Reaction and diffusion at a gas/liquid interface, II [1]

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ABSTRACT: We consider a reaction/diffusion system consisting of parabolic partial differential equations coupled through boundary conditions with ordinary differential equations. The specific model example arises in connection with the 'film model' for mass transport in a chemical bubble reactor. We show well-posedness for the general system and convergence to steady state for the specific problem.

KEY WORDS: *partial differential equation, system, reaction-diffusion, well-posedness, asymptotics.*

[1]This research has been partially supported by the National Science Foundation under the grant ECS-8814788 and by the U.S. Air Force Office of Scientific Research under the grant AFOSR-91-0008.

1. INTRODUCTION

We will primarily be concerned with the approach to steady state for the reaction/diffusion system

$$
\begin{aligned}
u_t &= Du_{xx} - \lambda uv - \mu uw \\
v_t &= Ev_{xx} - \lambda uv \\
w_t &= Fw_{xx} + \lambda uv - \mu uw
\end{aligned}
\tag{1.1}
$$

with the boundary conditions

$$
u = u^*, \qquad v_x = 0, \qquad w_x = 0 \tag{1.2}
$$

at $x = 0$ and with boundary conditions at $x = 1$ of the form:

$$
\begin{aligned}
-Du_x &= [u_t + \lambda uv + \mu uw]/\sigma \\
-Ev_x &= [v_t + \lambda uv]/\sigma \\
-Fw_x &= [w_t - \lambda uv + \mu uw]/\sigma.
\end{aligned}
\tag{1.3}
$$

The general form of the system (1.1), (1.3) is suggested by the 'film model' [9] for a gas/liquid interface. The involvement of the time derivatives on the right hand side of (1.3) is the most unusual feature here. If we were to introduce auxiliary scalar variables

$$
U := u\big|_{x=1} \qquad V := v\big|_{x=1} \qquad W := w\big|_{x=1}
$$

then these boundary conditions would take the form of a system of ordinary differential equations for U, V, W involving as 'sources' the *transport terms*

$$
\zeta_1 := -\sigma\left[Du_x\big|_{x=1}\right], \qquad \zeta_2 := -\sigma\left[Ev_x\big|_{x=1}\right], \qquad \zeta_3 := -\sigma\left[Fw_x\big|_{x=1}\right].
$$

The physical interpretation, here, is that U, V, W represent chemical concentrations in the (stirred, homogeneous) 'bulk liquid' while u, v, w are concentrations within a 'film' at a gas/liquid interface so, actually, it is U, V, W and the transport terms ζ_j which are of primary interest to the chemical engineer. A related 'surface renewal' model suggests the possible consideration of an (additional) distributed transport interaction in which a term $-\gamma_1[u - U]$

would be included on the right hand side of the first reaction/diffusion equation in (1.1) with the corresponding transport term ζ_1 modified to be now

$$\zeta_1 := \sigma \left[-Du_x\Big|_{x=1} + \int_0^1 \gamma_1 u \, dx \right]$$

and a new term $-\Gamma_1 U$ (with $\Gamma_1 = \sigma \int \gamma_1 \, dx$) included in the ordinary differential equation for U — with similar treatment of the other components.

In the following we will mainly discuss the well-posedness of the original specific system (1.1), as well as the approach to steady state. We will also discuss corresponding results for systems of more general form. In addition, we make some comments in Section 5 (following [4]) on the modeling and related computation.

The particular system discussed here corresponds to a (comparatively simple) chemical process:

$$A + B \xrightarrow{\lambda} C, \qquad A + C \xrightarrow{\mu} \text{`product'} \tag{1.4}$$

with $[u, v, w]$ representing concentrations for the reactants $[A, B, C]$; our eventual hypotheses will reflect the consideration that concentrations must be non-negative.

There is no real surprise as to the eventual steady state to be reached. Since the first reaction uses up the reactant B without replenishment and since 'after this' there would be no replenishment for C, used up then by the second reaction, one can expect ultimate depletion of B, C while A continues to be supplied at $x = 0$ at the level u^*; obviously, then, the steady state should be

$$u \equiv u^*; \qquad v \equiv 0; \qquad w \equiv 0. \tag{1.5}$$

Nevertheless, the mathematical arguments for well-posedness of the system and for the approach to steady state are not entirely trivial and these will be our present concern. We can consider a system such as (1.1), (1.3) as an example of a more general abstract form — see (2.5), (2.6) or (4.1), below — and will formulate the problem in this context, since it readily provides insight as to the significant aspects of the nonlinearities. The arguments for convergence to the steady state (1.5) and for the exponential decay rate of that convergence are a bit more specialized and will be presented specifically in the context of (1.1), (1.3) — although it is clear that variations on the argument would apply to systems with suitably similar properties.

The technical difficulties associated with well-posedness are related to the lack of a uniform Lipschitz bound for the nonlinearity; one cannot, then, *a priori* exclude the possibility of blowup in finite time. In particular, the positive term $+\lambda uv$ in the third equation of (1.1) makes it more difficult to obtain a uniform bound for w: there seems to be no (fixed) invariant set. From (1.4), we expect to obtain bounds by 'conservation' but these are inherently L^1 bounds and some effort is needed to see that we will actually have exponential decay to the steady state in L^∞. Further, it is not clear that the regularity of the transport terms supports a classical interpretation for the ordinary differential equations governing the bulk concentrations and it will be necessary to reformulate the problem so as to defer consideration of this regularity.

2. Formulation of the problem

We wish to formulate our problem in a slightly more general form. Denote

$$\mathbf{u} := [u_1, \ldots, u_m], \qquad \mathbf{U} := [U_1, \ldots, U_m], \qquad \mathbf{D} := \operatorname{diag}\{D_1, \ldots, D_m\}$$

and let $\boldsymbol{\zeta} := [\zeta_1, \ldots, \zeta_m]$, with

$$\zeta_j : \;=\; \sigma\left[-D_j[u_j]_x\Big|_{x=1} + \int_0^1 \gamma_j u_j\,dx\right] \tag{2.1}$$

$$\boldsymbol{\Gamma} : \;=\; \operatorname{diag}\left\{\sigma\int_0^1 \gamma_1\,dx, \ldots, \sigma\int_0^1 \gamma_m\,dx\right\} \tag{2.2}$$

be the the coupling terms. Here we suppose that σ and each D_j is a positive constant and that each $\gamma_j = \gamma_j(\cdot)$ is in $L^\infty[0,1]$:

$$|\gamma_j(x)| \le M \qquad \text{ae on } [0,1]. \tag{2.3}$$

[Remark: We do not pursue the possibility of a more refined treatment which could permit, e.g., $\gamma_j \in H^{-1}(0,1)$ with a one-sided bound; compare [11].] Next, we introduce functions

$$\mathbf{f}^0 : \mathbb{R}_+ \times [0,1] \times \mathbb{R}^m \to \mathbb{R}^m, \qquad\qquad \mathbf{f}^1 : \mathbb{R}_+ \times \mathbb{R}^m \to \mathbb{R}^m, \tag{2.4}$$

and consider systems of the form

$$\dot{\mathbf{u}} \;=\; [\mathbf{D}\mathbf{u}_x]_x - \boldsymbol{\gamma}[\mathbf{u} - \mathbf{U}] + \mathbf{f}^0(\cdot, \mathbf{u}) \tag{2.5}$$

$$\dot{\mathbf{U}} \;=\; \boldsymbol{\zeta} - \boldsymbol{\Gamma}\mathbf{U} + \mathbf{f}^1(\cdot, \mathbf{U}) \tag{2.6}$$

together with the further coupling $\mathbf{U} = \mathbf{u}\big|_{x=1}$. To this we must adjoin either Dirichlet or Neumann boundary conditions at $x = 0$. Of course, we must also impose initial conditions:

$$\mathbf{u}\big|_{t=0} = \overset{\circ}{\mathbf{u}}, \qquad \mathbf{U}(0) = \overset{\circ}{\mathbf{U}}\,. \tag{2.7}$$

Note that we do not *a priori* require that the initial data be consistent with either the boundary conditions (taken at $t = 0$) or the coupling condition $\mathbf{U} = \mathbf{u}\big|_{x=1}$ — or even that $\overset{\circ}{\mathbf{u}}$ be regular enough for such consistency to be meaningful.

If we now introduce a linear operator $\mathbf{A}$, given (formally) by

$$\begin{aligned} \mathbf{A} : [\mathbf{y}, \mathbf{Y}] \;\; &\mapsto \;\; [(\mathbf{D}\mathbf{y}')' - \boldsymbol{\gamma}(\mathbf{y} - \mathbf{Y}),\, \boldsymbol{\zeta} - \boldsymbol{\Gamma}\mathbf{Y}\,] \\ &\qquad \text{with } \boldsymbol{\zeta} := \boldsymbol{\sigma}\left[[-\mathbf{D}\mathbf{y}']\big|_{x=1} + \int_0^1 \boldsymbol{\gamma}\mathbf{y}\,dx\right] \end{aligned} \tag{2.8}$$

for suitable $[\mathbf{y}, \mathbf{Y}] \in \mathcal{X} := [L^2(0,1) \times \mathbb{R}]^m$, and a nonlinearity

$$\mathbf{F} : \mathbb{R}_+ \times [0,1] \times \mathcal{X} \to \mathcal{X} : [t, \cdot, [\mathbf{y}, \mathbf{Y}]] \mapsto [\mathbf{f}^0(t, \cdot, \mathbf{y}), \mathbf{f}^1(t, \mathbf{Y})], \tag{2.9}$$

then, setting $\mathbf{z} := [\mathbf{u}, \mathbf{U}]$ taking values in $\mathcal{X}$, we can write the system more succinctly as

$$\dot{\mathbf{z}} = \mathbf{A}\mathbf{z} + \mathbf{F}(t, \mathbf{z}) \tag{2.10}$$

along with the boundary and initial conditions.

We introduce the norm on $\mathcal{X} := [L^2(0,1) \times \mathbb{R}]^m$ given by

$$\|\mathbf{z}\|^2 := \sum_{j=1}^m \left[\sigma_j \int_0^1 |y_j|^2\,dx + |Y_j|^2\right] \text{ for } \mathbf{z} = [\mathbf{y}, \mathbf{Y}] \in \mathcal{X} \tag{2.11}$$

and also make the definition (2.8) more precise by setting

$$\mathcal{D}_{\mathbf{A}} := \left\{ [\mathbf{y}, \mathbf{Y}] \in \mathcal{X}\!: \begin{array}{l} Y_j = y_j(1) \text{ and} \\ y_j \in H^2(0,1) \text{ so } (\mathbf{D}\mathbf{y}')' \in [L^2(0,1)]^m; \\ \text{one has } \begin{cases} y_j(0) = 0 & \text{for Dirichlet conditions;} \\ y_j'(0) = 0 & \text{for Neumann conditions} \end{cases} \end{array} \right\} \tag{2.12}$$

where $'$ denotes d/dx. Note that for $\mathbf{z} = [\mathbf{y}, \mathbf{Y}]$, $\hat{\mathbf{z}} = [\hat{\mathbf{y}}, \hat{\mathbf{Y}}]$ in $\mathcal{D}_{\mathbf{A}}$ one has, using the inner product of $\mathcal{X}$ and a bit of manipulation,

$$\begin{aligned}\langle \mathbf{z}, \mathbf{A}\hat{\mathbf{z}} \rangle &= \sum_{j=1}^{m} \left[\sigma_j \int_0^1 y_j \left(\left(D_j \hat{y}_j' \right)' - \gamma_j \hat{y}_j \right) \, dx + Y_j \left([\hat{\zeta}_j - \Gamma_j \hat{Y}_j] \right) \right] \\ &= -\sum_{j=1}^{m} \sigma_j \left[\int_0^1 D_j \hat{y}_j' y_j' \, dx + \int_0^1 \gamma_j \left(\hat{y}_j - \hat{Y}_j \right) (y_j - Y_j) \right]\end{aligned}$$

since the definition of $\mathcal{D}_{\mathbf{A}}$ ensures that $y_j \hat{y}_j'$ vanishes at $x = 0$ for either Dirichlet or Neumann conditions and the terms at $x = 1$ cancel. It follows that $\mathbf{A}$ is a self-adjoint operator on the Hilbert space $\mathcal{X}$ and is semi-bounded since we have assumed that $D_j > 0$ and that γ_j is bounded. It follows that $\mathbf{A}$ is the infinitesimal generator [6] of an analytic semigroup $\mathbf{S}(\cdot)$ on $\mathcal{X}$ (a contraction semigroup if the γ_j's are non-negative, as is physically reasonable for our application.)

It is not difficult to show that the above system has a unique solution, provided that $\mathbf{F}$ is uniformly Lipschitzian. In our case, however, we do not know this *a priori* for $\mathbf{F}$ as given. We will therefore formulate a modified problem and show that that has a unique solution which is a solution of the original problem. In the subsequent section the original problem is shown to have a unique solution.

We now return to the specific system (for simplicity we set $\gamma_i = \gamma$ for $i = 1, 2, 3$),

$$\begin{aligned} u_t &= Du_{xx} - \lambda uv - \mu uw - \gamma(u - U) \\ v_t &= Ev_{xx} - \lambda uv - \gamma(v - V) \\ w_t &= Fw_{xx} + \lambda uv - \mu uw - \gamma(w - W) \end{aligned} \tag{2.13}$$

$$\begin{aligned} U_t &= \sigma[-Du_x|_{x=1} + \int_0^1 \gamma(u - U)] - \lambda UV - \mu UW \\ V_t &= \sigma[-Ev_x|_{x=1} + \int_0^1 \gamma(v - V)] - \lambda UV \\ W_t &= \sigma[-Fw_x|_{x=1} + \int_0^1 \gamma(w - W)] + \lambda UV - \mu UW \end{aligned} \tag{2.14}$$

with the boundary conditions

$$u = u^* = 1, \qquad v_x = 0, \qquad w_x = 0 \tag{2.15}$$

Note that shifting u, U (as the first and fourth components of $\mathbf{z}$) by u^* makes the boundary conditions for $\mathbf{z}$ homogeneous but does not alter $\mathbf{z}_t$ or $\mathbf{Az}$ at all.

A modified problem

$$\mathbf{z}_t = \mathbf{Az} + \hat{\mathbf{F}}(\mathbf{z}), \quad \mathbf{z}(t) \in \mathcal{D}(\mathbf{A}) \tag{2.16}$$

is constructed by using a 'restricted version' of $\mathbf{z}$ in the reaction terms — all of the components are restricted to be non–negative and, in addition, we require that u, v, U, $V \leq M$ with a fixed constant M — physically, such a restriction is perfectly natural: the concentrations u, v can be expected to take only values between zero and their initial values — and require that w, $W \leq \hat{M}(t) := M + \lambda M^2 t$. Our treatment allows generalization to other chemical kinetics with several components and different nonlinearity terms $\mathbf{F}(\cdot)$, as will be discussed in Section 7 below.

Fixing $M, \hat{M}$, we introduce the $[0, M]$–retract: $\chi(r) := r_+ \wedge M$, where $\wedge := min$, $\vee := max$, and $r_+ := r \vee 0$ and, similarly, the $[0, \hat{M}]$–retract $\hat{\chi}(r)$.

The modified terms become

$$z =: \begin{pmatrix} u-1 \\ v \\ w \\ U-1 \\ V \\ W \end{pmatrix}, \quad \hat{\mathbf{F}}(\mathbf{z}) = \lambda \begin{pmatrix} -\chi(u)\chi(v) \\ -\chi(u)\chi(v) \\ \chi(u)\chi(v) \\ -\chi(U)\chi(V) \\ -\chi(U)\chi(V) \\ \chi(U)\chi(V) \end{pmatrix} - \mu \begin{pmatrix} \chi(u)\hat{\chi}(w) \\ 0 \\ \chi(u)\hat{\chi}(w) \\ \chi(U)\hat{\chi}(W) \\ 0 \\ \chi(U)\hat{\chi}(W) \end{pmatrix}.$$

In the following, we shall repeatedly make use of the weak form of (2.16), which takes the form of the identities

$$\begin{aligned} \sigma \int \varphi u_t + \Phi U_t \quad &+ \quad \sigma \int D\varphi_x u_x + \sigma \int \gamma(\varphi - \Phi)(u - U) \\ &= \lambda[\sigma \int \varphi uv + \Phi UV] - \mu[\sigma \int \varphi uw + \Phi UW] \end{aligned} \tag{2.17}$$

$$\begin{aligned} \sigma \int \varphi v_t + \Phi V_t \quad &+ \quad \sigma \int E\varphi_x u_x + \sigma \int \gamma(\varphi - \Phi)(v - V) \\ &= -\lambda[\sigma \int \varphi uv + \Phi UV] \end{aligned} \tag{2.18}$$

$$\sigma \int \varphi w_t + \Phi W_t \quad + \quad \sigma \int F\varphi_x v_x + \sigma \int \gamma(\varphi - \Phi)(w - W)$$

$$= \lambda[\sigma \int \varphi uv + \Phi UV] - \mu[\sigma \int \varphi uw + \Phi UW] \tag{2.19}$$

valid for any φ, Φ with $\varphi|_{x=0} = 0$, $\varphi|_{x=1} = \Phi$.

Lemma 1: *Any solution of the modified problem (2.16) is a solution of the original problem (2.10).*

Proof: Take $\varphi = u_- = u \wedge 0$, $\Phi = U_-$ in (2.17). By a theorem of Stampacchia [12], we have

$$(u_-)_t = \{u_t = (u-1)_t \quad \text{if } u < 0; \quad 0 \quad \text{if } u \geq 0\} \qquad \text{a.e.},$$

etc. Thus $u_-(u-1)_t = (\frac{1}{2}{u_-}^2)_t$ and $(u_-)_x(u-1)_x = [(u_-)_x]^2$. Similarly, use $\varphi = v_-$, $\Phi = V_-$ and $\varphi = w_-$, $\Phi = W_-$, in (2.18) and (2.19), respectively. Taking into account the facts that $u_-\chi(u)\chi(v) \equiv 0$, $w_-\chi(u)\chi(v) \leq 0$, etc, we get

$$\begin{aligned}
\left(\frac{1}{2}\int_0^1 {u_-}^2\right)_t + D\int_0^1 [(u_-)_x]^2 + \frac{1}{2\sigma}\left({U_-}^2\right)_t + \int_0^1 \gamma(u-U)(u_- - U_-) &= 0 \\
\left(\frac{1}{2}\int_0^1 {v_-}^2\right)_t + E\int_0^1 [(v_-)_x]^2 + \frac{1}{2\sigma}\left({V_-}^2\right)_t + \int_0^1 \gamma(v-V)(v_- - V_-) &= 0 \\
\left(\frac{1}{2}\int_0^1 {w_-}^2\right)_t + F\int_0^1 [w_-]_x^2 + \frac{1}{2\sigma}\left({W_-}^2\right)_t + \int_0^1 \gamma(w-W)(w_- - W_-) &\leq 0
\end{aligned}$$

An easy inspection shows that the terms with the mixed products are non–negative. Adding and integrating with respect to t (noting that u_-, U_-, etc., all vanish at $t = 0$), one sees that u_-, v_-, w_-, U_-, V_-, W_- all vanish identically, showing that $u \geq 0$, $v \geq 0$, $w \geq 0$, $U \geq 0; V \geq 0; W \geq 0$ a.e.

Next, to obtain the corresponding upper bounds we use $\varphi = u_M := (u-M)_+ = [(u-1) \vee (M-1)] - (M-1)$, $\Phi = U_M$; note that now $u_M \geq 0$, $u_M(u-1)_t = (\frac{1}{2}[u_M]^2)_t$, etc. We have

$$\left(\frac{1}{2}\int_0^1 [u_M]^2\right)_t + D\int_0^1 [(u_M)_x]^2 + \frac{1}{2\sigma}\left({U_M}^2\right)_t + \int_0^1 \gamma(u-U)(u_M - U_M) \leq 0$$

and similarly for v_M, V_M. As above, one sees that u_M, v_M, U_M, V_M all vanish identically, which shows that $u \leq M$, $v \leq M$, $U \leq M$, $V \leq M$ a.e.

Finally, to study the components w, W we set $\varphi = (w - \hat{M})_+$, $\Phi = (W - \hat{M})_+$, obtaining

$$\begin{aligned}
\varphi w_t &= (w-\hat{M})_+ (w_t - \lambda M^2) + (w - \hat{M})_+ \lambda M^2 \\
&= \left(\frac{1}{2}\varphi^2\right)_t + \lambda M^2 \varphi.
\end{aligned}$$

Since $w_t \le Fw_{xx} + \lambda M^2 - \gamma(w - W)$, it follows that $(\frac{1}{2}\varphi^2)_t \le \varphi[Fw_{xx} - \gamma(w - W)]$ whence

$$\int_0^1 \left(\frac{1}{2}\varphi^2\right)_t \le F\varphi w_x\Big|_0^1 - F\int_0^1 \varphi_x w_x - \int_0^1 \varphi\gamma(w - W)$$

so

$$\left(\frac{1}{2}\|\varphi\|^2\right)_t + F\|\varphi_x\|^2 \le F\Phi w_x|_{x=1} - \int_0^1 \varphi\gamma(w - W).$$

Similarly, for Φ we have

$$\begin{aligned} \Phi W_t &= \left(\frac{1}{2}\Phi^2\right)_t + \lambda M^2\Phi \\ &\le -\sigma\Phi F w_x\Big|_{x=1} + \lambda M^2\Phi + \int_0^1 z\gamma(w - W). \end{aligned}$$

Combining, we conclude that these φ and Φ also vanish identically.

In conclusion, we observe that this means that $\hat{f}_1(u, v, w) = f_1(u, v, w)$, etc., so the modified problem coincides with the original one at the solution. ■

3. Well-posedness for the modified problem

In this section we study the existence of a solution for the modified problem by formulating an integral equation in terms of the 'variation of parameters' formula associated with the semigroup for the leading linear part of the system: $\mathbf{z}_t = \mathbf{A}\mathbf{z}$ underlying the nonlinear system (2.10). The operator $\mathbf{A}$ is as given in Section 2, and we now simply write u, U for the first and fourth components of $\mathbf{z}$ so u^* is replaced by 0 in (2.15) while u, U are replaced by $(u - 1)$, $(U - 1)$ in the definitions of $\mathbf{F}$, $\hat{\mathbf{F}}$.

From semigroup theory we know that solving the nonlinear problem is equivalent to solving the integral equation

$$\mathbf{z}(t) = \mathbf{S}(t)\mathbf{z}(0) + \int_0^t \mathbf{S}(t - s)\mathbf{F}(\mathbf{z}(s))\, ds \tag{3.1}$$

obtained by the variation of parameters formula — having a solution of (3.1) precisely corresponds to having a solution of the original system (2.13)–(2.14). We now show that the modified problem does indeed have a unique solution.

Theorem 1: *The Picard map* $\mathbf{T}$ *for the modified system (2.16), given by*

$$[\mathbf{T}z](t) := \mathbf{S}(t)\mathbf{z}(0) + \int_0^t \mathbf{S}(t-s)\hat{\mathbf{F}}(\mathbf{z}(s))\, ds,$$

is contractive for a suitable norm on $\mathcal{W} = \mathcal{W}_\mathcal{T} := \mathcal{C}([\prime, \mathcal{T}] \to \mathcal{X})$ *with* $T > 0$ *arbitrary.*

Proof: One easily sees that $\hat{\mathbf{F}}$ is Lipschitzian with a uniform constant L. For any $\mathbf{z}_0$ – say, $\mathbf{z}_0 \equiv \mathbf{z}(0)$ – write, as usual, $\mathbf{z}_{j+1}(t) = [\mathbf{T}\mathbf{z}_j](t)$. This iteration will converge to a unique solution provided the map $\mathbf{T}$ is contraction. We define the $\mathcal{W}$-norm as

$$\|\mathbf{z}\|_\mathcal{W} := \sup\{e^{-as}\|\mathbf{z}(s)\|_\mathcal{X} : \quad 0 \leq s \leq T\},$$

with $a := L/\vartheta$ for some $\vartheta < 1$. To show contractivity in this norm, let $\mathbf{z}$, $\mathbf{z}'$ be *any* functions in $\mathcal{W}$. Then

$$\begin{aligned} \|e^{-at}[\mathbf{T}\mathbf{z} - \mathbf{T}\mathbf{z}'](t)\|_\mathcal{X} &\leq \textstyle\int_0^t e^{-a(t-s)}\, \|\mathbf{S}(t-s)\, e^{-as}[\hat{\mathbf{F}}(\mathbf{z}(s)) - \hat{\mathbf{F}}(\mathbf{z}'(s))]\,\|\, ds \\ &\leq \textstyle\int_0^t e^{-a(t-s)} L\|e^{-as}[\mathbf{z}(s) - \mathbf{z}'(s)]\,\|\, ds \\ &\leq L\|\mathbf{z} - \mathbf{z}'\|_\mathcal{W} \textstyle\int_0^t e^{-a(t-s)}\, ds \\ &\leq L\|\mathbf{z} - \mathbf{z}'\|_\mathcal{W} \textstyle\int_0^\infty e^{-ar}\, dr = \vartheta\|\mathbf{z} - \mathbf{z}'\|_\mathcal{W}. \end{aligned}$$

Taking the sup over t on the left, we obtain: $\|\mathbf{T}\mathbf{z} - \mathbf{T}\mathbf{z}'\|_\mathcal{W} \leq \vartheta\|\mathbf{z} - \mathbf{z}'\|_\mathcal{W}$ so $\mathbf{T}$ is contractive in this norm. Thus there exists a unique solution on $(0, T)$ to the modified problem. We have already shown that this is necessarily also a solution of the original problem. ■

Corollary 1: *The solution depends Lipschitz continuously on the initial data.*

Proof: We consider solutions $\mathbf{z}$, $\mathbf{z}'$ with different initial data and estimate essentially as in the proof above:

$$\begin{aligned} \|e^{-at}[\mathbf{z} - \mathbf{z}'](t)\| &\leq \|e^{-at}\mathbf{S}(t)[\mathbf{z} - \mathbf{z}'](0)\| + \\ &\qquad \int_0^t e^{-a(t-s)}\, \|\mathbf{S}(t-r)e^{-as}[\hat{\mathbf{F}}(\mathbf{z}(s)) - \hat{\mathbf{F}}(\mathbf{z}'(s))\,]\,\|\, ds \\ &\leq \|[\mathbf{z} - \mathbf{z}'](0)\| + \int_0^t e^{-a(t-s)} L\|e^{-as}[\mathbf{z}(s) - \mathbf{z}'(s)]\,\|\, ds \\ &\leq \|\mathbf{z}(0) - \mathbf{z}'(0)\| + \vartheta\|\mathbf{z} - \mathbf{z}'\|_\mathcal{W}. \end{aligned}$$

so $\|\mathbf{z}-\mathbf{z}'\|_{\mathcal{W}} \le \|\mathbf{z}(0)-\mathbf{z}'(0)\|/(1-\vartheta)$. ■

Corollary 2: *A unique global solution exists on* $[0,\infty)]$.

Proof: Since $T>0$ was arbitrary, existence on $(0,\infty)$ follows by a standard Zorn's Lemma argument, ordering solutions by inclusion of domain. No finite interval gives maximality since the uniqueness shows that such a solution coincides with the restriction of one with a still larger domain. ■

4. Uniqueness for the original problem

Note that we have so far only proved existence of a solution for the original problem, although for the modified problem the argument gives uniqueness as well. Indeed, if $\hat{\mathbf{z}}$ is the solution we have just found then it is also obvious from what we know that there cannot be another distinct solution $\tilde{\mathbf{z}}$ with the same data if this would also be nonnegative and (pointwise) bounded — these would then both be solutions of the modified problem. In this section we wish to rule out any possibility that the system might also have other (non-physical) solutions in some wider class.

We try to interpret what we will mean by saying that "$\tilde{\mathbf{z}}$ is a solution" as weakly as possible and so, e.g., interpret the pair of equations for $\tilde{u}$, $\tilde{U}$ as requiring that

$$\langle y, \tilde{u}_t\rangle + D\langle y_x, \tilde{u}_x\rangle + \lambda Y\tilde{U}_t + \langle y, \lambda\tilde{u}\tilde{v} + \mu\tilde{u}\tilde{w}\rangle + \lambda Y[\tilde{U}\tilde{V} + \tilde{U}\tilde{W}] \tag{4.1}$$

vanish for suitable test functions $[y,\, Y]$ (for simplicity, we drop the additional transport terms here). The first two products $\langle\cdot\cdot\rangle$ are initially interpreted distributionally (for the first, in particular, we note that the identity (1) is to hold when integrated over time intervals with t-dependent $y\,, Y$) and the third as an integral over $(0,h)$; we thus require *a priori* that $\tilde{u}$, $\tilde{v}$, $\tilde{w} \in L^2(0,h)$ so the products $\tilde{u}\tilde{v}$, $\tilde{u}\tilde{w}$ are each integrable (when multiplied by a smooth function y). It is then not too difficult to justify going to the limit here with a sequence of smooth $[y,\, Y]$ converging (say, distributionally) to $[u-1,\, U-1]$ and so to obtain in the usual way the usual regularity: $\tilde{U}_t$, $\|\tilde{u}_t\|_{H^{-1}}$, $\|\tilde{u}_x\|$ all in $L^2(0,T)$ and $\|\tilde{u}\|$ in $L^\infty(0,T)$ so that one has the usual weak interpretation of (1). The same considerations apply, of course, to $[\tilde{v},\, \tilde{V}]$ and to $[\tilde{w},\, \tilde{W}]$ and we already know more than enough regularity for the previously obtained solution $\hat{\mathbf{z}}$ to justify the same weak interpretation there.

The proof of uniqueness is now a fairly straightforward, if messy, computation — setting $\mathbf{z} := \hat{\mathbf{z}} - \tilde{\mathbf{z}}$ and applying the Gronwall Inequality to estimate $\mathbf{z}$ so as to show $\mathbf{z} = 0$. We begin by taking $y = 2u$, $Y = 2U$ in (1) and also in the corresponding weak form of the equation for $[\hat{u},\, \hat{U}]$ and subtracting to obtain

$$\begin{aligned}(\|u\|_t)^2 + 2D\|u_x\|^2 + \lambda(U^2)_t &= -\lambda\left[\int_0^1 u(u\hat{v} + v\tilde{u}) + \lambda U(U\hat{V} + V\tilde{U})\right] \\ &\quad -\mu\left[\int_0^1 u(u\hat{w} + w\tilde{u}) + \lambda U(U\hat{W} + W\tilde{U})\right]\end{aligned}$$

Noting that $\hat{v}, \hat{V}, \hat{w}, \hat{W}$ are non-negative and that $u \equiv 0 = U$ at $t = 0$, we can integrate over $(0, t)$ to obtain the inequality

$$\|u\|^2 + D\int_0^t \|u_x\|^2 + \lambda U^2 \le K\int_0^t \left[\int_0^1 |uv\tilde{u} + uw\tilde{u}| + \lambda\left|UV\tilde{U} + UW\tilde{U}\right|\right]$$

with $K := \max\{\lambda,\, \mu\}$. We observe that since $u = 0$ at $x = 0$, we have $\|u\|_\infty \le \|u_x\|$ so

$$\int_0^1 |uv\tilde{u}| \le \|u\|_\infty \|v\| \|\tilde{u}\| \le \varepsilon\|u_x\|^2 + \frac{1}{4\epsilon}\|v\|^2\|\tilde{u}\|^2.$$

Choose $\varepsilon := \delta/2K$ (with $\delta := \min\{D, E, F\}$) to obtain

$$\|u\|^2 + \delta\int_0^t \|u_x\|^2 + \lambda U^2 \le K\int_0^t [C_\varepsilon\|\tilde{u}\|^2(\|v\|^2 + \|w\|^2) + \lambda|\tilde{U}|(U^2 + V^2 + W^2)].$$

For $[v,\, V]$ and for $[w,\, W]$ we can argue almost similarly. Since they satisfy $v_x = w_x = 0$ at $x = 0$ we use the inequality

$$\|y\|_\infty^2 \le \|y\|^2 + \|y_x\|^2,$$

(valid for all functions y on $[0, 1]$ with $y_x \in L^2$) and get, for example

$$\begin{aligned}-\int_0^1 v[\lambda\hat{u}\hat{v} - \lambda\tilde{u}\tilde{v}] &= -\lambda\int_0^1 v[\hat{u}v + u\tilde{v}] = -\lambda\int_0^1 \hat{u}v^2 - \lambda\int_0^1 vu\tilde{v} \\ &\le -\lambda\int_0^1 vu\tilde{v} \le K\int_0^1 |vu\tilde{v}| \le K\|v\|_\infty\|u\|\|\tilde{v}\| \\ &\le K(\epsilon\|v\|_\infty^2 + \frac{1}{4\epsilon}\|u\|^2\|v\|^2) \\ &\le K\epsilon\|v_x\|^2 + 2K\epsilon\|v\|^2 + \frac{K}{4\epsilon}\|u\|^2\|\tilde{v}\|^2\end{aligned}$$

Adding all the inequalities, we obtain an estimate of the form

$$\eta(t) \leq \int_0^t \beta\eta$$

with

$$\begin{aligned}\eta(t) \;:=\; & \|u\|^2 + \|v\|^2 + \|w\|^2 \\ & +\delta \int_0^t [\|u_x\|^2 + \|v_x\|^2 + \|w_x\|^2] + \lambda[U^2 + V^2 + W^2]\end{aligned}$$

and $\beta(\cdot)$ an integrable function, by our assumptions. The Gronwall Inequality then gives $\eta \equiv 0$, proving uniqueness.

5. Long–term behavior

In this section we study the asymptotic behavior of the specific system given by the formulas (2.13)–(2.14). Again, we drop the additional transport terms – keeping them would only cause notational changes. Heuristically, one can anticipate what might happen: 'first' the reactant B will be 'used up' in reaction with A, creating C; then, with no more C produced, all of the C available will react with A; finally, with no remaining reaction, A diffuses to a constant value: the fixed boundary value $u^* = 1$ at $x = 0$. The expected steady state $\mathbf{z}_*$ is thus as in (5.2), below. Note, however, that the correctness of this naive reasoning is not self–evident — certainly this 'sequencing' cannot be literally true. Further, we note that the estimates used in the previous sections do not even give a uniform bound for the component C – the estimates provided for w, W grow unboundedly with t.

To prove convergence, we begin by defining the following functions of t:

$$\begin{aligned}\varphi_1 &= \int_0^1 v\,dx + \alpha V, \\ \varphi_2 &= \varphi_1 + \int_0^1 w\,dx + \alpha W \\ \varphi_3 &= \|u-1\|^2 + \alpha(U-1)^2\end{aligned} \tag{5.1}$$

where $\alpha = 1/\sigma$. The function φ_1 describes the total amount of the component B at a given time so we expect it to be decreasing and finally vanishing.

This and similar statements for φ_2 and φ_3 are more exactly formulated in the following lemma.

Lemma 3: *Each of the functions φ_1, φ_2 and φ_3 converges as $t \to \infty$. The functions φ_1, φ_2 are decreasing with φ_1', φ_2' integrable in t on $(0, \infty)$. Moreover, the functions $\|w\|$, W are bounded and $\|u_x\|^2$, $\|v_x\|^2$, $\|w_x\|^2$ are integrable in t on $(0, \infty)$.*

Proof: Set $v_\nu := Ev_x|_{x=1}$. Noting the boundary conditions, we have

$$\left(\int_0^1 v\, dx\right)_t = v_\nu - \lambda \int_0^1 uv\, dx.$$

and, since $(\alpha V)_t = -v_\nu - \alpha\lambda UV$, we have

$$\varphi_1' = -\lambda \left(\int_0^1 uv\, dx + \alpha UV\right) \leq 0.$$

As a non–negative decreasing function, φ_1 has a limit φ_1^* as $t \to \infty$. The integrability of φ_1' then follows from the observation that, for arbitrary $t > 0$,

$$-\int_0^t \varphi_1' = \varphi_1(0) - \varphi_1(t) \leq \varphi_1(0) - \varphi_1^* < \infty.$$

A similar calculation with analogous conclusion is then possible for the function φ_2. It follows that $\int_0^1 uv$, UV, $\int_0^1 uw$, UW must each be an integrable function of t on $(0, \infty)$.

We next consider the function φ_3. Multiplying the equations for u and U in (2.13), (2.14), by $u - 1$ and $U - 1$, respectively, and integrating, we easily see that

$$\varphi_3(t) - \varphi_3(s) + 2D \int_s^t \|u_x\|^2 \leq 2\lambda \int_s^t \left(\int_0^1 uv + \alpha UV + \int_0^1 uw + \alpha UW\right).$$

Denote the integrand $(\cdots)$ on the right hand side by G and note that we have just shown that G is integrable in t on $(0, \infty)$. Taking $s = 0$ it follows that $\int_0^t \|u_x\|^2 \leq \varphi_3(0) + \int_0^t G$. Thus we see that the function $\|u_x\|^2$ is also integrable in t on $(0, \infty)$. For $s \leq t$ we have the inequality

$$|\varphi_3(t) - \varphi_3(s)| \leq 2D \int_s^\infty \|u_x\|^2 + \lambda \int_s^\infty G$$

which goes to 0 as $s \to \infty$ so $\lim_{t\to\infty} \varphi_3(t)$ does exist.

It remains to prove the boundedness of $\|w\|$ and W as functions of t. Multiplying the equations for w, W in (2.13), (2.14) by w, W and integrating by parts, we readily obtain the estimate

$$\|w\|^2 + 2F\int_0^t \|w_x\|^2 + \alpha W^2 \le 2\lambda \int_0^t \left(\int_0^1 uvw + \alpha UVW\right) + \|w_0\|^2 + \alpha W_0^2.$$

Since $H^1(0,1)$ embeds compactly in $C[0,1]$, one has, for $\varepsilon > 0$, an inequality $\|w\|_\infty \le C_\varepsilon + \varepsilon(\|w_x\|^2 + W^2)$, etc. Thus we can obtain

$$0 \le \int uvw + \alpha UVW \le \varepsilon M^2 \|w_x\|^2 + \beta\eta + C_\varepsilon$$

where we have set

$$\begin{aligned} \eta(t) &:= \|w\|^2 + F\int_0^t \|w_x\|^2 + \alpha W^2 \\ \beta(t) &:= \lambda\left[\int_0^1 uv + \alpha UV\right]. \end{aligned}$$

Choosing ε so $\varepsilon M^2\lambda \le F$, we then have $\eta(t) \le const + \int \beta\eta$. By Gronwall's Inequality this gives

$$\eta(t) \le (const)\exp[\int_0^t \beta]$$

which is uniformly bounded as $\beta = -\varphi_1'$ is integrable. This shows that $\|w\|$, W are uniformly bounded and that $\|w_x\|^2$ is integrable in t on $(0,\infty)$.

We are now ready to state the theorem describing the long–term behavior of our system.

Theorem 2: *The solution (u, v, w, U, V, W) of the system (2.13)–(2.14) converges uniformly to the steady state $(u_*, v_*, w_*, U_*, V_*, W_*)$ given by*

$$u_* \equiv 1 = U_*, \quad v_* \equiv 0 = V_*, \quad w_* \equiv 0 = W_*. \tag{5.2}$$

Proof: As earlier, let $\mathbf{z} = (u-1, v, w, U-1, V, W)$ and write the state of the system at time t as

$$\mathbf{z}(t) = \mathbf{S}(t-s)\mathbf{z}(s) + \int_s^t \mathbf{S}(t-r)\mathbf{F}(\mathbf{z}(r))\,dr.$$

where $\mathbf{S}$ is the analytic semigroup given by the linear system, etc. We first show that u, v, w belong to a compact subset of $C[0,1]$. To this end, we first consider the operators $\mathbf{A}^\vartheta$, $0 \le \vartheta < 1$, for which we hav e

$$\mathbf{A}^\vartheta \mathbf{z}(t) = \mathbf{A}^\vartheta \mathbf{S}(t-s)\mathbf{z}(s) + \int_s^t \mathbf{A}^\vartheta \mathbf{S}(t-r)\mathbf{F}(\mathbf{z}(r))\, dr.$$

Using the fact that $\mathbf{A}$ generates an analytic semigroup, we have $\|\mathbf{A}^\vartheta \mathbf{S}(\tau)\| \le M_1 \tau^{-\vartheta}$ (see e.g. [3], p.26) and obtain the estimate

$$\|\mathbf{A}^\vartheta \mathbf{z}(t)\| \le M(t-s)^{-\vartheta}\|\mathbf{z}(s)\| + \int_s^t M(t-r)^{-\vartheta}\|\mathbf{F}(\mathbf{z}(r))\|\, dr.$$

By Lemma 3 we know that $\mathbf{z}(\cdot)$ and so also the term $F(z)$ are bounded in t (one has $\|-\mu uw\|_{L^2} \le \mu M \|w\|_{L^2} \le const$, etc.). Now let M_1 be a bound so $\|z(\cdot)\|, \|\mathbf{F}(\mathbf{z}(\cdot))\| \le M_1$ and fix $\varepsilon > 0$. For any given $t \ge \varepsilon$, take $s = t - \varepsilon$ and one has

$$\|\mathbf{A}^\vartheta \mathbf{z}(t)\| \le M M_1 \left(\varepsilon^{-\vartheta} + \int_0^\varepsilon r^{-\vartheta}\, dr\right),$$

where the right hand side is a fixed constant for $\vartheta < 1$.

Consider, then, the continuous projection operator $\mathbf{P} : W \mapsto \mathcal{X}^3$. Since $\mathbf{A}$ is a closed operator, the restriction $\mathbf{P} : \mathcal{D}(\mathbf{A}) \mapsto (H^2)^3$ is continuous as well and by an interpolation argument (see e.g. [9]) we thus have for $\mathbf{z}' = (u, v, w)$

$$\|\mathbf{z}'\|_{H^{2\vartheta}} \le const \|\mathbf{A}\|_{\mathcal{D}(\mathbf{A}^\vartheta)}$$

from which we see that u, v, w are bounded in $H^{2\vartheta}$. By the Sobolev Embedding Theorem, u, v, w take values (for $t \ge \varepsilon$) in a compact subset of $C[0,1]$ if $\vartheta > 1/4$. The boundedness of U, V, W has already been noted. Hence, for any sequence $t_n \to \infty$ we can find a subsequence (t_k) for which $\mathbf{z}(t_k)$ converges to some state $\mathbf{z}_*$. It remains to show that this limit state is always as given by (1.5) — which also shows that the convergence is independent of any extraction of a subsequence.

Consider a new initial value problem, with the original initial state $\mathbf{z}_0$ replaced by the state $\mathbf{z}_*$. Denote by φ_1^* the corresponding function (1). The function φ_1^* is again decreasing; we show that it is in fact constant. Suppose, to the contrary, that there would be some $\hat{t}$ for which $\varphi_1^*(\hat{t}) < \varphi_1^*(0)$. Since $\varphi_1(\hat{t})$ clearly depends continuously on $\mathbf{z}(t)$ which, in turn, depends continuously on $\mathbf{z}(0)$ by Corollary 2 to Theorem 3.1, we may consider 'initial value problems' starting with $\mathbf{z}(t_k)$ and with $\mathbf{z}_*$, respectively, and observe that we must then have $\varphi_1(t_k+\hat{t}) \to \varphi_1^*(\hat{t})$ since $\mathbf{z}(t_k) \to \mathbf{z}_*$. On the other hand, $\varphi_1(t_k+\hat{t}) \to \lim_{t\to\infty} \varphi_1(t) = \varphi_1^*(0)$ so $\varphi_1^*(\hat{t}) \equiv \varphi_1^*(0)$.

It follows that $(\varphi_1^*)_t = -\lambda(\int_0^1 u_*(t)v_*(t) + \alpha U_*(t)V_*(t))$ vanishes identically. Hence, noting their nonnegativity, we see that $u_*v_*(t) \equiv 0$, $U_*V_*(t) \equiv 0$ and, from the equation, we conclude that $v_*(t,\cdot)$ and $V_*(t)$ remain constant. These constants must each be 0, since otherwise one would necessarily have $u_* \equiv 0$, contradicting the boundary condition at $x = 0$. The steady state for the components v, V has thus been found and the asymptotics for w, W and u, U are subsequently found in a similar way — using φ_2 and φ_3, respectively, in place of φ_1. ■

We next show that the decay to the steady state is exponential. We know at this point that a unique solution exists with $0 \le u, v, w$, $0 \le U, V, W$, with u, v, w taking values in a given compact subset of $C([0,1])$ such that $u \to u^*$, $v \to 0$, $w \to 0$ uniformly on $[0,1]$ as $t \to \infty$. We first deal with v and V. Fixing $\epsilon > 0$ arbitrary, there is some $\tau = \tau(\epsilon)$ and $M > 0$ such that

$$|u - u^*| \le \epsilon, \qquad 0 \le v \le M, \qquad 0 \le w \le M' \text{ for } \qquad x \in [0,1], \quad t \ge \tau$$

Define now $\bar{\lambda} := \lambda(u^* - \epsilon)$ so that $\lambda u \ge \bar{\lambda}$ for $t \ge \tau$ and $\bar{v}(t,\cdot) = \bar{V}(t) := Me^{-\bar{\lambda}(t-\tau)}$. We set

$$\varphi := (v - \bar{v})_+, \qquad \Phi := (V - \bar{V})_+.$$

Note that $\Phi = \varphi|_{x=1}$, if $\varphi_x \neq 0$ one has $v_x = \varphi_x$ (ae) and that where $\varphi \neq 0$ one has

$$\begin{aligned}
\varphi_t &= v_t - \bar{v}_t = v_t + \bar{\lambda}\bar{v} = v_t - \lambda\varphi + \lambda v \\
\Phi_t &= V_t - \lambda\Phi + \lambda V
\end{aligned}$$

Hence, using these φ, Φ in the identity (2.18), one has

$$\begin{aligned}
\tfrac{1}{2}[\sigma\|\varphi\|^2 + \Phi^2]_t &+ \bar{\lambda}[\sigma\|\varphi\|^2 + \Phi^2] + \sigma E\|\varphi_x\|^2 \\
&= -[\sigma \int \varphi(\lambda u)v + \Phi(\lambda U)V] + \bar{\lambda}[\sigma \int \varphi v + \Phi V] \le \quad 0
\end{aligned}$$

which, since $\varphi, \Phi = 0$ at $t = \tau$, gives $\varphi, \Phi \equiv 0$, or

$$0 \le v(t, \cdot), V(t) \le Me^{-\lambda(t-\tau)}$$

Next choose $\bar{\mu} \le \mu(u^* - \epsilon)$ so that also $\bar{\mu} \le \lambda$ and then set $\bar{c} := \lambda(u^* + \epsilon)/(\lambda - \bar{\mu})$ so that $\mu u \ge \bar{\mu}$, $(\lambda - \bar{\mu}\bar{c}\bar{V} \ge \lambda uv$. Now set

$$\varphi := ([w + \bar{c}\bar{V}] - [M' + \bar{c}M]e^{-\bar{\mu}(t-\tau)})_+, \qquad \Phi := \varphi_{x=1},$$

and note $\varphi|_{t=\tau} = (w|_{t=\tau} - M')_+ = 0$ and, as above, that $w_x = \varphi_x$ where $\varphi_x \ne 0$ and, where $\varphi \ne 0$ one has (ae)

$$\varphi_t = w_t - \bar{\lambda}\bar{c}\bar{V} + \bar{\mu}[M' + \bar{c}M]e^{-\bar{\mu}(t-\tau)} = w_t - \bar{\lambda}\bar{c}\bar{V} - \bar{\mu}[\varphi - (w + \bar{c}\bar{V})],$$

so

$$w_t = \varphi_t + \bar{\mu}\varphi + [(\bar{\lambda} - \bar{\mu})\bar{c}\bar{V} - \bar{\mu}w], \qquad \varphi \ne 0.$$

Similarly,

$$W_t = \Phi_t + \bar{\mu}\Phi + [(\bar{\lambda} - \bar{\mu})\bar{c}\bar{V} - \bar{\mu}W], \qquad \Phi \ne 0.$$

Using this in (2.19) gives

$$\begin{aligned}\tfrac{1}{2}[\sigma\|\varphi\|^2 + \Phi^2]_t \quad &+ \quad \bar{\mu}[\sigma\|\varphi\|^2 + \Phi^2] + \sigma F\|\varphi_x\|^2 \\ &= \quad -[\sigma \int \varphi(\bar{\lambda} - \bar{\mu})\bar{c}\bar{V} - \lambda uV] + \Phi[(\bar{\lambda}\bar{\mu})\bar{c}\bar{V} - \lambda UV]) \\ &\quad\; -\sigma \int \varphi[\mu u - \bar{\mu}]w + \Phi[\mu U - \bar{\mu}]W \le \quad 0\end{aligned}$$

Thus $\varphi, \Phi \equiv 0$ and we have

$$0 \le w, W \le (M' + \bar{c}M)e^{-\bar{\mu}(t-\tau)} =: \bar{W}(t).$$

We next proceed to show exponential decay for $u - u^*$, $U - u^*$. First, however, a small diversion is necessary.

LEMMA: *Let y be given on $[0, 1]$ with $y(0) = 0$. Then*

$$\sigma\|y\|^2 + y(1)^2 \le \beta(\sigma)\|y'\|^2,$$

where $\beta = \sigma/\rho^2$ where $\rho$is the smallest positive root of the equation $\rho\tan\rho = \sigma$.

Proof: Define $\mathbf{L} : z \to [y, y(1)]$ with $y(x) = \int_0^x z$ and note that the adjoint $\mathbf{L}^*$ is given by $\mathbf{L}^* : [\hat{y}, \hat{Y}] \to \hat{Y} + \sigma \int_x^1 \hat{y}$ (using the inner product $\langle [\hat{y}, \hat{Y}], [y, Y] \rangle := \sigma \int \hat{y} y + \hat{Y} Y$). Then β is the largest eigenvalue of the (positive, selfadjoint) operator $\mathbf{L}^*\mathbf{L} : L^2(0,1) \to L^2(0,1)$. Thus $\mathbf{L}^*\mathbf{L}z = \beta z$. With $z = y'$ this gives $y(1) + \sigma \int_x^1 y = \beta y'$. On the other hand, we get the boundary conditions $y(0) = 0$ and $y(1) = \beta y'(1)$. Differentiating, we also get the equation $-\sigma y = \beta y''$. Since $\beta > 0, \sigma > 0$, we have $y(x) = \sin\left(\sqrt{\sigma/\beta}\, x\right)$ and at $x = 1$ the condition $\sin \sqrt{\sigma/\beta} = \beta \sqrt{\sigma/\beta} \cos \sqrt{\sigma/\beta}$, from which the claim follows. Observe that $\rho \sim \sqrt{\beta}$ as $\sigma \to 0$, so $\beta(\sigma) \to 1$ as $\sigma \to 0$. ■

Perhaps the simplest way to treat the exponential decay for $\hat{u} := u - u^*$, $\hat{U} := U - u^*$ is to use semigroup methods, noting that we have

$$
\begin{aligned}
\hat{u}_t &= D\hat{u}_{xx} + g, \qquad \hat{u}|_{x=0} = 0, \quad \hat{u}_{x=1} = \hat{U} \\
\hat{U}_t &= \sigma[-D\hat{u}_x|_{x=1}] + G
\end{aligned}
\tag{5.3}
$$

where $g = -\lambda uv - \mu uw$, $G = -\lambda UV - \mu UW$. From our previous estimates, we have (with a suitable M)

$$0 \le g, G \le Me^{-\bar{\lambda}(t-\tau)} \qquad \text{for } t \ge \tau.$$

We may write (5.3) in semigroup form. Let $\mathcal{X}' = L^2(0,1) \times R$ with the inner product given in the lemma above and set

$$\hat{\mathbf{A}}[y, Y] := [-Dy'', \sigma D y'|_{x=1}]$$

with the domain $\mathcal{D}_{\hat{\mathbf{A}}} := \{[y, Y] : y'' \in L^2(0,1), y(0) = 0, y(1) = Y\}$. We observe that $\hat{\mathbf{A}}$ is a selfadjoint positive definite operator on $\mathcal{X}'$. Any eigenvalue $\hat{\lambda}$ for $\hat{\mathbf{A}}$ satisfies

$$\hat{\lambda} \|[y, Y]\|^2 \ge \sigma D \|y'\|^2 \ge \sigma D \frac{1}{\beta(\sigma)} \|[y, Y]\|^2,$$

i.e., $\hat{\lambda} \ge \sigma D \beta(\sigma)$. Letting $\hat{\mathbf{S}}(t)$ denote the semigroup generated by $-\hat{\mathbf{A}}$, one then has

$$
\begin{aligned}
\|\hat{\mathbf{A}}^{\vartheta} \hat{\mathbf{S}}(t)\| &= \sup\{\hat{\lambda}^{\vartheta} e^{-\hat{\lambda} t} : \hat{\lambda} \text{ an eigenvalue of } \hat{\mathbf{A}}\} \\
&\le \sup\{\hat{\lambda}^{\vartheta} e^{-\hat{\lambda} t} : \lambda \ge \sigma D \beta(\sigma)\}.
\end{aligned}
$$

By the semigroup solution of (5.3) we have with $0 \leq \vartheta \leq 1$

$$\begin{aligned}
\|\hat{\mathbf{A}}^{\vartheta}[\hat{u},\hat{U}](t)\| &\leq \|\hat{\mathbf{A}}^{\vartheta}\hat{\mathbf{S}}(t-\tau)\|\|[\hat{u},\hat{U}](\tau)\| + \int_{\tau}^{t} \|\hat{\mathbf{A}}^{\vartheta}\hat{\mathbf{S}}(t-s)\|\|[g,G](s)\|ds \\
&\leq K\left(r^{-\vartheta}e^{-\bar{\beta}r} + \int_0^r (r-\rho)^{-\vartheta}e^{-\bar{\beta}(r-\rho)}e^{-\bar{\mu}\rho}d\rho\right) \\
&\leq Ke^{-\bar{\beta}r}\left(r^{-\vartheta} + \int_0^r (r-\rho)^{-\vartheta}e^{-\bar{\mu}-\bar{\beta})\rho}d\rho\right)
\end{aligned}$$

provided $\bar{\beta} < \sigma D\beta(\sigma)$ so that one has an estimate

$$\|\hat{\mathbf{A}}^{\vartheta}\hat{\mathbf{S}}(t)\| \leq K(\beta)t^{-\vartheta}e^{-\bar{\beta}t}.$$

The term above will be bounded – uniformly in $r \geq r_0 > 0$ – if $\bar{\beta} < \bar{\mu}(< \bar{\lambda})$. As before, we have $\|\hat{u}\|_\infty \leq K\|\hat{\mathbf{A}}^{\vartheta}[\hat{u},\hat{U}]\|$ for $\vartheta > 1/4$, so we obtain

$$\|\hat{u}\|_\infty, |\hat{U}| \leq Ke^{-\bar{\beta}t} \qquad \text{for } t \geq \tau + r_0$$

provided $\bar{\beta} < \bar{\mu}$ and also $\bar{\beta} < \sigma D\beta(\sigma)$. We have now obtained the desired asympotically exponential convergence:

Theorem 3:

$$\begin{aligned}
V, \|v\|_\infty &\rightarrow 0 \text{ at a rate } e^{-\bar{\lambda}t} \quad (\text{ any } \bar{\lambda} < \lambda) \\
W, \|w\|_\infty &\rightarrow 0 \text{ at a rate } e^{-\bar{\mu}t} \quad (\text{ any } \bar{\mu} < \min\{\lambda,\mu\}) \\
U-u^*, \|u-u^*\|_\infty &\rightarrow 0 \text{ at a rate } e^{-\bar{\beta}t} \quad (\text{ any } \bar{\beta} < \min\{\lambda,\mu,\sigma D\beta(\sigma)\})
\end{aligned}$$

It is not difficult to see that the 'shape' of $u - u^*$ is asymptotically proportional to the eigenfunction we found earlier, $\sin\sqrt{\sigma/\beta}\ x$. Thus, if σ is taken to be a small parameter we have $\sin\sqrt{\sigma/\beta}\,x \sim \sqrt{\sigma/\beta}\,x$ for $0 \leq x \leq 1$ and, uniformly for large t,

$$\begin{aligned}
u(t,x) &= u^* + (U-u^*)x + o(e^{-\bar{\beta}t}), \\
u_x(t,1) &= (U-u^*) + o(e^{-\bar{\beta}t}).
\end{aligned} \tag{5.4}$$

The usual 'film theory' analysis takes u as corresponding to its quasi–steady–state form which (for $v, w \sim 0$) is just a straight line. This analysis (neglecting v, w) takes

$$U_t = \sigma D u_x|_{x=1} \sim -\sigma D(U-u^*)$$

giving

$$U - u^* \sim ce^{-\sigma D t} \qquad \text{as } t \to \infty.$$

Comparing this to the decay rate obtained above, we see that $\beta(\sigma) \searrow 1$ so $\sigma D\beta(\sigma) > \sigma D$ and we actually get (slightly) faster decay than the film theory indicates (assuming $\lambda, \mu > \sigma D\beta(\sigma)$), with asymptotic agreement as $\sigma \to 0$.

6. Modeling and simulation

In chemical literature the film theory is used as a tool for the calculation of gas/liquid reactions, especially in accounting for the enhancement of the mass transfer from gas to liquid due to the reaction already taking place 'at the interface'. From this point of view, the 'film' is a theoretical construct since only the bulk concentrations, determined by the reactions in the bulk and by the mass transfer between the gas and bulk liquid, are of practical interest. In the film theory this mass transfer is given by the source terms in the equations for the bulk concentrations, i.e., by the gradients at $x = 0$ and $x = 1$. Proportional to the gradient at $x = 0$ is the so called 'enhancement factor' which gives the increase of mass transfer from gas to liquid due to reaction as compared to the mass transfer obtained with pure diffusion. Approximate ways of computing this enhancement factor in special cases with steady state and simple kinetics are found in the chemical literature [15]. Alternative ways to model transient gas/liquid mass transfers are the 'penetration theory' and the 'surface renewal theory', cf. [7].

In fact, the use of the film theory in chemical engineering is mainly restricted to steady–state cases. We remark that the treatments in the literature and discussions with chemical engineers have not resolved the question of whether, as is implicit here, one actually has a physically 'real' film of liquid moving with the bubble or whether, as suggested by P. Fife [3], this model may be a metaphor for a singular perturbation analysis involving a boundary layer. In the former case, of course, our treatment has practical implications as well as its intrinsic mathematical interest. Closest to our treatment are some articles dealing with examples of transient film models under the title 'film–penetration theory', cf. [7].

We have here assumed the system to be *dynamic*, with a given initial state at $t = 0$. Such a system models adequately two types of reactors: (i) a fully 'batch' reactor characterized by fixed amount of reactants in which the gas is brought into the liquid all at once, so all the bubbles begin the reaction with the same initial conditions at $t = 0$. (ii) steady state operation of a co–current column reactor for which the role of the time variable t is played by the height coordinate of the column. A practical example is discussed in [5].

In the more common 'semi–batch' reactor the bubbles are fed into the liquid continuously and we note that our model does not quite fit this. The situation differs from the full–batch one in that the bubbles have varying initial conditions: a bubble coming in at time $t = \tau$ has the initial conditions as in (2.7) where the right hand sides are to be replaced by $U(\tau)$, $V(\tau)$, $W(\tau)$. One then has $u = u(t, x, \tau)$ for $t \geq \tau$, and the flux into U involves an integral with respect to τ, etc. We intend to treat such systems elsewhere.

As noted above, film models are used to compute the enhancement factor, i.e. the gradient at the film boundaries. Perhaps the most straightforward way to solve the parabolic system of equations numerically is to use the method of lines: discretize the system with respect to the spatial variable with a finite difference formula, and integrate the resulting ODE system with any standard ODE solver. One may encounter numerical problems of accuracy with very fast reactions, and one expects that some care in selection of the difference scheme will be needed. Useful difference formulae are discussed, e.g., in [10].

In systems like $A + B \mapsto C$ the concentrations are bounded by the initial values. In such cases the algorithm described should satisfy the *discrete maximum principle*: the computed solutions also stay between the limits given by the initial values. For more details, see [13], [4].

7. Discussion

In our treatment we have only considered the specific system (2.13)–(2.14) but the approach here is not restricted to this. Other kinetics can be handled by the same methods. The number of components may be arbitrarily large. The essential properties of the nonlinearity $\mathbf{F}$ appearing in Sections 2 and 3 are that the modified $\hat{\mathbf{F}}$ be Lipschitzian and that its components satisfy such conditions as $u_-\hat{f}_1(u, v, w) \leq 0$, $v_-\hat{f}_2(u, v, w) \leq 0$, $\hat{f}_3 \leq const.$ The boundary conditions may also be modified.

A special case of interest is to consider the situation when the first reaction $A+B \to C$ is 'very fast' compared to $A+C \to ..$ With an increasing reaction rate constant λ, the concentration profiles of A and B in the film become more and more v–shaped (cf. Figure 3), since the reactants 'eat' each other almost immediately. In the limit we can expect A and B to meet at one moving point only. This naive picture thus leads to (i) a free boundary problem for the 'reduced problem', (ii) a singular perturbation problem for the asymptotics of the relation between the problems. These questions will be studied in [8].

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