On the dissolution-growth process of a grain: large time behavior and special solutions.

Françoise Issard-Roch
Analyse Numérique et EDP
Université Paris-Sud, Batiment 425
91405 ORSAY Cedex, FRANCE
e-mail: ⟨Francoise.Issard-Roch@math.u-psud.fr⟩

Thomas I. Seidman
Department of Mathematics and Statistics
University of Maryland Baltimore County,
Baltimore, MD 21250, USA
e-mail: ⟨seidman@math.umbc.edu⟩

ABSTRACT: We study here the large time behavior of the radius $R(t)$ of a spherical grain in a dilute solution of the same substance. The evolution in time of the grain is governed by a reaction-diffusion process in the liquid phase and by a dissolution/accretion process located at the interface which determines the interface kinetics; a discussion of this modelling is provided. When there is no reaction, the order of $R(t)$ is rather independent of the interface kinetics; we prove that $R(t) = \mathcal{O}(\sqrt{t})$ and construct special solutions with $R(t) = \beta\sqrt{t}$ for the interface kinetics of interest. In the situation with nontrivial chemistry, we obtain a general upper bound $R(t) = \mathcal{O}(t^{3/2})$; for the particular kinetics there is an easy linear upper bound and we obtain a complementary linear lower bound for $R(t)$, clearly distinguishing this from the situation without reaction.

AMS SUBJECT HEADINGS: *35B40, 35E15, 35K55, 35K57, 35R35.*

1. Introduction

We are studying here a simple model of a solid/liquid interface which forms a free boundary for the problem. This model is composed of an amorphous solid phase of a single substance and an incompressible liquid phase which is a dilute solution of the same substance involving both diffusion and possible chemical reaction. One interpretation of this model is the corrosion of a material in water — with both dissolution of the material into the water and accretion of dissolved material to the solid possible so the interface motion need not have a fixed direction.

The evolution in time of the system consists of two interacting processes: the dissolution/accretion process at the interface and the reaction/diffusion process in the liquid phase, which occupies a time-varying spatial region $\Omega(t) \subset \mathbb{R}^d$ — i.e., $\Omega(t)$ is an unbounded exterior domain and $\partial\Omega(t)$ is the interface. In this paper, we assume radial symmetry in an unbounded domain with $d = 2, 3$, i.e., the solid is and remains a spherical 'grain' in 2 or 3 dimensions. We denote by $R(t)$ the radius of the grain and by $r := |x|$ the distance from the center of the grain so $\Omega(t) = \{x : |x| = r > R(t)\}$. Our intent here is to study the large time behavior of the growth rate $R(\cdot)$ for the unbounded domain and, if possible, to try to find a simple determination of the precise growth rate.

The reaction/diffusion process is governed by the usual conservation equation for the concentration C, which in radial geometry takes the form

$$C_t = C_{rr} + \frac{d-1}{r}C_r + F(C) \qquad \text{in } \mathcal{Q} := \left\{ (t,r) : \begin{array}{c} 0 < t < \tau^* \\ r > R(t) \end{array} \right\} \tag{1.1}$$

or, if we exclude consideration of any chemical reaction in the fluid, by

$$C_t = C_{rr} + \frac{d-1}{r}C_r \quad \text{in } \mathcal{Q}. \tag{1.2}$$

In either case, we impose a conservation boundary condition at the interface[1]

$$C_r = (1 - C)\dot{R} \qquad \text{at } r = R(t) \tag{1.3}$$

For reasons described in Section 5 (see also [8]), the constitutive law for the interface motion may be expected to take the form

$$\dot{R} = \Lambda\left[\omega - h(1/R)\right] \quad \text{with } \omega := C\Big|_{r=R(t)}, \tag{1.4}$$

where Λ is a rate constant, ω is the concentration in the adjacent liquid phase (for which we note the physical constraint: $0 \le \omega \le 1$), and $h(\cdot)$ is a suitable nonnegative given function of the local mean curvature κ of $\partial\Omega$ — taken as positive when the solid phase would be convex so in our radial case we have simply: $\kappa = 1/R$. Physically, $\Gamma^* := h(0)$ is related to the saturation concentration and $h'(0) > 0$ is proportional to the interfacial 'surface tension'.

The physical derivation originally leading to [5],[8], [12], [13] and [15], was due to M. Cournil [6] and specifically employed the Ostwald-Freundlich Law

$$h(\kappa) = \Gamma^* e^{\gamma\kappa} \tag{1.5}$$

with $\gamma > 0$; alternatively one might consider the frequently used linear law

$$h(\kappa) = \Gamma^*(1 + \gamma\kappa). \tag{1.6}$$

These 'laws' match to first order, but each certainly requires correction for larger $|\kappa|$. The physical derivation of (1.4) given in Section 5 presumably is also reliable only for a limited range of κ, but shows that (1.5), (1.6) are reasonable approximations so long as $|\kappa|$ remains small.

As we are considering an unbounded domain in this paper, we must also specify a 'boundary condition at infinity', which we impose in the form

$$[C(t,\cdot) - \Gamma] \in H^1(R(t), \infty) \tag{1.7}$$

[1] We note that the concentration C is necessarily positive and is typically quite small ($0 \le C \ll 1$) so that one also will find in the literature a 'simplification' of the boundary condition (1.3), replacing $(1 - C)$ by 1, to get: $C_r = \dot{R}$ (or, later, (1.11) simplified to $\partial C/\partial n = V_n$). However, not only is (1.3) physically more correct as stated, but this form was essential in [13] to the argument showing that C takes only physically meaningful values: in the range $[0, 1]$.

for a constant[2] Γ corresponding to the spatially uniform concentration one would have if there were no grain at all.

We also impose appropriate initial conditions:

$$R(0) = R_0 \quad \text{and} \quad C(0,r) = C_0(r) \text{ for } r > R_0. \tag{1.9}$$

The complete problem, then, is the coupled system

(P) $\{\ (1.1), (1.7), (1.3), (1.4), (1.9)\ \}$

or the system $(\mathbf{P}_0)$ in which (1.1) is replaced by (1.2) so we would be considering the situation 'without chemistry', i.e., the special case $F \equiv 0$.

In [13], we have shown that **(P)** is well-posed and have studied the regularity of the solution as well as its maximal time of existence. Those results complemented the analysis of F. Conrad, D. Hilhorst, and T.I. Seidman [5] who considered this problem on a bounded domain, more precisely: (1.1) in $0 < R(t) < r < 1$ with (1.3), (1.4) at $r = R$ and with a Dirichlet condition $C(t,1) = \alpha(t)$ specified at the outer boundary $r = 1$.

Well-posedness results have also been obtained for certain non-radial settings in [1], [2], [15]. Note that in the non-radial case the equation and the boundary condition at the interface take the forms

$$C_t = \Delta C + F(C) \ \text{ in } \mathcal{Q} := \left\{ (t,x) \in \mathbb{R}^{1+d} : \begin{array}{c} 0 < t < \tau^* \\ x \in \Omega(t) \end{array} \right\}, \tag{1.10}$$

$$\frac{\partial C}{\partial n} = (1-C)V_n \ \text{ on } \Sigma := \left\{ (t,x) \in \mathbb{R}^{1+d} : \begin{array}{c} 0 < t < \tau^* \\ x \in \partial\Omega(t) \end{array} \right\} \tag{1.11}$$

In (1.11), both the rate of motion of the interface $-V_n$ in its normal direction and $\partial C/\partial n$ are taken as oriented inward to $\Omega(t)$ so the constitutive law (1.4)

[2]In [13] this was taken, somewhat more generally, as a time-varying 'concentration at infinity' $\Gamma = \Gamma(t)$ satisfying the ODE

$$\dot\Gamma(t) = F(\Gamma(t)) \text{ for } t > 0; \qquad \Gamma(0) = \Gamma_0 \tag{1.8}$$

which corresponds to the chemistry in a well-mixed reactor with no grain appearing but not yet in equilibrium; compare the discussion in subsection 5.3. It is classical [11] that (1.8) would have global $C^{1,1}$ solutions under the conditions we shall impose on F. Our present situation is a special case of this in which the concentration at infinity is already in equilibrium so $\Gamma \equiv \Gamma_0$, given that $F(\Gamma_0) = 0$. This is, of course, the only possibility in considering (1.2) where $F \equiv 0$.

has the form $V_n = \Lambda\,[C - h(\kappa)]$. These studies considered the problem in a bounded region with no-flux boundary conditions at the far boundary. Numerical studies for this model are done in [15], [8].

A. Friedman [9] has studied several free boundary problems for the equation (1.2) with Dirichlet boundary conditions at the interface and various kinetics laws for its motion. He proved the monotonicity of $R(\cdot)$ and behavior of the form $R = \mathcal{O}(\sqrt{t})$.

A quite similar problem, corresponding to the growth of a spherical crystal in a supersaturated solution with no reaction was studied by J. Chadam, S.D. Howison, and P. Ortoleva [4]. Their version also replaces (1.4) by the Dirichlet boundary condition

$$C = \Gamma^*(1 + \gamma\kappa). \tag{1.12}$$

Formally, using the linear law (1.6) in (1.4) and dividing by Λ, we obtain (1.12) as $\Lambda \to \infty$; this problem appears as the scaled evolution of a perturbed shape. In [4] they first prove the existence of special solutions of the form

$$R(t) = \beta\sqrt{t}, \quad C(t,r) = w_0\left(\frac{r}{R(t)}\right) + \frac{1}{\sqrt{t}} w_1\left(\frac{r}{R(t)}\right). \tag{1.13}$$

and then (under suitable assumptions on the initial data, expressing in particular that the solution is supersaturated) they also obtain, following [9], that the free boundary grows like $\beta\sqrt{t}$. This behavior seems to be a consequence of the reactionless equation (1.2) and of the constraint $0 \le C \le 1$ without any consideration of the interface kinetics. Our results in section 3 are an extension of this analysis.

In section 2 we recall the main results of [13] on the well-posedness and the regularity of the solutions of Problem **(P)**. Sections 3 and 4 are devoted to the large time behavior of the growth rate $R(t)$. In section 3, we give upper bounds for $R(t)$ without any use of the constitutive law for the interface kinetics. More precisely, when there is no chemistry in the reaction/diffusion process, that is when (R, C) satisfies (1.2), the growth of the grain is limited primarily by the rate of diffusive mass transfer so the rate of growth is somewhat independent of the interface kinetics; we give in dimensions 2 and 3 an upper bound for $R(t)$ of the form $A + B\sqrt{t}$. Next considering the situation 'with chemistry' ($F \not\equiv 0$), we show (under suitable assumptions) that the growth of the grain radius is now limited to $\mathcal{O}(t^{3/2})$ for $d = 3$ — although it is easily observed that the particular interface kinetics (1.4) together with $0 \le C \le 1$ immediately implies that the growth is then limited to $R = \mathcal{O}(t)$. In section 4, we consider the problem with the constitutive law for the interface kinetics and suppose that the liquid phase is supersaturated at infinity, to obtain solutions with the expected growth rate. First, in the case 'without chemistry' ($F \equiv 0$) we give a lower bound for $R(t)$ in the form $D + E\sqrt{t}$, and when the constitutive function h is analytic near $\kappa = 0$ we compute in dimension 2 or 3 special solutions with the precise rate $R(t) = \beta\sqrt{t}$. Then in the situation 'with chemistry' we show a linear growth rate for $R(t)$. Finally in section 5 we describe the physical background of this model.

2. Preliminaries

Before proceeding further, we pause to state the hypotheses which we will impose throughout — on the constitutive functions $\{F, h\}$ of the problem:

$$\text{(2.1)} \qquad \begin{aligned} i)&\quad F \text{ is Lipschitzian on } [0,1] \text{ with } F(1) \le 0 \le F(0);\\ ii)&\quad h \in C^1((0,\infty)), \quad h \ge 0 \text{ on } (0,\infty) \end{aligned}$$

and on the data $\{R_0, \Gamma, C_0\}$:

$$\text{(2.2)} \qquad \begin{aligned} i)&\quad 0 < R_0 < \infty;\\ ii)&\quad F(\Gamma) = 0 \text{ and } 0 < \Gamma < 1 \text{ so } 0 < \vartheta := \max\{\Gamma,\, 1-\Gamma\} < 1;\\ iii)&\quad 0 \le C_0 \le 1 \text{ with } [C_0(\cdot) - \Gamma] \in H^1(R_0,\infty);\\ iv)&\quad \int_{R_0}^{\infty} |C_0(r) - \Gamma|^2\, r^{d-1}\, dr < \infty. \end{aligned}$$

The requirement in (2.1-ii) that $h \ge 0$ means physically that the grain cannot grow when there is no material supply. The fact that Γ is a zero of the function $F(\cdot)$ is essential when $F \not\equiv 0$: physically, we want the concentration at infinity Γ to be a stable equilibrium for the chemistry (e.g., as expressed by (1.8)). A standard sufficient condition for this would be to have assumed F regular and strictly decreasing — so Γ would be the unique root of $F(\Gamma) = 0$ with $F'(\Gamma) < 0$. An immediate consequence of that condition would be that

$$\text{(2.3)} \qquad \begin{cases} 0 \le \alpha^-(\Gamma - s) \le F(s) \le \alpha^+(\Gamma - s) & \text{for } s \le \Gamma\\ F(s) \le 0 & \text{for } s \ge \Gamma \end{cases}$$

for some $0 < \alpha^- < \alpha^+$ and we take this (with $0 < \Gamma < 1$) as characterizing the case of nontrivial chemistry ($F \not\equiv 0$) without actually requiring the strict decrease. Note also that we will later be assuming that F is 'smooth', but here have required only Lipschitz continuity since (2.1-i) is sufficient for the well-posedness Theorem 2.1 and it will later be useful to have allowed the case of (3.2.7) for comparison.

We next recall the main results given in [13] on the well-posedness and regularity of the solution of Problem **(P)**.

THEOREM 2.1: *Assume the hypotheses (2.1) for the constitutive functions F, h and (2.2) for the data R_0, Γ, C_0. Then there exist a time interval $[0,\tau]$ (with $\tau = \tau(R_0) > 0$) and a unique solution pair (R, C) of Problem* **(P)**= { (1.1), (1.7), (1.3), (1.4), (1.9) } *on $[0,\tau]$ with $0 \le C \le 1$. More precisely, if one sets $y = r - R(t), u(t,y) := C(t,r) - \Gamma$, then*

$$u \in \boldsymbol{U} := L^\infty([0,\tau] \to \mathcal{H}) \cap L^2([0,\tau] \to \mathcal{V}),$$

where $\mathcal{H} = L^2(0,\infty)$ and $\mathcal{V} = \{v \in \mathcal{H} : v_y \in \mathcal{H}\}$, with continuous dependence of $u \in \boldsymbol{U}$ on the initial data R_0 and $u_0 \in \mathcal{H}$. From (2.2-iv) we actually have $u_0 \in \mathcal{H}_* = L^2_\mu(0,\infty)$ with $\mu(y) := (1+y)^{d-1}$ and then obtain

$$u \in \boldsymbol{U}_* := L^\infty([0,\tau] \to \mathcal{H}_*) \cap L^2([0,\tau] \to \mathcal{V}_*)$$

where $\mathcal{V}_* = \{v \in \mathcal{H}_* : v_y \in \mathcal{H}_*\}$ with continuous dependence of $u \in \boldsymbol{U}_*$ on R_0 and $u_0 \in \mathcal{H}_*$.

The choice of μ gives a norm equivalent to the r^{d-1}-weighted norm coming from the use of polar coordinates in the context of $L^2(\mathbb{R}^d \setminus [\,\text{grain}\,])$ and we recall that the assumption (2.2-iv) was used in [13] in showing that $0 \le C \le 1$ for $t > 0$.

Theorem 2.1 gives unique existence for **(P)** locally in time for some interval $[0,\tau_1]$ with $\tau_1 = \tau(R_0)$. As is standard for ODEs, we note that the problem may be restarted at $t = \tau_1$ to get existence of a solution on $[\tau_1, \tau_2]$, where $\tau_2 = \tau_1 + \tau(R(\tau_1))$, with a simple verification that this provides, by concatenation, a (unique) solution on $[0,\tau_2]$ ... and, of course, this construction can be iterated. A Zorn's Lemma argument gives existence of a unique solution (R, C) of the problem with a maximal interval of existence $(0,\tau^*)$.

In this paper we assume Hypothesis (2.1-*ii*) for the function h so the constitutive law for the interface kinetics $H(r,\omega) = \Lambda(\omega - h(1/r))$ satisfies a linear growth condition $H(r,\omega) \leq K(1+r)$ for $r > 0$ and $0 \leq \omega \leq 1$. This constrains the behavior of the radius $R(t)$ as $t \to \tau^*$ if one were to have $\tau^* < \infty$.

THEOREM 2.2: *Assume the hypotheses (2.1) for the constitutive functions F, h and (2.2) for the data R_0, Γ, C_0 and denote by τ^* the maximal time of existence. Then $\tau^* < \infty$ could be possible only with $R(t) \to 0$ as $t \nearrow \tau^*$.*

Finally we recall additional regularity for the solutions of **(P)**.

THEOREM 2.3: *Let (R, C) be the solution of* **(P)** *on $(0,T)$; we assume that $T < \tau^*$ and that we know $R \geq \eta > 0$ on $[0,T]$. Suppose the constitutive functions F and h are infinitely differentiable. Then R and C are infinitely differentiable on $(0,T]$ and on $\mathcal{Q}_T := \{(t,r) : 0 < t \leq T,\ r > R(t)\}$, respectively.*

In the following we will suppose for simplicity that the constitutive functions F and h are, indeed, infinitely differentiable so we have infinite differentiability throughout for R, C.

3. Asymptotics of the grain radius: upper bounds for the growth rate

In this section we give upper bounds for the rate of growth of the grain radius $R(t)$. We must separately consider the two cases of interest: first without chemistry ($F \equiv 0$), so we are considering (1.2), and then with chemistry as in (1.1). These upper bounds are obtained without any use of the specific constitutive law (1.4) for the interface kinetics.

Physically, this shows that substance simply cannot be supplied to the interface fast enough to support more rapid growth than we are indicating — by diffusion alone in the first case or by the combination of diffusion and chemistry in the second. E.g., even if one were to ignore any constitutive law (while retaining the conservation condition (1.3)) and would treat $\dot{R}$ as a *control*, at our disposal, the state constraint $0 \leq C \leq 1$ necessarily limits the admissible controls as in (3.1.2) or (3.2.1).

3.1. Upper bounds for $R(t)$ when $F \equiv 0$

In this subsection we consider (1.2) which corresponds to a diffusion process without reaction.

THEOREM 3.1: *For dimension $d = 2$ or 3, let (R, C) be a solution in $\mathcal{Q}$ of (1.2), (1.3), (1.9) and suppose that the data R_0, Γ, C_0 satisfy (2.2) and*

$$J_0 := \int_{R_0}^{\infty} |C_0 - \Gamma| r \, dr < \infty. \tag{3.1.1}$$

Then there exist positive constants A (depending on Γ, R_0, J_0) and B (depending only on Γ) such that

$$0 \leq R(t) \leq A + B\sqrt{t} \qquad \text{for all } 0 < t < \tau^*. \tag{3.1.2}$$

The argument very slightly generalizes that of [9], [4] in not assuming monotone increase of $R(\cdot)$. We proceed by proving first that (3.1.2) holds at *'exposed points'* of the graph, from which the general case follows.

DEFINITION 3.2: *A point (τ, b) is an* **exposed point** *for $R(\cdot)$ if $b = R(\tau) \geq R_0$ and $R(t) \leq b$ for all $0 \leq t \leq \tau \leq \tau^*$ so $\mathcal{Q} \supset \mathcal{Q}_b := (0, \tau) \times (b, \infty)$.*

Note that if $R(\cdot)$ is *a priori* assumed increasing, then *all* the points $(\tau, R(\tau))$ are exposed points.

Following [9], [4], it will be convenient to introduce the functions V, I defined by

$$V(t, r) := r[C(t, r) - \Gamma], \quad I(t) := \int_{R(t)}^{\infty} V(t, r) \, dr \tag{3.1.3}$$

Note that (3.1.1) implies $|I(0)| \leq J_0 < \infty$ and, thanks to (2.2-iii), we have $V(0, \cdot) \in L^2(R_0, +\infty)$.

We first give a technical lemma estimating $I(\tau)$, noting at this point that it will later be important for us that (1.3) is not needed in the proof of this lemma. Recall that $\vartheta := \max\{\{\Gamma, 1 - \Gamma\} \in (0, 1)$.

LEMMA 3.3: *Let $R(\cdot)$ be a positive smooth function on $[0,\tau]$ such that $(\tau, R(\tau))$ is an exposed point and, with $d = 2$ or 3, let C be a solution on $\mathcal{Q}$ of (1.2). Assume (2.2), (3.1.1) and that $0 \le C \le 1$ for $0 \le t \le \tau$. Then*

$$|I(\tau)| \le \begin{cases} 2\vartheta R(\tau)\sqrt{\tau/\pi} + J_0 + \vartheta\tau & \text{for } d = 2 \\ 2\vartheta R(\tau)\sqrt{\tau/\pi} + J_0 & \text{for } d = 3. \end{cases} \tag{3.1.4}$$

PROOF: Set $\omega(t) := V(t,b)$ with $b := R(\tau)$, noting that this is smooth, and set $V_0(r) := V(0,r) = r[C_0(r) - \Gamma]$ (taking $V_0 := 0$ for $0 \le r < R_0$), noting that this is integrable by (3.1.1). Since we have assumed that (τ, b) is an exposed point, we have $\mathcal{Q}_b \subset \mathcal{Q}$ so V is defined on $\mathcal{Q}_b$. From (1.2) we see that V satisfies in $\mathcal{Q}$, hence in $\mathcal{Q}_b$,

$$\begin{aligned} V_t &= r^{-(d-2)}\left(r^{d-2}V_r - r^{d-3}V\right)_r \\ &= r^{-(d-3)}\left(r^{d-3}V_r\right)_r - \frac{d-3}{r^2}V. \end{aligned} \tag{3.1.5}$$

We now also introduce V_i, W_i, which are defined for $i = 1,2$ as the respective solutions of

$$\begin{aligned} &V_{it} = V_{irr} \text{ on } \mathcal{Q}_b \text{ and} \\ &\quad \begin{cases} V_1 = \omega, \quad V_2 = 0 & \text{at } r = b,\ 0 \le t \le \tau \\ V_1 = 0, \quad V_2 = V_0 & \text{at } t = 0,\ b \le r \end{cases} \\ &W_{it} = W_{irr} \text{ on } (0,\tau) \times \mathbb{R}_+ \text{ and} \\ &\quad \begin{cases} W_1 = 1, \quad W_{2r} = 0 & \text{at } r = 0,\ 0 \le t \le \tau \\ W_1 = 0, \quad W_2 = |V_0| & \text{at } t = 0,\ 0 \le r \end{cases} \end{aligned} \tag{3.1.6}$$

Note that

$$W_1(t,y) = (1/\sqrt{\pi}) \int_{y/\sqrt{t}}^{\infty} e^{-z^2/4}\, dz$$

so $\int_0^\infty W_1(t,y)\, dy = 2\sqrt{t/\pi}$. Observe also that if we redefine V_0 on all of $\mathbb{R}$ as an even function across $r = b$ we have $V_0 \in L^1(\mathbb{R})$ whence, as $V_2(t,\cdot)$ is the convolution of this with the heat kernel, we see that it is integrable; similarly considering an extension of $|V_0|$ as even across $r = 0$, the same convolution argument shows integrability of $W_2(t, \cdot)$.

(Case 1: $d = 3$) In this case (3.1.5) simplifies to $V_t = V_{rr}$ so we have $V = V_1 + V_2$ on $\mathcal{Q}_b$ and $I(\tau) = \int_b^\infty [V_1 + V_2]\, dr$.

Since the constraint $0 \le C \le 1$ in (3.1.3) gives $|\omega(t)| \le b\vartheta$ on $[0, \tau]$, the Maximum Principle gives $|V_1(t, r)| \le b\vartheta W_1(t, r - b)$, whence

$$\int_b^\infty |V_1(t,r)|\, dr \le b\vartheta \int_0^\infty W_1(t,r)\, dr = 2b\vartheta\sqrt{t/\pi}. \tag{3.1.7}$$

Comparing V_2, W_2, the Maximum Principle gives, first, $W_2 \ge 0$ (so, in particular, $W_2(t, b) \ge 0 = V_2(t, b)$) whence $|V_2| \le W_2$ and

$$\int_b^\infty |V_2(t,r)|\, dr \le \int_0^\infty W_2(t,r)\, dr = \int_0^\infty W_2(0,r)\, dr = J_0. \tag{3.1.8}$$

Combining (3.1.7), (3.1.8) gives (3.1.4), as desired, for $d = 3$.

(Case 2: $d = 2$) Now (3.1.5) becomes $V_t - V_{rr} = -C_r$ so we additionally introduce $V_3 = -Z_r$ where $Z \in H^1(b, \infty)$ is the solution of

$$\begin{aligned} &Z_t = Z_{rr} + [C - \Gamma] &&\text{on } \mathcal{Q}_b \\ &Z_r = 0 \text{ at } r = b &&Z = 0 \text{ at } t = 0. \end{aligned} \tag{3.1.9}$$

One easily sees that

$$\begin{gathered} V_{3t} = V_{3rr} - C_r \text{ on } \mathcal{Q}_b \text{ with} \\ V_3 = 0 \text{ if } r = b \text{ or} t = 0 \end{gathered} \tag{3.1.10}$$

and that we have $V = V_1 + V_2 + V_3$ on $\mathcal{Q}_b$ with V_1, V_2 exactly as above, with the same estimates[3] (3.1.7), (3.1.8). Noting that further convolution arguments show first that $[C(t, \cdot) - \Gamma] \in L^1(b, \infty)$ and then integrability of $Z_r(t, \cdot)$, one obtains

$$\int_b^\infty V_3(t,r)\, dr = -Z(t,\cdot)\Big|_b^\infty = Z(t,b). \tag{3.1.11}$$

[3]Although we have restricted our attention here to dimensions $d = 2, 3$, one may note that essentially the same argument gives the same result for $d > 3$ since the coefficient of V in (3.1.5) is then positive: the same Maximum Principle arguments continue to be valid, although one now has a different W_1, depending on d, so the constant must then be altered.

By assumption, $|C - \Gamma| \le \vartheta$ and, since $\hat{Z} := \vartheta t$ satisfies (3.1.9) with $C - \Gamma$ replaced by ϑ, we have $|Z| \le \vartheta t$. Combining this with (3.1.7), (3.1.8), (3.1.11) gives (3.1.4), as desired, for $d = 2$. ■

Proof (of Theorem 3.1): Note that $V_0 \in L^2(R_0, +\infty)$ from (2.2-*iii*) and (3.1.1) so $V(t,\cdot) \in H^1(R(t), +\infty)$. Hence, from (3.1.3), (1.2), (1.3), we have

$$\begin{aligned} I'(t) &= \int_{R(t)}^{\infty} rC_t(t,r)\,dr - \dot{R}(t)R(t)[C(t,R(t)) - \Gamma] \\ &= (d-2)[\Gamma - C(t,R(t)] - \frac{1-\Gamma}{2}\frac{d}{dt}R^2(t) \end{aligned} \tag{3.1.12}$$

and integrating this last on $(0,t)$ gives the first estimate

$$(1-\Gamma)R^2(t) \le 2(d-2)\Gamma\, t - 2I(t) + (1-\Gamma)R_0^2 + 2I(0), \tag{3.1.13}$$

since we have $C \ge 0$. Using (3.1.4) in (3.1.13) gives

$$R^2(\tau) \le \frac{2\Gamma}{1-\Gamma}\tau + \frac{4}{\sqrt{\pi}}\frac{\vartheta}{1-\Gamma}R(\tau)\sqrt{\tau} + \left[R_0^2 + \frac{4J_0}{1-\Gamma}\right],$$

from which one easily obtains

$$0 \le R(\tau) \le A + B\sqrt{\tau} \tag{3.1.14}$$

whenever $(\tau, R(\tau))$ is an exposed point, with

$$B = \frac{4}{\sqrt{\pi}}\frac{\vartheta}{1-\Gamma} + \sqrt{\frac{2\Gamma}{1-\Gamma}}, \quad A = \sqrt{R_0^2 + 4\frac{J_0}{1-\Gamma}}.$$

Finally, we note that (3.1.14) actually holds not only for the exposed points $(\tau, R(\tau))$ but *for all* $(t, R(t))$ with $0 < \tau < \tau_*$. [Otherwise there would exist $t, \varepsilon > 0$ with $R(t) > [A + B\sqrt{t}] + \varepsilon$ and, fixing $\varepsilon > 0$, we may let τ minimize t for which $R(t) \ge [A + B\sqrt{t}] + \varepsilon$. This $(\tau, R(\tau))$ must be an exposed point which would contradict (3.1.14), as obtained above.] ■

3.2. Upper bounds for $R(t)$ when $F \not\equiv 0$

Having considered in section 3.1 the situation with $F \equiv 0$, we now return to the situation (1.1), assuming (2.3).

THEOREM 3.4: *For dimension $d = 3$, suppose that the reaction term F satisfies (2.3) with $0 \le \alpha^- \le \alpha^+ =: \alpha$. Assume $R(\cdot)$ is known to be nondecreasing and let C be a solution in $\mathcal{Q}$ of (1.1), (1.3) for $0 \le t < \infty$ such that $0 \le C \le 1$ in $\mathcal{Q}$ Assume the initial data R_0, Γ, C_0 satisfy (2.2) and (3.1.1). Then*

(3.2.1) $$0 \le R(t) \le A + \tilde{B}\sqrt{t} + \alpha \hat{D} t^{3/2}$$

with

$$A = \sqrt{R_0^2 + 4\frac{J_0}{1-\Gamma}}, \quad \tilde{B} = \frac{4}{\sqrt{\pi}}\frac{\vartheta}{1-\Gamma} + \sqrt{\frac{2(\Gamma + \alpha J_0)}{1-\Gamma}}, \quad \hat{D} = \frac{8}{3\sqrt{\pi}}\frac{\vartheta}{1-\Gamma}$$

We observe that (3.2.1) reduces to (3.1.14) for $\alpha = 0$ and further remark, since $\sqrt{t} \le t^{3/2} + 2/(3\sqrt{3})$ for all $t > 0$, that (3.2.1) implies that there exist positive constants $\tilde{A}$ (depending on Γ, R_0, J_0, α) and $\tilde{C}$ (depending only on Γ, J_0, α) such that

(3.2.2) $$0 \le R(t) \le \tilde{A} + \tilde{D}\, t^{3/2} \quad \text{for all t } > 0.$$

Physically, this shows that substance simply cannot be supplied to the interface, now by the combination of reaction and diffusion, fast enough to support a more rapid growth. As in the situation without reaction treated in Theorem 3.1, this shows that even if one were to ignore any constitutive law (while retaining the conservation condition (1.3)) and treat $\dot{R}$ as a *control*, completely at our disposal except for the state constraint $0 \le C \le 1$, then that constraint restricts the admissible controls as in (3.2.2).

When one *does* impose the constitutive law (1.4), of course, this state constraint gives an immediate *linear* bound on the growth rate in the form:

(3.2.3) $$0 \le R(t) \le R_0 + \Lambda t \quad \text{for all } t > 0,$$

for *any* constitutive function $h \ge 0$ — and in the sharper form:

(3.2.4) $$0 \le R(t) \le R_0 + \Lambda(1 - \Gamma^*)t \quad \text{for all } t > 0$$

when h satisfies (1.5). We will return to this in section 4.

PROOF (of Theorem 3.4): Much as in section 3.1, we now see from (3.1.3) that

$$V_t = V_{rr} + rF(\Gamma + V/r) \quad \text{in } \mathcal{Q} \tag{3.2.5}$$

and

$$\begin{aligned} I'(t) &= \int_{R(t)}^{\infty} V_t \, dr - \dot{R}(t)V\Big|_{r=R(t)} \\ &= -\left[V_r + \dot{R}V\right]\Big|_{r=R(t)} + \int_{R(t)}^{\infty} rF(\Gamma + V/r)\, dr. \end{aligned}$$

Then, using (1.3) to get $V_r + \dot{R}V = (C - \Gamma) + R\dot{R}(1 - \Gamma)$ at $r = R(t)$,

$$\begin{aligned} (1-\Gamma)R^2(t) &= \left[(1-\Gamma)R_0^2 + 2I(0) + 2\int_0^t \left(\Gamma - C\Big|_{r=R(t)}\right)\, dt\right] \\ &\qquad - 2I(t) + 2\int_0^t \int_{R(s)}^{\infty} rF(\Gamma + V/r)\, dr\, ds \\ &\le [(1-\Gamma)R_0^2 + 2I(0) + 2\Gamma\, t] \\ &\qquad + 2\left[-\int_{R(t)}^{\infty} V(t,r)\, dr + \alpha \int_0^t \int_{R(s)}^{\infty} [-V(s,r)]_+ \, dr\, ds\right] \end{aligned} \tag{3.2.6}$$

(where $[\cdot]_+$ indicates the 'nonnegative part') since we have $C \ge 0$ and (2.3) with $\alpha \ge \alpha^- \ge 0$.

We now introduce the auxiliary function $\tilde{F}$, defined by

$$\tilde{F}(s) := \begin{cases} -\alpha s & \text{for } s \le 0 \\ 0 & \text{for } 0 \le s \le \Gamma \\ \min\{F(\sigma) : \sigma \le s\} & \text{for } s \ge \Gamma \end{cases} \tag{3.2.7}$$

and note that $\tilde{F}$ is nonincreasing, positive for $s < 0$, and that $\tilde{F}(s) \le F(s)$ on $\mathbb{R}$ (where we are extending F to $\mathbb{R}$, e.g., as $F(s) := F(0) - \alpha s$ for $s < 0$ and as $F(s) := F(1)$ for $s > 1$). Next, we define $\tilde{V}$ as the solution of

$$\begin{aligned} &\tilde{V}_t = \tilde{V}_{rr} + r\tilde{F}(\Gamma + \tilde{V}/r) \ \text{ on } \mathcal{Q} \text{ with} \\ &\tilde{V}(t,\cdot) \in H^1(R(t),\infty), \quad \tilde{V}\Big|_{r=R(t)} = \tilde{\omega}, \quad \tilde{V}\Big|_{t=0} = \tilde{V}_0. \end{aligned} \tag{3.2.8}$$

where we have set

$$\omega(t) := V\Big|_{r=R(t)} \qquad \tilde{\omega} := \omega_- := \min\{0,\omega\} \qquad \tilde{V}_0 := [V_0]_- := \min\{0, V_0\}.$$

Note that $-R(t)\Gamma \leq \tilde{\omega}(t) \leq 0$ for all $t \in (0, \infty)$ and $-r\Gamma \leq \tilde{V}_0(r) \leq 0$ for all $r \geq R_0$ so standard arguments give $-r\Gamma \leq \tilde{V}(t,r) \leq 0$ on $\mathcal{Q}$; similarly, comparing to (3.2.5), we get $\tilde{V} \leq V$ on $\mathcal{Q}$. We now introduce $\tilde{C} := \Gamma + \tilde{V}/r$ (so $\tilde{V} = r[\tilde{C} - \Gamma]$) and note that $\tilde{C}$ satisfies (1.1) with F replaced by $\tilde{F}$ and, since $-r\Gamma \leq \tilde{V}(t,r) \leq 0$, (3.2.7) gives $\tilde{F}(\tilde{C}) = \tilde{F}(\Gamma + \tilde{V}/r) \equiv 0$ so $\tilde{C}$ satisfies (1.2). Further, $-r\Gamma \leq \tilde{V}$ gives $0 \leq \tilde{C}$ and $\tilde{V} \leq V$ gives $\tilde{C} \leq C \leq 1$. By our assumptions, $\tau^* = \infty$ and each $(t, R(t))$ is an exposed point so[4] we may apply Lemma 3.3 to $\tilde{C}$ whence, returning to (3.2.6), we have

$$
\begin{aligned}
(1-\Gamma)R^2(t) &\leq [(1-\Gamma)R_0^2 + 2I(0) + 2\Gamma t] \\
&\qquad + 2\left[-\int_{R(t)}^{\infty} \tilde{V}(t,r)\,dr - \alpha \int_0^t \int_{R(s)}^{\infty} \tilde{V}(s,r)\,dr\,ds\right] \\
&\leq [(1-\Gamma)R_0^2 + 2I(0) + 2\Gamma t] \\
&\qquad + 2\left[\vartheta 2R(t)\frac{\sqrt{t}}{\sqrt{\pi}} + J_0 + \alpha \int_0^t \left[\vartheta 2R(s)\frac{\sqrt{s}}{\sqrt{\pi}} + J_0\right] ds\right] \\
&\leq (1-\Gamma)R_0^2 + 2[I(0) + J_0] + 2[\Gamma + \alpha J_0]t \\
&\qquad + \frac{4\vartheta}{\sqrt{\pi}}\left[t^{1/2} + (2/3)\alpha t^{3/2}\right] R(t).
\end{aligned} \tag{3.2.9}
$$

One then easily obtains (3.2.1), as desired. ■

4. Solutions with the expected growth rates

In this section we re-impose the constitutive law (1.4) for the interface kinetics:

$$\dot{R}(t) = \Lambda\left[C(t, R(t)) - h(1/R(t))\right] \quad \text{for all } 0 < t < \tau^*.$$

We also assume that initially the liquid phase is a 'supersaturated solution' for large r: that is, with $\Gamma^* := h(0) > 0$ we have

$$\Gamma^* < \Gamma < 1. \tag{4.1}$$

We then can expect continued growth of the grain from some time on.

[4] At this point we recall that (1.3) was fortunately not required for Lemma 3.3.

Our objective is to obtain, from this constitutive law, results which complement the upper bounds of section 3. When $F \equiv 0$ we first give a lower bound in the same form as the upper bound (3.1.2), then we find solutions exhibiting the $\mathcal{O}(t^{1/2})$ growth rate of Theorem 3.1. Then, when $F \not\equiv 0$ (satisfying (2.3)), i.e., in the presence of chemistry, we construct solutions of (1.1) which have linear growth rates, showing that (3.2.3) or (3.2.4) give the correct asymptotic order of growth in that case.

4.1. A lower bound on the growth rate for $R(t)$ when $F \equiv 0$

In this subsection we will seek an $O(\sqrt{t})$ lower bound for the growth rate of the grain radius when $F \equiv 0$, complementing the upper bound (3.1.2) obtained in Theorem 3.1; the results are then quite similar to those of [4].

THEOREM 4.1: *Let (R, C) be a solution in $\mathcal{Q}$ of (1.2), (1.3), (1.9), and the constitutive law (1.4); assume also that $h(\cdot)$ is a smooth increasing function of κ. Suppose the data R_0, Γ, C_0 satisfy (2.2), (4.1) and*

(4.1.1) $h(1/R_0) < C_0(R_0), \quad C_0(R_0) \le C_0(r) \le 1 \qquad$ *a.e. on* $[R_0, \infty)$.

Then $\dot{R}(t) > 0$ — i.e., $C(t, R(t)) > h(1/R(t))$ — for all $t > 0$ so $R(\cdot)$ is strictly increasing.

Next, suppose also that R_0, Γ, C_0 satisfy (3.1.1) and that

$$C_0(r) \le \Gamma \qquad \text{a.e. on } [R_0, \infty). \tag{4.1.2}$$

Then $C(t, r) \le \Gamma$ for $t > 0$, $r > R(t)$; for $d = 3$, there then exist positive constants A', B' such that

$$R(t) \ge B'\sqrt{t} - A' \quad \text{for } t > 0. \tag{4.1.3}$$

PROOF: If, as in [13], we set $y = r - R(t)$ and $u(t, y) = C(t, r) - \Gamma$, then $u(t, \cdot)$ is in $H^1(\mathbb{R}_+)$ for each $0 < t \le \tau^*$ and satisfies

$$\begin{array}{lrll} i) & \dot{R} = & \Lambda[u\big|_{y=0} + \Gamma - h(1/R)] & (t > 0) \\ ii) & u_t = & u_{yy} + \psi u_y & (t, y > 0) \\ iii) & u_y = & \dot{R}[1 - \Gamma - u] & (y = 0;\ t > 0) \\ iv) & u = & u_0 := C_0(y + R_0) - \Gamma & (y > 0;\ t = 0) \end{array} \tag{4.1.4}$$

with $\psi(t,y) := \dot{R}(t) + 2/[y+R(t)]$.

From assumption (4.1.1), we have $\dot{R}(0) > 0$. If we did not have $\dot{R}(t) > 0$ always, set

$$\tau = \min\{t : \dot{R}(t) \le 0\} \quad \mu = \min\{u(t,y) : 0 \le t \le \tau,\ y \ge 0\}.$$

Then $\dot{R}(\tau) = 0$ and μ is attained at $(\hat{\tau}, \hat{y})$ with $0 \le \hat{\tau} \le \tau, \hat{y} \ge 0$. By the Strong Maximum Principle, $(\hat{\tau}, \hat{y})$ cannot occur in the interior unless u were constant, which is clearly not the case here. On the other hand if u attains its minimum at $\hat{y} = 0$ for $0 \le \hat{\tau} < \tau$ one has $\dot{R}(t) > 0$ for all $0 \le t < \tau$ so (4.1.4-i) gives

$$u(\hat{\tau}, 0) + \Gamma > h(1/R(\hat{\tau})) > h(1/R(\tau)) = u(\tau, 0) + \Gamma$$

which contradicts the choïce of $\hat{\tau}$. Thus u attains its minimum at $\hat{\tau} = 0$ with $\hat{y} \ge 0$, but the assumption (4.1.1) for C_0 implies that $\hat{y} = 0$ — which is, as above, impossible. These contradictions show that $\dot{R}(t) > 0$ for all $0 \le t < \tau^*$ whence $R(\cdot)$ is strictly increasing and $\tau^* = \infty$.

Under the additional hypotheses, a simple Maximum Principle argument gives $C \le \Gamma$ globally and we need only show the lower bound (4.1.3) for the growth rate when $d = 3$, complementing (3.1.2). Note, from (1.4), that $[h(1/R(t)) - C(t, R(t))] = -\dot{R}(t)/\Lambda$. Again using the functions of (3.1.3) and Lemma 2.5, we integrate (3.1.12) to obtain

$$\text{(4.1.5)} \quad \begin{aligned} \frac{1-\Gamma}{2}\left[R^2(t) - R_0^2\right] &= I(0) - I(t) + \int_0^t [\Gamma - h(1/R) - \dot{R}/\Lambda]\, dt \\ &\ge I(0) + [R_0 - R(t)]/\Lambda + [\Gamma - h(1/R_0)]\, t \end{aligned}$$

since $h(1/R) \le h(1/R_0)$ and $I(t) \le 0$ as R and h increase and $C \le \Gamma$. This quadratic inequality ($[aR^2 + bR \ge ct + d]$ with $c = \Gamma - h(1/R_0) > 0$) gives (4.1.3), as desired. ■

4.2. Exact solutions with $R(t) = \beta\sqrt{t}$ for $F \equiv 0$

In this subsection we consider the problem (1.2), (1.3), (1.4), assuming that at the initial time we have a supersaturated solution: (4.1) and that

R_0, Γ, C_0 satisfy (2.2). We further assume that the constitutive function h in (1.4) is analytic near $\kappa = 0$ with a series expansion

$$h(\kappa) = \sum_{j=0}^{\infty} \gamma_j \kappa^j, \qquad \gamma_0 = h(0) =: \Gamma^*,\ \gamma_1 = h'(0) > 0. \tag{4.2.1}$$

We then seek, in the form of a corresponding expansion, special solutions of the system which precisely exhibit the behavior described in the last two subsections. These solutions would be characterized by having $R\dot{R} \equiv \alpha$ — for a constant α depending (only) on the *supersaturation ratio*

$$\rho := \frac{\Gamma - \Gamma^*}{1 - \Gamma^*}\ . \tag{4.2.2}$$

through (4.2.9) below — which gives $R(t) = \beta\sqrt{t}$ for $\beta = \sqrt{2\alpha}$ (obviously 'starting' at some $t = t_0 > 0$) or, equivalently, $R(t) = \beta\sqrt{t + t_0}$ starting at $t = 0$ with $t_0 = (R_0/\beta)^2$.

Our approach is to introduce a 'similarity variable' ξ and then to expand everything in powers of the curvature $\kappa = \kappa(t)$ to match (4.2.1):

$$C(t, r) =: w(t, \xi) \equiv \sum_{j=0}^{\infty} \kappa^j w_j(\xi), \qquad \xi := r/R(t). \tag{4.2.3}$$

Noting that $\dot{\kappa} = (1/R)^{\cdot} = -\dot{R}\kappa^2$, we then have

$$\begin{array}{llll} i) & w_t & = \kappa^2 \left[w_{\xi\xi} + \left(\dfrac{d-1}{\xi} + R\dot{R}\xi \right) w_\xi \right] & \text{on } (1, \infty) \\ ii) & w_\xi & = R\dot{R}[1 - w] & \text{at } \xi = 1 \\ iii) & R\dot{R}\kappa & = \Lambda \left[w\Big|_{\xi=1} - h(\kappa) \right] & \\ iv) & & [w(t, \cdot) - \Gamma] \in H^1(1, \infty). & \end{array} \tag{4.2.4}$$

If $R\dot{R} \equiv \alpha$, then $\dot{\kappa} = -\alpha\kappa^3$, so (4.2.4-*i*, *ii*, *iii*) become, on expansion,

$$\begin{array}{lll} i) & -\alpha \sum_0^\infty j\kappa^j w_j & = \sum_0^\infty \kappa^j \left[w_j'' + \left(\dfrac{d-1}{\xi} + \alpha\xi \right) w_j' \right] \quad \text{on } (1, \infty) \\ ii) & \sum_0^\infty \kappa^j w_j'(1) & = \alpha \left[1 - \sum_0^\infty \kappa^j w_j(1) \right] \\ iii) & \alpha\kappa & = \Lambda \sum_0^\infty \kappa^j \left[w_j(1) - \gamma_j \right]. \end{array} \tag{4.2.5}$$

On separating by powers of κ, this system decouples completely so

$$(4.2.6)\qquad \begin{aligned} &i) && w_j'' + \left(\frac{d-1}{\xi} + \alpha\xi\right) w_j' + \alpha j w_j = 0 \quad \text{on } (1,\infty) \\ &ii) && w_j'(1) + \alpha w_j(1) = \begin{cases} \alpha & j = 0 \\ 0 & j > 0 \end{cases} \\ &iii) && w_j(1) = \begin{cases} \gamma_1 + \alpha/\Lambda & j = 1 \\ \gamma_j & j \neq 1 \end{cases} \end{aligned}$$

independently for each $j = 0, 1, \ldots$; to this we adjoin, from (4.2.4-iv),

$$(4.2.7)\qquad [w_0 - \Gamma] \in H^1(1,\infty), \qquad w_j \in H^1(1,\infty) \text{ for } j > 0.$$

Note that at this point α in (4.2.6) is an unknown constant which we will determine through (4.2.7). We must show that, for each $j = 0, 1, \ldots$, the system (4.2.6), has a unique solution satisfying (4.2.7) with estimates ensuring that the power series (4.2.3) converges.

Consider, first, the case $j = 0$. Setting $z := w_0'$, we have

$$z' + \left(\frac{d-1}{\xi} + \alpha\xi\right) z = 0 \qquad \text{for } \xi > 1 \qquad z(1) = \alpha(1 - \Gamma^*)$$

whence

$$\begin{aligned} z(\xi) &= \alpha(1-\Gamma^*) \exp\left[-\int_1^\xi \left(\frac{d-1}{\eta} + \alpha\eta\right) d\eta\right] \\ &= \alpha(1-\Gamma^*) e^{-(\alpha/2)\left(\xi^2-1\right)} \xi^{-(d-1)}. \end{aligned}$$

This is integrable and, using (4.2.6-iii), we obtain

$$(4.2.8)\qquad w_0(\xi) = \Gamma^* + \alpha(1-\Gamma^*) \int_1^\xi e^{-(\alpha/2)\left(\eta^2-1\right)} \eta^{-(d-1)}\, d\eta.$$

To satisfy (4.2.7) we must have $w_0(\xi) \to \Gamma$ as $\xi \to \infty$ so we must have

$$(4.2.9)\qquad \begin{aligned} \rho &= \alpha \int_1^\infty e^{-(\alpha/2)\left(\eta^2-1\right)} \eta^{-(d-1)}\, d\eta \\ &= \int_0^\infty \frac{e^{-\zeta}\, d\zeta}{[1 + 2\zeta/\alpha]^{d/2}} \qquad [\zeta = \tfrac{\alpha}{2}(\eta^2 - 1)] \end{aligned}$$

with ρ as in (4.2.2). The final integral, as a function of $\alpha \in \mathbb{R}_+$, is increasing (and continuous, by the Dominated Convergence Theorem) with values 0 at

$\alpha = 0+$ and 1 at ∞. Thus, (4.1) ensures that (4.2.9) can be solved uniquely for α — i.e., the growth rate depends only on ρ, independently of any other aspect of $h(\cdot)$, and this also determines $w_0(\cdot)$ as the asymptotic 'shape' of the distribution when $\kappa \to 0$.

To consider $j \geq 1$, we introduce $z := \xi^{\vartheta} w_j / w_j(1)$, which satisfies

$$
(4.2.10)\qquad
\begin{array}{ll}
i) & z'' + [\alpha + (d-1-2\vartheta)\xi^{-2}]\,\xi z' \\
 & \qquad + [\alpha(j-\vartheta) + \vartheta(\vartheta - d + 2)\xi^{-2}]\,z = 0 \quad \text{for } \xi > 1 \\
ii) & z(1) = 1, \qquad z'(1) = \vartheta - \alpha
\end{array}
$$

with α already determined from (4.2.9) and the value of ϑ still to be suitably chosen.

(Case 1: $d = 3$) In this case we take $\vartheta = 1$ so (4.2.10-i) becomes $z'' + \alpha\xi z' + \alpha(j-1)z = 0$. For $j = 1$, this gives $z' = ce^{-(\alpha/2)\xi^2}$ which is integrable and we obtain, explicitly,

$$
(4.2.11)\qquad w_1(\xi) = \left(\gamma_1 + \frac{\alpha}{\Lambda}\right)\left(1 + (1-\alpha)\int_1^{\xi} e^{-(\alpha/2)(\eta^2-1)}\,d\eta\right)\frac{1}{\xi}.
$$

Note that both z and z' are bounded: $|z|, |z'| \leq M$.

For $j > 1$ we do not seek an explicit solution, but only an estimate to verify (4.2.7) and to ensure convergence (in the $H^1(1,\infty)$-norm) for the expansion (4.2.3) to define $w(t,\xi)$. Multiplying (4.2.10-i) by $2z'$ and integrating gives

$$
[z'(\xi)]^2 + 2\alpha\int_1^{\xi} \eta[z'(\eta)]^2\,d\eta + \alpha(j-1)z^2(\xi) = (1-\alpha)^2 + \alpha(j-1).
$$

Again we get the estimates

$$
\begin{array}{ll}
|z| \leq M, & |z'| \leq Mj, \\
|w_j(\xi)| \leq |w_j(1)|M/\xi, & |w_j'(\xi)| \leq |w_j(1)|M\left[\dfrac{1}{\xi^2} + \dfrac{j}{\xi}\right]
\end{array}
$$

with M independent of j. Noting (4.2.6-ii, iii), this bounds each w_j in the $H^1(1,\infty)$-norm:

$$
(4.2.12)\qquad \|w_j\|_{(1)} \leq jM|\gamma_j| \quad \text{for } j = 1, \ldots
$$

with a different M, but still independent of j. This is sufficient to ensure validity of the expansion in (4.2.3) for the same radius of convergence as one has in (4.2.1).

(Case 2: $d = 2$) In this case we choose $1/2 < \vartheta < \min\{1, (1+\alpha)/2\}$ so $\alpha + (1 - 2\vartheta) > 0$ and $j \geq \vartheta$. Multiplying (4.2.10-i) by $2z'$ and integrating, including an integration by parts, then gives

$$\begin{aligned} 0 \; &= z'^2\Big|_1^\xi + 2\int_1^\xi \left[\alpha + (1-2\vartheta)\eta^{-2}\right] \eta[z'(\eta)]^2\, d\eta \\ &\quad + \alpha(j-\vartheta)z^2\Big|_1^\xi + \vartheta^2\eta^{-2}z^2\Big|_1^\xi + 2\vartheta^2 \textstyle\int_1^\xi \eta^{-3} z^2(\eta)\, d\eta \\ &\geq \left[z'^2 + \left(\alpha[j-\vartheta] + \vartheta^2\eta^{-2}\right) z^2\right]\Big|_1^\xi \end{aligned}$$

Thus,

$$z'^2 + \alpha(j-\vartheta)z^2 \leq (\vartheta - \alpha)^2 + \alpha(j-\vartheta) + \vartheta^2$$

so again we have bounds for z, z'. Since $\vartheta > 1/2$, this suffices, as above, to give (4.2.12).

In either of these cases, then, one has (4.2.12) and the analyticity of $h(\cdot)$ then ensures the convergence, for small κ, of the scalar series $\sum Mj|\gamma_j|\kappa^j$ and so the H^1 convergence of the series in (4.2.3). This justifies the construction as giving a solution of the problem from some t_0 on (making $\kappa = 1/(\beta\sqrt{t})$ small enough). Looking back over this construction, we observe that the coefficient $\beta = \sqrt{2\alpha}$ and the solution $C(t,r) = w(t, r/\beta\sqrt{t})$ were uniquely determined. Summarizing, we see that we have proved the following result:

THEOREM 4.2: *Consider the problem (1.2), (1.3), (1.4) with $h(\cdot)$ analytic near $\kappa = 0$ and as in (4.2.1); assume also that the data R_0, Γ, C_0 satisfy (2.2) and (4.1).*

Then there is a unique solution (R, C) with $R(t)/\sqrt{t} \equiv$ constant; this constant depends only on the supersaturation ratio defined in (4.2.2).

At this point we note that when the constitutive function $h(\cdot)$ is linear — i.e., for $h(\kappa) = \gamma_0 + \gamma_1\kappa$, so $\gamma_j = 0$ in (4.2.1) for all $j > 1$ — the expansion (4.2.3) reduces to the form (1.13) and the explicit computation of w_0, w_1 for $d = 3$ already appears, for this case, in [4]. Our contribution here is primarily the shift from (1.12), used in [4], to (1.3), (1.4), i.e., generalizing to nonlinear $h(\cdot)$.

4.3. The linear growth rate for $R(t)$ when $F \not\equiv 0$

In this final subsection we obtain one of the principal results of the paper: a linear lower bound for the growth rate, complementing (3.2.4), when we have nontrivial chemistry and the constitutive law (1.4). Thus, we are considering the problem (1.1) with (1.3), (1.4) in dimension 3 with a nontrivial reaction term F satisfying (2.3) for some $0 < \alpha^- < \alpha^+$ and we suppose that at the initial time the supersaturation condition (4.1) is satisfied. Note that Theorem 3.4 applies to give an upper bound for $R(t)$ but, as we are working with the constitutive law and have $0 \leq C \leq 1$, we obviously have the stronger bound (3.2.4). Our objective here is to show existence of a positive lower bound σ — depending on α^-, α^+, etc. — for the speed $\dot{R}$. Thus the grain radius grows so as to complement (3.2.3) by the linear growth rate: $R(t) \geq R_0 + \sigma t$.

We also impose some additional conditions beyond (2.1) and (2.2). The first of these is that R_0 is large enough so that the effect of curvature is already sufficiently reduced:

$$\Lambda[h(1/R_0) - \Gamma^*] =: \bar{\gamma} < \frac{\Lambda\sqrt{\alpha^-}}{\Lambda + \sqrt{\alpha^-}}[\Gamma - \Gamma^*]. \tag{4.3.1}$$

We then introduce, as functions of $s \geq 0$,

$$\begin{aligned} \lambda(s) &:= \left[s + \sqrt{s^2 + 4\alpha^-}\right]/2 \quad \text{so} \\ &\lambda^2(s) - s\lambda(s) - \alpha^- = 0 \qquad (\lambda(s) - s = \alpha^-/\lambda(s) > 0) \\ \eta(s) &:= \frac{s + \bar{\gamma}}{\Lambda} + [s(1-\Gamma) + \bar{\gamma}]\,\frac{\lambda(s)}{\alpha^-} \\ &:= \frac{\Gamma}{\Lambda}s + \left(\frac{1}{\Lambda} + \frac{\lambda(s)}{\alpha^-}\right)[s(1-\Gamma) + \bar{\gamma}]\,. \end{aligned} \tag{4.3.2}$$

Note that $\lambda(\cdot)$ is strictly increasing on $\mathbb{R}_+$ with $\lambda(0) = \sqrt{\alpha^-}$ so $\eta(\cdot)$ is also strictly increasing with $\eta(0) = \bar{\gamma}\left(1/\Lambda + 1/\sqrt{\alpha^-}\right)$. Thus, (4.3.1) is just sufficient to ensure that we can find (uniquely) $\sigma > 0$ such that

$$\eta(\sigma) = [\Gamma - \Gamma^*]. \tag{4.3.3}$$

Using this σ and $\lambda = \lambda(\sigma)$, we define $v = v(y)$ (depending, of course, on α^- and $\bar{\gamma}$) by

$$v(y) := -ce^{-\lambda y} \qquad \text{with } c := [\sigma(1-\Gamma) + \bar{\gamma}]\,\lambda/\alpha^- \tag{4.3.4}$$

and note that it satisfies

$$
(4.3.5)\qquad
\begin{gathered}
v'' + \sigma v' - \alpha^- v = 0 \qquad \text{for } y > 0 \\
v' + \sigma v = \sigma(1-\Gamma) + \bar{\gamma} \text{ at } y = 0; \qquad v \to 0 \text{ as } y \to \infty \\
\sigma = \Lambda[v(0) + \zeta] \qquad \text{with } \zeta := \Gamma - \Gamma^* - \bar{\gamma}/\Lambda = \Gamma - h(1/R_0).
\end{gathered}
$$

We also introduce the Hilbert spaces $\mathcal{X}, \mathcal{Y}$ of functions on $\mathbb{R}^+$ with norms

$$
(4.3.6)\qquad
\begin{aligned}
\|f\|_{\mathcal{X}} = \|f\|_\sigma &:= \left[\int_0^\infty |f(y)|^2 e^{\sigma y}\, dy\right]^{1/2} \\
\|f\|_{\mathcal{Y}} &:= \left[\|f'\|_\sigma^2 + \alpha^- \|f\|_\sigma^2\right]^{1/2} \\
&:= \left[\int_0^\infty \left[|f'(y)|^2 + \alpha^- |f(y)|^2\right] e^{\sigma y}\, dy\right]^{1/2}
\end{aligned}
$$

and note that (4.3.4) gives $v \in \mathcal{Y}$ as $\lambda = \lambda(\sigma) > \sigma$.

LEMMA 4.3: *For $f \in \mathcal{Y}$ and $\lambda = \lambda(\sigma)$ we have: $\sqrt{\lambda}|f(0)| \le \|f\|_{\mathcal{Y}}$.*

PROOF: Set $\varphi(y) := [f(y)]^2 e^{\sigma y}$ so $\varphi' = [2ff' + \sigma f^2]e^{\sigma y}$. Then

$$
\begin{aligned}
[f(0)]^2 &= \varphi(0) = -\int_0^\infty \varphi'\, dy \\
&= -2\langle f, f'\rangle_\sigma - \sigma\|f\|_\sigma^2 \le 2\|f\|_\sigma \|f'\|_\sigma - \sigma\|f\|_\sigma^2 \\
&\le \left[\lambda\|f\|_\sigma^2 + (1/\lambda)\|f'\|_\sigma^2\right] - \sigma\|f\|_\sigma^2.
\end{aligned}
$$

Finally, multiply by λ and note from (4.3.2) that $\lambda(\lambda - \sigma) = \alpha^-$. ■

At this point we collect the conditions to be imposed on the initial data Γ and C_0 in addition to (2.2) and (4.1) — as in (4.1.4), we state these in terms of $u_0(y) := [C_0(y + R_0) - \Gamma]$ and $y = r - R(t)$:

$$
(4.3.7)\qquad
\begin{aligned}
&i) \;\; u_0 \in \mathcal{Y} \\
&ii) \;\; u_0' \ge 0 \;\text{ for } y \ge 0 \\
&iii) \;\; u_0(y) \ge v(y) \;\text{ for } y \ge 0.
\end{aligned}
$$

Note that from (4.3.7-*iii*), (1.4), and (4.3.5) we get

$$
\dot{R}(0) = \Lambda\left[C_0(R_0) - h(1/R_0)\right] \ge \Lambda\left[\Gamma + v(0) - h(1/R_0)\right] = \sigma
$$

and we now explicitly assume that R_0 is large enough to make this a strict inequality.

THEOREM 4.4: *Let (R, C) be a solution of* **(P)** *on $(0, \tau^*)$ with $h(\cdot)$ strictly increasing from $h(0) =: \Gamma^*$ and with F decreasing and satisfying (2.3). Suppose the data (R_0, Γ, C_0) satisfy (2.2), (4.1), (4.3.1) and (4.3.7) where σ is uniquely defined by (4.3.3) and that $\dot{R}(0) > \sigma$.*

Then the solution exists for $0 < t < \tau^* = \infty$ and we have $R(t) \geq R_0 + \sigma t$ for all $t > 0$.

PROOF: Since $\dot{R}(0) > \sigma$, we may introduce

$$T_0 := \sup\left\{T > 0 : \dot{R}(t) \geq \sigma \text{ for } 0 \leq t \leq T\right\} > 0. \tag{4.3.8}$$

Our intention will be to show that $T_0 = \tau^* = \infty$.

Step 1 We first show that $C_r \geq 0$ for all $0 < t \leq T_0$ and $r \geq R(t)$.

Set $Z := C_r$. Differentiating equation (1.1) with respect to r we have

$$\begin{gathered} Z_t = Z_{rr} + \frac{d-1}{r} Z_r - G(t,r)Z \qquad r \geq R(t),\ t \in (0, \tau^*), \\ Z(t, R(t)) = g(t),\ t \in (0, \tau^*); \qquad Z(0, r) = Z_0(r),\ r \geq R_0. \end{gathered}$$

with

$$G(t,r) := \frac{d-1}{r^2} - F'(C)(t,r); \qquad g(t) := \dot{R}(t)(1 - C(t, R(t))); \qquad Z_0 := C_0'.$$

Note that $G > 0$ as F is decreasing, that $g \geq 0$ as $\dot{R} > 0$ on $[0, T_0]$ and $C \leq 1$, and that $Z_0 \geq 0$ by (4.3.7-*ii*).

Set $W := Z_- := \min\{Z, 0\} \leq 0$ and note that $W = 0$ at $r = R(t)$ since $g \geq 0$. We have

$$\begin{aligned} &\frac{1}{2}\frac{d}{dt}\int_{R(t)}^{\infty} W^2(t,r) r^{d-1}\, dr \\ &\quad = -\frac{1}{2}\dot{R}(t) W^2(t, R(t)) R(t)^{d-1} + \int_{R(t)}^{\infty} W(t,r) Z_t(t,r)\, r^{d-1}\, dr \\ &\quad = \int_{R(t)}^{\infty} W(t,r) \left(r^{d-1} Z_r(t,r)\right)_r\, dr \\ &\qquad - \int_{R(t)}^{\infty} W(t,r) G(t,r) Z(t,r)\, r^{d-1}\, dr \\ &\quad = -\int_{R(t)}^{\infty} \left[(W_r(t,r))^2 + G(t,r) W^2(t,r)\right] r^{d-1}\, dr \leq 0. \end{aligned}$$

We have $W(0,\cdot) \equiv 0$ as $Z_0 \geq 0$, whence $W(t,r) = 0$ for $r \geq R(t), 0 \leq t \leq T_0$.

Step 2 As for (4.1.4), set $u(t,y) = C(t,r) - \Gamma, y = r - R(t)$. We first prove that $u(t,y) \geq v(y)$ for all $t \in [0,T_0)$ and $y \geq 0$. The function u now satisfies

$$
(4.3.9)\quad
\begin{aligned}
i) \quad u_t &= u_{yy} + \left[\dot{R}(t) + \frac{d-1}{y+R(t)}\right] u_y + F(u+\Gamma) \\
&= u_{yy} + \sigma u_y - \alpha^- u + \hat{G} && (t, y > 0) \\
ii) \quad u_y &= \dot{R}(1 - [u+\Gamma]) \\
&= -\sigma u(t,0) + \sigma[1-\Gamma] + \hat{g} && (y = 0;\ t > 0) \\
iii) \quad u &= u_0 := C_0(y+R_0) - \Gamma && (y > 0;\ t = 0)
\end{aligned}
$$

with

$$
\begin{aligned}
\hat{G}(t,y) &:= \left[(\dot{R}(t) - \sigma) + \frac{d-1}{y+R(t)}\right] u_y + \left[F(u+\Gamma) + \alpha^- u\right] \\
\hat{g}(t) &:= (\dot{R}(t) - \sigma)[1 - \Gamma - u(t,0)] = (\dot{R}(t) - \sigma)[1 - C(t, R(t))].
\end{aligned}
$$

We set $w := u - v$ and, $\hat{w} := w_- := \min\{u - v, 0\}$. The function w satisfies

$$w_t = w_{yy} + \sigma w_y - \alpha^- w + \hat{G} \qquad t > 0, y > 0.$$

Multiplying this equation by $\hat{w}e^{\sigma y}$ and integrating on $(0,\infty)$ we obtain

$$(4.3.10) \qquad \frac{1}{2}\frac{d}{dt}\left(\|\hat{w}(t,\cdot)\|_\sigma^2\right) = \left\langle \hat{w}, e^{-\sigma y}\left(e^{\sigma y}\hat{w}_y\right)_y - \alpha^- \hat{w} + \hat{G}\right\rangle_\sigma.$$

Since we are considering $t \in [0,T_0]$, we have $(\dot{R}(t) - \sigma) \geq 0$ for all $t \in [0,T_0]$ and from step 1 $u_y(t,y) \geq 0$ for all $t \in [0,T_0], y \geq 0$. By (2.3), we also have $[F(u+\Gamma) + \alpha^- u] \geq 0$ when $u \leq 0$ so $\hat{G} \geq 0$ when $u \leq 0$ and thus $\langle \hat{w}, \hat{G}\rangle_\sigma \leq 0$ on $[0,T_0]$. From (4.3.10) we obtain

$$
(4.3.11)\quad
\begin{aligned}
\frac{1}{2}\frac{d}{dt}\left(\|\hat{w}(t,\cdot)\|_\sigma^2\right) &\leq \int_0^\infty \hat{w}(t,y)\left(\hat{w}_y e^{\sigma y}\right)_y\, dy - \alpha^- \|\hat{w}(t,\cdot)\|_\sigma^2 \\
&\leq -\hat{w}(t,0) w_y(t,0) - \|\hat{w}\|_{\mathcal{Y}}^2.
\end{aligned}
$$

Moreover at $y = 0, w_y(t,0) = -\sigma w(t,0) + \hat{g} - \bar{\gamma}$. Since $C \geq 0$ we have

$$
(4.3.12)\quad
\begin{aligned}
\hat{g}(t) \leq \dot{R}(t) - \sigma &= \Lambda\left[w(t,0) + h(1/R_0) - h(1/R(t))\right] \\
&\leq \Lambda w(t,0) + \bar{\gamma}.
\end{aligned}
$$

This implies that for all $t \in [0, T_0]$ we have

$$\hat{w}(t,0)w_y(t,0) \geq (\Lambda - \sigma)\hat{w}^2(t,0) \geq -\sigma\hat{w}^2(t,0)$$

and

$$\frac{d}{dt}\left(\frac{1}{2}\|\hat{w}(t,\cdot)\|_\sigma^2\right) \leq \left(\frac{\sigma}{\lambda} - 1\right)\|\hat{w}\|_{\mathcal{Y}}^2$$

by means of Lemma 4.3. Since $\lambda > \sigma$ and $\hat{w} = 0$ at $t = 0$, we deduce that $\hat{w} \equiv 0$ on $[0, T_0] \times [0, \infty)$ so $u(t, y) \geq v(y)$ for all $(t, y) \in [0, T_0] \times [0, \infty)$. Somewhat as in (4.3.12), one then has

$$\begin{aligned} \dot{R}(t) - \sigma &= \Lambda\left[u(t,0) + \Gamma - h(1/R(t))\right] - \Lambda\left[v(0) + \Gamma - h(1/R_0)\right] \\ &\geq \Lambda\left[h(1/R_0) - h(1/R(t))\right] > 0 \end{aligned} \tag{4.3.13}$$

for $0 < t \leq T_0$. If we were to suppose $T_0 < \tau^*$, then we would get $\dot{R}(T_0) > \sigma$ which contradicts the definition of T_0. Thus $T_0 = \tau^*$ and $\dot{R}(t) \geq 0$ for all $t \in [0, \tau^*)$. It then follows from Theorem 2.2 that $\tau^* = \infty$ and $\dot{R} \geq \sigma$ for all $t \geq 0$. Indeed from (4.3.13), since $R(t) \to \infty$ as $t \to \infty$, the growth rate $\dot{R}(t)$ is greater than $\sigma + \bar{\gamma}$ for large t. ■

5. Modelling

In this section we wish to discuss briefly the physical background underlying the mathematical problems we have been considering. Our thrust is twofold: to interpret the elements which have been included in this model and to indicate the restrictive assumptions made and aspects which would require modification in a still more detailed treatment. We comment separately on four elements of the model: the reaction/diffusion equation in the fluid, the boundary conditions at the grain surface, the boundary conditions away from the grain, and the constitutive law governing the interface motion.

5.1. The equation

The partial differential equation (1.10) is a quite standard conservation equation, describing reaction and diffusion of a single substance in solution with concentration C in a fluid solvent. Diffusion in the solvent is isotropic, so one has a scalar diffusion coefficient D and, for a homogeneous fluid, we may take $D =$ constant if the solution is sufficiently dilute that concentration-dependent effects may be ignored. It will also be significant later that we are implicitly assuming an effectively constant temperature in not coupling this with another conservation equation for the generation and diffusion of heat; compare [17].

Assuming the time-scale associated with the normalization (choice of units) for (1.10) is already appropriate, we have scaled space $[D^{1/d}x \mapsto x]$ to make $D \equiv 1$. This also scales the grain radius, of course, $[R/D^{1/d} \mapsto R]$ so in taking R macroscopic we will later be effectively assuming that the grain radius is large compared to the diffusive length scale — i.e., that we are concerned with a setting well past nucleation and, correspondingly, that we could not expect this analysis to provide an adequate modelling of complete dissolution of the grain if that were to occur.

The term $F(C)$ represents a lumped rate for the set of chemical reactions $[\textit{other species}] \overset{F}{\longmapsto} A^0$ where C is the concentration of the particular chemical species A^0 under consideration. This is only incompletely modeled in (1.10) as we have not coupled the equation with concentrations for other species $A^1, \dots, A^N$ which may be involved. More plausibly, there would be a *system*

$$\overline{u}_t = \nabla \cdot \overline{D} \nabla \overline{u} + \overline{F}(\overline{u}) \tag{5.1.1}$$

with $\overline{u} = (u^0, \dots, u^N)$ a vector of concentrations for $N+1$ interacting species where $C = u^0$ represents the concentration of interest. If we were to have an equilibrium: $\overline{F}(\bar{\Gamma}, \bar{\Gamma}^1, \dots, \bar{\Gamma}^N) = 0$ and we had uniform concentrations $u^k \equiv \bar{\Gamma}^k$ for $k = 1, \dots, N$, then we would have $F(C) := \overline{F}^0(C, \bar{\Gamma}^1, \dots, \bar{\Gamma}^N)$. Such a uniform concentration is not entirely consistent with motion of the grain boundary and also neglects variations of the concentrations $u^1, \dots, u^N$ near $\bar{\Gamma}^1, \dots, \bar{\Gamma}^N$ due to reactions involving $u = u^0$, although this is plausible if this perturbation effect is small compared to those other concentrations. Hence, the inclusion of the term F in (1.10) must be viewed as a reminder of the possible relevance of chemical reactions and as a shorthand for (5.1.1), but not as a full model.

5.2. Boundary conditions at the grain

The equation (1.10) is a 'conservation equation' for mass of the species; even the reaction term, as we have noted, represents interspecies conversion.

Thus, we also expect mass conservation at the interface.

If the grain were to grow by dR, then the motion of any area differential dA gives a local volume increase $dV = dR\,dA$. Prior to this growth the volume already contained the amount $C\,dV$ of the species and, since the grain is to be pure substance, must afterward contain the amount dV, requiring a local mass flux $(1-C)dR\,dA$ for this to occur in the time dt. A similar description would apply for a shrinking grain. Thus, we necessarily have

$$\text{[flux]} = (1-C)dR/dt, \tag{5.2.1}$$

corresponding to conservation of mass at the interface, which is just the condition we have imposed in (1.3); essentially the same argument gives (1.11) for more general geometry. As already noted, we are considering a dilute solution ($C \ll 1$) and the grain volume is quite small compared to the total solvent volume so we neglect the small volumetric effects due to displacement of fluid by accretion to the solid grain and conversely.

5.3. Boundary conditions away from the grain

We are considering an isolated grain in a uniform bulk fluid. Ignoring the grain, for the moment, the bulk fluid has a concentration Γ which, presumably, is subject to the same chemistry as noted above. Thus, as an ODE (neglecting any spatial variation far from the grain), one would have (1.8). This could be neglected if the fluid were assumed already at equilibrium: $\Gamma = \bar{\Gamma} =$constant with $F(\bar{\Gamma}) = 0$ as we have been considering throughout this paper, presumably with $F'(\bar{\Gamma}) < 0$ for stability. With respect to the grain, this now becomes a 'condition at infinity' that $C \to \Gamma$ as $r = |x| \to \infty$ — with the interpretation that we actually require $[C - \Gamma] \in H^1$, as in (1.7), so relevant 'boundary terms at infinity' will vanish when we apply the Divergence Theorem in getting a weak formulation.

This becomes conceptually clearer as we turn to a variant case: considering a continuum of similar grains with positive spatial density ρ, each quasi-isolated in that the distances between grains are assumed very large[5] compared to the diffusive spatial scale. The mass flux for each grain is then given by $-D\partial C/\partial R$, measured in volume per unit surface area, so the volume

[5]This may limit the relevant time period in considering the asymptotics of grain growth.

flux per grain (at radius r) is proportional to $-r^{d-1}\partial C/\partial R$ and this, multiplied by the grain density ρ_g, gives a contribution to the bulk concentration. Thus, (1.8) would become coupled:

$$\dot{\Gamma} = F(\Gamma) + \bar{\rho} \lim_{r\to\infty} \left[-r^{d-1}C_r\right] \tag{5.3.1}$$

where $\bar{\rho}$ is just ρ_g, scaled by a constant determined by the units for surface/volume conversion. We have, in this paper, effectively taken $\rho_g = 0$ so the coupling with (5.3.1) may be viewed as a potential generalization.

In each of these cases we considered the bulk liquid as a stationary passive medium within which material transport was entirely diffusive. For comparison, we consider a well-stirred bulk liquid in which one again has a density ρ_g of quasi-isolated grains. The hypothesis of 'well-stirring' again means that there is a uniform global concentration Γ associated with the bulk fluid. From fluid dynamics, we now have a boundary layer (film) of fluid around each grain with negligible motion relative to the grain. Within the film one again has diffusive transport: the equation (1.10) holds. The thickness δ of the layer provides another characteristic length for the problem and we need another boundary condition for (1.10) at the 'outer boundary' of the film. The simplest form for this, as in the Nernst 'film theory' (cf. [14] or, e.g., [7]), is to use a matching Dirichlet condition

$$C\Big|_{r=R+\delta} = \Gamma,$$

although, noting that this outer boundary of the 'film' is not really precise at $r = R + \delta$, other variations are available (cf., e.g., [10]). For this film model with a positive grain density $\rho_g > 0$, one would also have a flux coupling

$$\dot{\Gamma} = F(\Gamma) + \bar{\rho} \left[-C_r\Big|_{r=R+\delta}\right]. \tag{5.3.2}$$

Note that the scaling of $\bar{\rho}$ would now involve $R + \delta$, so in this form it would no longer remain constant.

5.4. The constitutive law

The constitutive law for growth/dissolution at the solid/liquid interphase interface provides the most interesting part of our physical modelling. We describe it in a slightly more general nonradial form, considering an interface

$\Sigma = \Sigma(t)$ which now need not be spherical and letting $\dot{\Sigma}$ (pointwise on Σ) be the 'surface velocity' $-V_n$ so, to first order,

$$\Sigma(t+dt) \approx \Sigma(t) + \dot{\Sigma}\, dt\, \vec{\boldsymbol{n}}$$

where $\vec{\boldsymbol{n}}$ is the unit normal to Σ. While one could present an argument based on a gradient flow involving the surface component of the Gibbs free energy (cf., e.g., [3]), we will here use an argument expressed more closely in terms of statistical mechanics.

At this point we remind ourselves of the purely geometric facts that surface area is the first variation and mean curvature κ is the second variation of 'volume enclosed' with respect to a small normal perturbation $dh(\cdot)$ of the bounding surface (parametrized by the surface Σ itself). Thus, a change $\Sigma \mapsto \hat{\Sigma} := \Sigma + dh(\cdot)\vec{\boldsymbol{n}}$ gives, to first order,

$$\begin{aligned} \hat{V} - V &\approx \langle 1, dh\rangle &:= \int_\Sigma (dh)\, dS \\ \hat{A} - A &\approx \langle \kappa, dh\rangle &:= \int_\Sigma \kappa(dh)\, dS, \end{aligned} \tag{5.4.1}$$

integrating with respect to surface area dS so $A = A(\Sigma) = \int_\Sigma dS$. For our present purposes, $dh = \dot{\Sigma}\, dt$ and our normalization identifies a volume change dV with a mass change, exactly as in subsection 5.2. The interpretation of (5.4.1), then, is that one has a local change $\Delta A = \kappa \Delta V$ corresponding to the adhesion of a mass ΔV (or dissolution, if ΔV is negative).

The interface motion is given by the balance between two competing surface reactions: dissolved molecules of our substance in the adjacent fluid binding to the solid grain and molecules in the grain boundary dissolving into the fluid. Noting that the concentration of such molecules in the fluid is C and in the grain is 1, we have $dV = [MC - N]\, dt\, dS$ or, since $\dot{V} = \dot{\Sigma}\, dS$ locally,

$$\dot{\Sigma} = MC - N \tag{5.4.2}$$

where (including a surface/volume scaling of C relative to the notion of 'adjacent') $M\, dt$ gives the probability of molecules in the adjacent fluid binding to the grain in time dt (essentially as a Poisson process) and $N\, dt$ gives the probability of bound molecules dissolving into the fluid.

We observe that the solid form is stable so bound molecules must have a lower energy level than free ones. Thus, no free energy is required for adherence (indeed, energy is released) so M is constant, independent of local energy availability.

In contrast, the dissolution reaction opposes an energy barrier and the reaction rate N is thus proportional to the frequency of local fluctuations of free energy exceeding this barrier. For a flat surface ($\kappa = 0$) we have $N = N_0$ (with N_0 dependent on the temperature; since, as noted earlier, we are assuming a constant ambient temperature, this N_0 is simply a constant). However, using an analysis reminiscent of the Jackson theory for melting (cf., e.g., [19]), we note that the chemical bonds of the molecules at the surface of the grain are already open in the direction of the liquid so these surface molecules have higher energy than those in the interior, i.e., there is an energy differential $\delta_S > 0$ between the interior and the surface layer. As in (5.4.1), dissolution changes the surface area and the energy barrier is therefore effectively reduced by $\kappa\delta_S$ whence the frequency with which that is overcome is, to first order, increased proportionally to this: we have

$$N \approx N_0 + \alpha\kappa\delta_S \tag{5.4.3}$$

and (5.4.2) takes the form — as in (1.4) —

$$\dot{\Sigma} = H(\kappa, \omega) = \Lambda\left[\omega - h(\kappa)\right] \qquad \omega = C\Big|_{\Sigma} \tag{5.4.4}$$

with $\Lambda = M$ and $h(\kappa) = \left[N_0 + \alpha\kappa\delta_S\right]/M$.

Note that this analysis gives $h(\cdot)$ nominally of the affine form (1.6) and increasing in κ (as in the hypotheses of Theorem 3.4) since α, δ_S are positive. In addition to our observation that the derivation of (5.4.3) is only correct to first order, we may further note that the surface energy differential δ_S may not be constant, but should be slightly geometry-dependent: molecules are more crowded where $\kappa < 0$, lateral bonds more 'stretched' where $\kappa > 0$ so we may anticipate that $\delta_S = \delta_S(\kappa)$. Indeed, this affine form cannot possibly be exact since, as already noted, it would give $h(\kappa) < 0$ — impossibly making $V_n > 0$ when $C = 0$ — for sufficiently negative curvature $\kappa < -1/\gamma$. Thus $h(\cdot)$ would not be precisely affine in κ and the more general treatment of Theorem 4.1 is relevant. It would also seem that the often-cited Ostwald-Freundlich Law (1.5) is only correct as providing a convenient approximate form for $\kappa \approx 0$.

It should be further noted that this discussion has implicitly assumed uniformity and isotropy at the interface, so we are considering an amorphous solid without any dependence on orientation to crystalline axes, as might otherwise be relevant.

References

[1] F. Abergel, D. Hilhorst, and F. Issard-Roch, *On a dissolution-growth problem with surface tension in the neighborhood of a stationary solution*, SIAM J. Math. Anal. **24**, pp. 299–316 (1993).

[2] F. Abergel, D. Hilhorst, F. Issard-Roch, and J.F. Scheid, *Local existence and uniqueness of a Stefan problem with surface tension*, Applicable Analysis **60**, pp. 219–240 (1996).

[3] J.W. Cahn and J.E. Hilliard, *Free energy of a nonuniform system, I: Interfacial free energy*, J. Chem. Phys. **28**, pp 258–267, (1958).

[4] J. Chadam, S.D. Howison, and P. Ortoleva, *Existence and stability for spherical crystals growing in a supersaturated solution*, IMA J. Appl. Math. **39**, pp. 1–15 (1987).

[5] F. Conrad, D. Hilhorst, and T.I. Seidman, *Well-posedness of a moving boundary problem arising in a dissolution–growth process,* Nonlinear Anal-TMA **15**, pp. 445–465 (1990).

[6] M. Cournil, *private communication.*

[7] E.L. Cussler, *Diffusion; Mass transfer in fluid systems,* Cambridge Univ. Press, Cambridge, (1984).

[8] C. Dupaix, D. Hilhorst, and J.F. Sheid, *On a dissolution–growth problem with surface tension: a numerical study,* preprint: Université de Paris–Sud, Orsay (1994).

[9] A. Friedman, *Free boundary problems for parabolic equations I. melting of solids,* J.Math. and Mech. **8**, pp. 499–517 (1959), *II. Condensation or evaporation of a liquid drop,* J. Math. and Mech. **9**, pp. 19–66 (1960), *III. Dissolution of a gas bubble in liquid,* J. Math. and Mech. **9**, pp. 327–345 (1960).

[10] H. Haario and T.I. Seidman, *A modification of the film model,* Chem. Eng. Sci. **49**, pp. 1477–1479 (1994).

[11] J. Hale, *Ordinary Differential Equations*, Krieger, New York, 1980.

[12] D. Hilhorst, F. Issard-Roch, and T.I. Seidman, *On a reaction–diffusion equation with a free boundary: the case of an unbounded domain*, pp. 232–236 in *Free Boundary Problems Involving Solids* (J. Chadam and P. Rasmussen, eds.), Longman, London, (1993).

[13] F. Issard-Roch, and T.I. Seidman, *Well–posedness of a dissolution-growth problem on an unbounded domain,* Applicable Analysis, **63**, pp. 183-205, (1996); also, *Erratum, ibid.* (1998).

[14] W. Nernst, *Theorie der Reaktionsgeschwindigkeit in heterogenen Systemer*, Z. Phys. Chem., **47**, pp. 52–55, (1904).

[15] J.F. Scheid, *Étude théorique et numérique de l'évolution morphologique d'interfaces*, Thesis: Université de Paris–Sud, Orsay, (1994).

[16] T.I. Seidman, *The transient semiconductor problem with generation terms, II,* in *Nonlinear Semigroups, PDE, and Attractors* (LNM #1394; T.E. Gill, W.W. Zachary, eds.), pp. 185–198, Springer-Verlag, New York (1989).

[17] T.I. Seidman, *Existence of optimal controls for a free boundary problem*, in *Differential Equations, Dynamical Systems, and Control Science: A Festschrift in Honor of Lawrence Markus* (K.D. Elworthy, W.N. Everitt, E.B. Lee, eds.), pp. 859–866, Marcel Dekker, N.Y. (1993).

[18] J.E. Taylor, *Mean curvature and weighted mean curvature*, Acta Met. Mat. **40**, pp. 1475–1485, (1992).

[19] D.P. Woodruff. *The Solid–Liquid Interface*, Cambridge Univ. Press, Cambridge, (1973).