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ASYMPTOTIC ANALYSIS OF DISSOLUTION OF A SPHERICAL BUBBLE (CASE OF FAST REACTION OUTSIDE THE BUBBLE)

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ABSTRACT. This paper analyzes the dissolution of a spherical gas bubble as the gas diffuses out of the bubble into a liquid and is consumed by a fast reaction in the liquid. Due to the fast reaction a small parameter ε appears in the problem formulation which makes the problem singularly perturbed. The boundary function method is used to derive uniform asymptotic approximations to the bubble's radius and gas concentration in the liquid. Existence, and uniqueness of the solution, as well as the asymptotic correctness of the approximations are shown.

1. Introduction. We consider a gas bubble moving through a liquid in a bubble reactor and shrinking as the gas is consumed in a reaction occurring near the surface of the bubble. In modeling different types of bubble reactors, catalytic bubble reactors, etc., the, so-called, film model [**2**] is widely used. According to this model it is assumed that the reactions accompanied by rapid spatial changes in concentration of the reacting components occur only in a 'thin film' near the surface of the bubble whereas concentrations of the reacting substances in the bulk of the liquid and inside the bubbles are constant in space and only change in time. In more complicated models, involving also the catalyst particles, the presence of two types of films is assumed: one near the surface of gas bubbles, and the other near the surface of catalyst particles. As of now, in practical calculations chemical engineers do not take into account the process of shrinking of the bubbles as they move through the reactor (the gas/liquid ratio is one of the parameters playing an important role in the reactor design, and it is assumed to be constant throughout the reactor in practical calculations [**4**]).

In this paper we attempt a more realistic approach that, in the case of fast reactions, allows us to eliminate the 'film' assumption. The concentrations will now be nonconstant in the bulk liquid but we

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will still have quite a simple description of the concentration profiles in the vicinity of the bubble surface. (The method that we discuss is very useful for real life applications since the reactions in bubble reactors are usually fast [**3**].) The equation we are going to work with is quasi-linear, subject to some initial conditions and the boundary conditions prescribed on a moving boundary whose position must also be determined during the solution process. One of the questions of interest that we are going to address is related to estimating the time it takes to completely dissolve the bubble.

The boundary function method [**5**] is used to construct the asymptotic approximation of the solution. The novelty of the result lies in the fact that the boundary function method has not been used so far for constructing asymptotic expansions for partial differential equations in domains with moving boundaries. The approach suggested in this paper is expected to also work for Stefan type problems, and the authors are planning such investigations in the future. In the case of the fast reaction the asymptotic procedure allows one to decouple the nonlinear conditions (originally coupled), which makes the resulting asymptotics very simple. (Note that the simpler the asymptotics the more useful it is in qualitative analysis of the reactor model and as an initial iterate for numerical calculations associated with the reactor design process.)

An important part of the analysis is the proof of the theorem on estimation of the remainder terms. It justifies the correctness of the asymptotic procedure used to construct the asymptotic expansion of the solution of the original problem. The method of successive approximations together with estimates for different types of Green's functions is used in proving this theorem. The new feature in the proof is the presence of two consecutive previous terms in the expression for the estimate of each current term in the successive approximations procedure. To handle this situation, the ideas related to solution of second order difference equations are used.

The paper is organized as follows. In Section 2 the statement of the problem is discussed. In Section 3 the asymptotic algorithm is presented. The theorem on estimation of the remainder terms is formulated and proved in Section 4. Brief discussion of the results can be found in Section 5.

2. Statement of the problem. We consider a gas bubble, containing a single species Y, in a liquid. The gas crosses the bubble's boundary, diffuses into the liquid, and is consumed in a fast reaction. We assume that the gas concentration k_1, as well as the pressure, and thus the gas density inside the bubble, are constant. Outside the bubble the concentration of Y drops off rapidly due to the reaction.

Let $\rho(\tau)$ be the radius of the gas bubble at time τ, with $\rho(0) = \rho_0$. Let $y(r, \tau)$ be the concentration of Y in the liquid at distance r from the bubble's center at time τ. The diffusion of Y away from the bubble together with the reaction that consumes the diffused gas is modeled by the equation

$$y_\tau - D\nabla^2 y = h(y).$$

Here D is a diffusion coefficient and ∇^2 is the Laplace operator. We consider $h(y)$ with $h(0) = 0$, that is, the reaction goes on only in the presence of Y. We assume that the gas is only being consumed in the reaction and not produced, and so $h(y) < 0$ for $y > 0$. We also assume that the reaction is fast. That is, the characteristic time of reaction proportional to $1/h'(y)$ is much smaller than characteristic diffusion time ρ_0^2/D (here ρ_0 is the initial radius of the bubble). Below, during the nondimensionalization, we will be using some other characteristic diffusion time assuming that its order is the same as the order of ρ_0^2/D. This will lead to appearance of a small parameter ε during nondimensionalization.

In the current statement of the problem we do not take into account hydrodynamic effects related to the motion of the bubble. We assume that the radius of the bubble is small and that the bubble moves slowly. We also assume that the shape of the gas bubble is spherical and that the concentration of Y in the liquid surrounding the bubble is radially symmetric. The *Laplacian* in the spatially three-dimensional radially symmetric case is given by

$$\nabla^2 y = \left(\frac{2}{r}\right) y_r + y_{rr}.$$

Assuming the flux across the bubble's boundary is proportional to the difference in concentrations of Y inside and outside the bubble, we get, using Fick's law, the boundary condition

$$-Dy_r\,(\rho(\tau), \tau) = k_2(k_1 - y(\rho(\tau), \tau)). \tag{2.1}$$

Here k_2 is the mass transfer coefficient. The initial concentration of Y in the liquid is assumed to be zero:

$$y(r,0) = 0 \quad \forall\, r \geq \rho_0.$$

We next derive an equation relating the bubble's radius to the concentration $y(\rho(\tau),\tau)$ of Y in the liquid at the bubble's boundary. We start with the conservation of mass relation

$$\begin{pmatrix}\text{initial amount of}\\ \text{Y in the bubble}\end{pmatrix} - \begin{pmatrix}\text{amount of Y}\\ \text{in the bubble}\\ \text{at time } \tau\end{pmatrix} = \begin{pmatrix}\text{amount of } Y \text{ which}\\ \text{has left the bubble}\\ \text{from time 0 to time } \tau\end{pmatrix}.$$

Assuming that the gas in the bubble acts in accordance with the perfect gas law, and recalling that the pressure and temperature are constant, we obtain

$$\frac{4}{3}\pi\rho_0^3 k_1 - \frac{4}{3}\pi\rho^3(\tau)k_1 = \begin{pmatrix}\text{amount of } Y \text{ which}\\ \text{has left the bubble}\end{pmatrix}.$$

By Fick's law, the total flux across the bubble's boundary at time τ is given by

$$[4\pi\rho^2(\tau)][-D\, y_r(\rho(\tau),\tau)],$$

so we get

$$\frac{4}{3}\pi(\rho_0^3 - \rho^3(\tau))k_1 = -\int_0^\tau 4\pi\rho^2(\tilde{\tau})D\, y_r(\rho(\tilde{\tau}),\tilde{\tau})\, d\tilde{\tau}.$$

Taking the derivative of the above relation with respect to τ, and using (2.1), we obtain

$$k_1\rho'(\tau) = -k_2(k_1 - y(\rho(\tau),\tau)).$$

We nondimensionalize the problem as follows. Let $s = (r-\rho(\tau))k_2/D$ be rescaled nondimensional distance from bubble's boundary; $s \geq 0$; let $R(t) = \rho(\tau)k_2/D$ be rescaled nondimensional bubble's radius; let $t = \tau k_2^2/D$ be rescaled nondimensional time; $0 \leq t < T$ where T is yet to be determined; and $u(s,t) = y(r,\tau)/k_1$ be rescaled nondimensional concentration. Also let $r_0 = \rho_0 k_2/D$, $\hat{g}(u) = h(k_1 u)/k_1$.

Then we get the nondimensionalized equation:

$$u_t = u_{ss} + \left[\frac{2}{s+R(t)} + R'(t)\right]u_s + \frac{D\hat{g}(u)}{k_2^2}.$$

To mathematically realize the fast reaction condition we can, e.g., define $g(u)$, and $0 < \varepsilon \ll 1$ by

$$g(u) = -\frac{\hat{g}(u)}{\hat{g}'(0)}, \qquad \varepsilon^2 = -\frac{k_2^2}{\hat{g}'(0)D}.$$

Here the parameter ε is squared for notational convenience, see the description of the asymptotic procedure below. Note that, as defined, $g'(0) = -1$.

We obtain the problem:

$$u_t = u_{ss} + \left[\frac{2}{s+R(t)} + R'(t)\right]u_s + \frac{g(u)}{\varepsilon^2}, \tag{2.2}$$

$$u(s,0) = 0, \tag{2.3}$$

$$u_s(0,t) - u(0,t) = -1, \tag{2.4}$$

$$R'(t) = u(0,t) - 1, \tag{2.5}$$

$$R(0) = r_0. \tag{2.6}$$

Note that since $h(0) = 0$ and $h(y) < 0$ for $y > 0$, similar properties will also hold for g: $g(0) = 0$, $g(u) < 0$ for $u > 0$. In what follows we assume that $g(u)$ is a sufficiently smooth function. Particular requirements on the smoothness of g will be introduced later (in the formulation of the theorem on estimation of the remainder).

Next, we apply the boundary function method to analyze (2.2)–(2.6).

3. Asymptotic approximation. We seek an asymptotic approximation, *uniform* in the domain ($0 \le s < \infty$, $0 \le t < T = \text{const}$), of the solution to the system (2.2)–(2.6) in the form

$$u = Q(\xi, t, \varepsilon) + P(\xi, \eta, \varepsilon), \tag{3.1}$$

where $\xi = s/\varepsilon$, $\eta = t/\varepsilon^2$ are the stretched variables, the function Q represents a boundary layer near the bubble's boundary; the, so-called, corner boundary function P is needed to compensate for the discrepancy introduced by Q in the initial condition in the vicinity of point $(0,0)$. We require boundary functions to be expandable in power series in ε, e.g., $Q(\xi,t,\varepsilon)=Q_0(\xi,t)+\varepsilon Q_1(\xi,t)+\cdots$. We also require all boundary functions to decay to zero as corresponding stretched variable tend to infinity, e.g., $Q_i(\xi,t)\to 0$ as $\xi\to\infty$.

Remark. Formally, according to boundary function method algorithm, we must seek the asymptotic approximation to the solution of (2.2)–(2.6) in the form $u=\bar{u}+\Pi+Q+P$, where $\bar{u}$ is the regular part of the asymptotics describing the concentration of Y in the bulk liquid away from the bubble's boundary and away from the initial instant of time, and Π is the boundary function describing the bulk liquid concentration of Y in the initial transition layer. This function must be important in the vicinity of the initial instant of time. However, for our particular formulation, zero initial concentration of Y in the bulk, $g(0)=0$, etc., it can be easily shown that $\bar{u}\equiv 0$ and $\Pi\equiv 0$. For example, to the leading order the regular part of the asymptotics, $\bar{u}_0(s,t)$, must satisfy the original equation with $\varepsilon=0$. In our case, it is simply $g(\bar{u}_0(s,t))=0$, and so $\bar{u}_0=0$. In a similar way analogous relations are obtained for regular functions in higher order approximations, and for the leading and higher order approximations for Π. Thus, we do not need to include these terms in our representation (3.1).

After substituting (3.1) into (2.2)–(2.6) we can separate the terms and get the following problems:

$$Q_{\xi\xi}+Qg=\varepsilon^2 Q_t-\varepsilon\left(R'(t)+\frac{2}{R(t)+\xi\varepsilon}\right)Q_\xi, \tag{3.2}$$

$$Q_\xi(0,t)=\varepsilon[Q(0,t)-1], \tag{3.3}$$

and

$$P_\eta-P_{\xi\xi}-Pg=\varepsilon\left[R'(\varepsilon^2\eta)+\frac{2}{R(\varepsilon^2\eta)+\xi\varepsilon}\right]P_\xi, \tag{3.4}$$

$$P(\xi,0)=-Q(\xi,0), \tag{3.5}$$

$$P_\xi(0,\eta)=\varepsilon P(0,\eta), \tag{3.6}$$

together with

$$R'(t)=Q(0,t)+P(0,\eta)-1, \tag{3.7}$$

$$R(0)=r_0. \tag{3.8}$$

Here

$$Qg = g(Q), \qquad Pg = g(Q+P) - g(Q),$$

so that $g = Qg + Pg$.

Now let us expand the functions Q, P, and R in power series in epsilon: $Q(\xi, t, \varepsilon) = Q_0(\xi, t) + \varepsilon Q_1(\xi, t) + \cdots$, $P(\xi, \eta, \varepsilon) = P_0(\xi, \eta) + \varepsilon P_1(\xi, \eta) + \cdots$, $R(t, \varepsilon) = R_0(t) + \varepsilon R_1(t) + \cdots$, and substitute these series into (3.2)–(3.8). We also use the following expansions for Qg and Pg: in (3.2)

$$\begin{aligned} Qg &= g(Q(\xi, t, \varepsilon)) \\ &= g(Q_0(\xi, t) + \varepsilon Q_1(\xi, t)) + O(\varepsilon^2) \\ &= g(Q_0(\xi, t)) + \varepsilon g'(Q_0(\xi, t)) Q_1(\xi, t) + O(\varepsilon^2), \end{aligned}$$

and in (3.4)

$$\begin{aligned} Pg &= g(Q(\xi, \varepsilon^2\eta, \varepsilon) + P(\xi, \eta, \varepsilon)) - g(Q(\xi, \varepsilon^2\eta, \varepsilon)) \\ &= g(Q_0(\xi, \varepsilon^2\eta) + \varepsilon Q_1(\xi, \varepsilon^2\eta) + P_0(\xi, \eta) + \varepsilon P_1(\xi, \eta)) \\ &\quad - g(Q_0(\xi, \varepsilon^2\eta) + \varepsilon Q_1(\xi, \varepsilon^2\eta)) + O(\varepsilon^2) \\ &= g(Q_0(\xi, \varepsilon^2\eta) + P_0(\xi, \eta)) - g(Q_0(\xi, \varepsilon^2\eta)) \\ &\quad + \varepsilon g'(Q_0(\xi, \varepsilon^2\eta) + P_0(\xi, \eta))[Q_1(\xi, \varepsilon^2\eta) + P_1(\xi, \eta)] \\ &\quad - \varepsilon g'(Q_0(\xi, \varepsilon^2\eta)) Q_1(\xi, \varepsilon^2\eta) + O(\varepsilon^2). \end{aligned}$$

Equating separately Q-, P-, and R- terms multiplying like powers of epsilon in resulting expressions, we arrive at the following problems. For Q_0 we have

$$Q_{0\,\xi\xi} - g(Q_0) = 0,$$

$$Q_{0\,\xi}(0, t) = 0, \qquad Q_0(\infty, t) = 0.$$

The trivial solution is the only solution that satisfies the equation and conditions. Thus, $Q_0 = 0$. For P_0 we have

$$P_{0\,\eta} - P_{0\,\xi\xi} + g(Q(\xi, 0, \varepsilon) + P) - g(Q(\xi, 0, \varepsilon)) = 0,$$

$$P_0(\xi, 0) = 0, \qquad P_{0\,\xi}(0, \eta) = 0, \quad P_0(\xi, \eta) \longrightarrow 0 \text{ as } \xi + \eta \longrightarrow \infty.$$

This also has only the trivial solution: $P_0 = 0$. The problem for the leading order approximation R_0 of the bubble's radius is

$$\begin{aligned} R_0'(t) &= -1, \\ R_0(0) &= r_0. \end{aligned}$$

This gives

$$R_0(t) = r_0 - t.$$

Equating the terms of order ε, we arrive at the following problems. For Q_1:

$$Q_{1\,\xi\xi} - Q_1 = 0, \qquad Q_{1\,\xi}(0,t) = -1, \qquad Q_1(\infty, t) = 0.$$

Thus

$$Q_1(\xi, t) = \exp[-\xi]. \tag{3.9}$$

Note that the boundary layer function Q_1 decays exponentially away from the bubble's boundary. For the corner boundary function P_1, we obtain

$$P_{1\,\eta} - P_{1\,\xi\xi} + P_1 = 0, \tag{3.10}$$

$$P_1(\xi, 0) = -Q_1(\xi, 0) = -\exp[-\xi], \tag{3.11}$$

$$P_{1\,\xi}(0, \eta) = 0, \qquad P_1(\infty, \eta) = 0. \tag{3.12}$$

Transformation of

$$w(\xi, \eta)\exp[-\eta] = P_1(\xi, \eta)$$

converts (3.10)–(3.12) into

$$w_{\xi\xi} = w_\eta, \tag{3.13}$$

$$w(\xi, 0) = -\exp[-\xi], \tag{3.14}$$

$$w_\xi(0, \eta) = 0. \tag{3.15}$$

The solution of (3.13)–(3.15) is, see, e.g., [**1**],

$$w(\xi, \eta) = \int_0^\infty G_1(\xi, x, \eta)(-\exp[-x])\,dx,$$

where

$$G_1(\xi, x, \eta) = \frac{1}{2\sqrt{\pi\eta}}\left(\exp\left[-\frac{(\xi + x)^2}{4\eta}\right] + \exp\left[-\frac{(\xi - x)^2}{4\eta}\right]\right).$$

So,

$$P_1(\xi,\eta) = \exp[-\eta]\int_0^\infty G_1(\xi,x,\eta)(-\exp[-x])\,dx.$$

It can be shown that P_1 decays exponentially away from the point $(\xi,\eta)=(0,0)$ (that is the same as the point $(s,t)=(0,0)$).

Consider now the problem for R_1:

$$R_1'(t) = Q_1(0,t) = 1,$$
$$R_1(0) = 0.$$

It has the solution

$$R_1(t) = t.$$

The asymptotic process can be continued in a similar way to obtain higher order terms of the expansion. To the first order in ε, we have the following approximations

$$u \approx \varepsilon Q_1 + \varepsilon P_1, \tag{3.16}$$
$$R \approx r_0 - t + \varepsilon t. \tag{3.17}$$

According to (3.17), the bubble's radius shrinks linearly in time. We can use (3.17) to estimate the time $\hat{T}$ it takes for the bubble to dissolve. Setting $R=0$ in (3.17), we obtain $0 = r_0 - \hat{T} + \varepsilon\hat{T}$, giving (to the first order in ε)

$$\hat{T} = \frac{r_0}{1-\varepsilon}. \tag{3.18}$$

On converting back to dimensional variables we get the approximation:

$$y \approx \varepsilon k_1 Q_1 + \varepsilon k_1 P_1, \tag{3.19}$$
$$\rho(\tau) \approx \rho_0 - (1-\varepsilon)k_2\tau. \tag{3.20}$$

4. Theorem on estimation of the remainder. Existence and uniqueness of the solution. In what follows, let

$$T = \hat{T} - \delta, \tag{4.1}$$

where $\delta > 0$ is a small constant of order $O(1)$, i.e., $\varepsilon \ll \delta \ll 1$. Here $\hat{T}$ is the first order approximation to bubble's dissolution time.

Theorem 4.1. *For sufficiently small ε and twice continuously differentiable $g(u)$ there exists a unique solution, u and R, to our original problem,* (2.2)–(2.6) *in the domain $0 \le s < \infty$, $0 \le t < T$. The approximation of this solution, $\varepsilon Q_1 + \varepsilon P_1$ and $R_0 + \varepsilon R_1$, is asymptotically accurate uniformly in this domain to order ε, i.e.,*

$$\|u - \varepsilon Q_1 - \varepsilon P_1\| = O(\varepsilon^2), \qquad \|R - R_0 - \varepsilon R_1\| = O(\varepsilon^2),$$

where $\|\cdot\|$ is the sup *norm.*

Before proceeding with the proof, it will be necessary to introduce some terms of order ε^2. These extra terms are added to our estimate only for purposes of this proof. They are not part of our approximate solution. In fact, they will not be defined exactly as the next terms of the approximation would be. Let $Q_2(\xi, t)$, $P_2(\xi, \eta)$, and $R_2(t)$ be defined by

$$\begin{gathered}
Q_{2\,\xi\xi} - Q_2 = 0, \qquad Q_{2\,\xi}(0,t) = Q_1(0,t) = 1, \qquad Q_2(\infty, t) = 0; \\
P_{2\,\eta} - P_{2\,\xi\xi} + P_2 = 0, \qquad P_2(\xi, 0) = -Q_2(\xi, 0), \qquad P_{2\,\xi}(0,\eta) = P_1(0,\eta); \\
R_2'(t) = Q_2(0,t), \qquad R_2(0) = 0.
\end{gathered}$$

Thus, $Q_2(\xi, t) = -\exp[-\xi]$, $R_2(t) = -t$, and P_2 can be expressed similarly to P_1:

$$\begin{aligned}
P_2 &= -\exp[-\eta] \int_0^\infty G_1(\xi, x, \eta) Q_2(x, 0)\, dx \\
&\quad - \exp[-\eta] \int_0^\eta G_1(\xi, 0, \eta - \tau) P_1(0, \tau)\, d\tau \\
&= -P_1 - \exp[-\eta] \int_0^\eta G_1(\xi, 0, \eta - \tau) P_1(0, \tau)\, d\tau.
\end{aligned}$$

It can be seen that $-1 \le P_1 \le 0$, and $0 \le P_2 \le 2$. We can also show that $\|P_{2\,\xi}\| \le 2$. Next, we define the remainder terms v and ψ by

$$\begin{aligned}
u &= \varepsilon Q_1 + \varepsilon P_1 + \varepsilon^2 Q_2 + \varepsilon^2 P_2 + v, \\
R &= R_0 + \varepsilon R_1 + \varepsilon^2 R_2 + \psi.
\end{aligned} \tag{4.2}$$

By proving that the problem for the remainder terms v and ψ has a unique solution and $\|v\| = O(\varepsilon^2)$, $\|\psi\| = O(\varepsilon^2)$, we will prove the theorem. Let us present an outline of the proof. After we derive the equations for the remainder terms v and ψ, we define sequences of successive approximations to v and ψ. We express the successive approximations by means of Green's functions. After that we estimate the asymptotic size of the successive approximations, and show the convergence of the corresponding sequences to v and ψ with $\|v\| = O(\varepsilon^2)$, and $\|\psi\| = O(\varepsilon^2)$.

Proof of the theorem. Let us introduce the notation $U = \varepsilon Q_1 + \varepsilon P_1 + \varepsilon^2 Q_2 + \varepsilon^2 P_2$, $\tilde{R}_2 = R_0 + \varepsilon R_1 + \varepsilon^2 R_2$. Substituting $u = U + v$ and $R = \tilde{R}_2 + \psi$, see (4.2), into equations (2.2)–(2.6), we obtain:

$$v_t = v_{ss} - \frac{v}{\varepsilon^2} + \left[\frac{2}{s + \tilde{R}_2 + \psi} + \tilde{R}_2' + \psi'\right][v_s + U_s] + \left[\frac{g(U+v) + (U+v)}{\varepsilon^2}\right] \tag{4.3}$$

$$v(s,0) = 0, \tag{4.4}$$

$$v_s(0,t) - v(0,t) = \varepsilon^2 [Q_2(0,t) + P_2(0,\eta)], \tag{4.5}$$

$$\psi'(t) = \varepsilon P_1(0,\eta) + \varepsilon^2 P_2(0,\eta) + v(0,t), \tag{4.6}$$

$$\psi(0) = 0. \tag{4.7}$$

Let us introduce successive approximations as follows. We define two sequences of functions, $v^1, v^2, v^3, \dots$ and $\psi^1, \psi^2, \psi^3, \dots$ by:

$$v^1(s,t) = 0, \qquad \psi^1(t) = 0;$$

and

$$v_t^{i+1} = v_{ss}^{i+1} - \frac{v^{i+1}}{\varepsilon^2} + f^i, \tag{4.8}$$

$$v_s^{i+1}(0,t) - v^{i+1}(0,t) = \lambda(t), \tag{4.9}$$

$$v^{i+1}(s,0) = 0, \tag{4.10}$$

$$\psi_t^{i+1}(t) = \varepsilon\, P_1(0,\eta) + \varepsilon^2\, P_2(0,\eta) + v^i(0,t), \tag{4.11}$$

$$\psi^{i+1}(0) = 0, \tag{4.12}$$

where

$$f^i = \theta^i[v_s^i + U_s] + \frac{g(U+v^i)+(U+v^i)}{\varepsilon^2},$$

$$\theta^i = \frac{2}{s+\tilde{R}_2+\psi^i} + \tilde{R}_2' + \psi_t^i, \qquad \lambda = \varepsilon^2\,[Q_2(0,t)+P_2(0,\eta)].$$

Solution to (4.8)–(4.12) can be written using Green's functions. Define $W(s,t)$ by

$$W(s,t) = \exp\left[\frac{t}{\varepsilon^2}\right](v^{i+1}(s,t)+\lambda(t)). \tag{4.13}$$

Then, using (4.8)–(4.10), we obtain:

$$W_t = W_{ss} + \exp\left[\frac{t}{\varepsilon^2}\right]\left[\lambda'(t) + \frac{\lambda(t)}{\varepsilon^2} + f^i(s,t)\right], \tag{4.14}$$

$$W(s,0) = 0, \tag{4.15}$$

$$W_s(0,t) - W(0,t) = 0. \tag{4.16}$$

According to [**1**], the solution of (4.14)–(4.16) can be written as:

$$\begin{aligned} W(s,t) &= \int_0^t\int_0^\infty G_3(s,\zeta,t-\tau)\exp\left[\frac{\tau}{\varepsilon^2}\right] \\ &\qquad\cdot\left[\lambda'(\tau)+\frac{\lambda(\tau)}{\varepsilon^2}+f^i(\zeta,\tau)\right]d\zeta\,d\tau \\ &= \int_0^t G_4(s,t-\tau)\exp\left[\frac{\tau}{\varepsilon^2}\right]\left[\lambda'(\tau)+\frac{\lambda(\tau)}{\varepsilon^2}\right]d\tau \\ &\quad + \int_0^t\int_0^\infty G_3(s,\zeta,t-\tau)\exp\left[\frac{\tau}{\varepsilon^2}\right]f^i(\zeta,\tau)\,d\zeta\,d\tau, \end{aligned}$$

where the Green's functions used here are

$$\begin{aligned} G_2(s,\zeta,t) &= \frac{1}{2\sqrt{\pi t}}\exp\left[-\frac{(s-\zeta)^2}{4t}\right], \\ G_3(s,\zeta,t) &= G_2(s,\zeta,t)+G_2(s,-\zeta,t) \\ &\quad - 2\int_{-\infty}^{-\zeta} G_2(s,\eta,t)\exp[\zeta+\eta]\,d\eta, \\ G_4(s,t) &= \int_0^\infty G_3(s,\zeta,t)\,d\zeta. \end{aligned}$$

Inverting (4.13), we obtain

$$\begin{aligned}
v^{i+1}(s,t) &= \exp\left[-\frac{t}{\varepsilon^2}\right]W(s,t)-\lambda(t)\\
&= \int_0^t G_6(s,t-\tau)\left[\lambda'(\tau)+\frac{\lambda(\tau)}{\varepsilon^2}\right]d\tau\\
&\quad+\int_0^t\int_0^\infty G_5(s,\zeta,t-\tau)f^i(\zeta,\tau)\,d\zeta\,d\tau\\
&\quad+\lambda(0)G_6(s,t)-\lambda(t),
\end{aligned}$$

where the following new Green's functions are used:

$$\begin{aligned}
G_5(s,\zeta,t) &= \exp\left[-\frac{t}{\varepsilon^2}\right]G_3(s,\zeta,t),\\
G_6(s,t) &= \exp\left[-\frac{t}{\varepsilon^2}\right]G_4(s,t).
\end{aligned}$$

Integrating by parts yields

$$\int_0^t G_6(s,t-\tau)\lambda'(\tau)\,d\tau = \lambda(t)-G_6(s,t)\lambda(0)-\int_0^t\left[\frac{d}{d\tau}G_6(s,t-\tau)\right]\lambda(\tau)\,d\tau.$$

Thus,

$$\begin{aligned}
v^{i+1}(s,t) &= -\int_0^t\left[\frac{d}{d\tau}G_6(s,t-\tau)\right]\lambda(\tau)\,d\tau\\
&\quad+\int_0^t G_6(s,t-\tau)\frac{\lambda(\tau)}{\varepsilon^2}\,d\tau\\
&\quad+\int_0^t\int_0^\infty G_5(s,\zeta,t-\tau)f^i(\zeta,\tau)\,d\zeta\,d\tau.
\end{aligned}\tag{4.17}$$

We will make use of the following bounds on G_6 and $G_{6\,s}$.

$$\|G_6\| = \left\|\exp\left[-\frac{t}{\varepsilon^2}\right]G_4\right\| \le \exp\left[-\frac{t}{\varepsilon^2}\right]2 \le 2.\tag{4.18}$$

$$\begin{aligned}
\left\|\int_0^t G_6(s,t-\tau)\,d\tau\right\| &\le \left\|\int_0^t 2\ \exp\left[-\frac{t-\tau}{\varepsilon^2}\right]d\tau\right\|\\
&= 2\varepsilon^2\left(1-\exp\left[-\frac{t}{\varepsilon^2}\right]\right) \le 2\varepsilon^2.
\end{aligned}\tag{4.19}$$

$$\|G_{6\,s}\| = \left\| \exp\left[-\frac{t}{\varepsilon^2}\right] G_{4\,s} \right\| \le \exp\left[-\frac{t}{\varepsilon^2}\right] \le 1. \tag{4.20}$$

$$\begin{aligned} \left\| \int_0^t G_{6\,s}(s, t-\tau)\, d\tau \right\| &\le \left\| \int_0^t \exp\left[-\frac{t-\tau}{\varepsilon^2}\right] d\tau \right\| \\ &= \varepsilon^2 \left(1 - \exp\left[-\frac{t}{\varepsilon^2}\right]\right) \le \varepsilon^2. \end{aligned} \tag{4.21}$$

We can now estimate the norm of v^{i+1}. The following bounds can be shown.

$$\|\lambda\| = \|\varepsilon^2 \left[Q_2(0,t) + P_2(0,\eta)\right]\| \le 3\varepsilon^2.$$

$$\left\| -\int_0^t \left[\frac{d}{d\tau} G_6(s, t-\tau)\right] \lambda(\tau)\, d\tau \right\| \le \|\lambda\| \left\| \int_0^t \left[\frac{d}{d\tau} G_6(s, t-\tau)\right] d\tau \right\| \le 3\varepsilon^2.$$

$$\left\| \int_0^t G_6(s, t-\tau) \frac{\lambda(\tau)}{\varepsilon^2}\, d\tau \right\| \le \left\| \frac{\lambda(\tau)}{\varepsilon^2} \right\| \left\| \int_0^t G_6(s, t-\tau) d\tau \right\| \le 6\varepsilon^2.$$

$$\begin{aligned} &\left\| \int_0^t \int_0^\infty G_5(s, \zeta, t-\tau) f^i(\zeta, \tau)\, d\zeta\, d\tau \right\| \\ &\qquad \le \|f^i\| \left\| \int_0^t \int_0^\infty G_5(s, \zeta, t-\tau)\, d\zeta\, d\tau \right\| \le \|f^i\| 2\varepsilon^2. \end{aligned}$$

Using these bounds we get

$$\|v^{i+1}(s,t)\| \le (9 + 2\|f^i\|)\varepsilon^2. \tag{4.22}$$

A similar inequality can be derived for v_s^{i+1} as follows. Using the Weirstrauss M-test it can be shown that the integrals in (4.17) converge uniformly. Thus, we can write

$$\begin{aligned} v_s^{i+1}(s,t) = &-\int_0^t \left[\frac{d}{d\tau} G_{6\,s}(s, t-\tau)\right] \lambda(\tau)\, d\tau \\ &+ \int_0^t G_{6\,s}(s, t-\tau) \frac{\lambda(\tau)}{\varepsilon^2}\, d\tau \\ &+ \int_0^t \int_0^\infty G_{5\,s}(s, \zeta, t-\tau) f^i(\zeta, \tau)\, d\zeta\, d\tau. \end{aligned}$$

Thus, using the bounds (4.20) and (4.21) stated above we get:

$$\|v_s^{i+1}(s,t)\| = \frac{1}{2}(9 + 2\|f^i\|)\varepsilon^2. \tag{4.23}$$

Lemma 4.2. *There exists a constant $M > 0$ such that for sufficiently small ε we have $\|f^i\| \le M$ for all $i \ge 0$.*

Proof. This proof uses the principle of mathematical induction. For the initial induction step we have

$$\|f^1\| = \left\|\theta^1 U_s + \frac{g(U)+U}{\varepsilon^2}\right\| \le \|\theta^1\|\,\|U_s\| + \left\|\frac{g(U)+U}{\varepsilon^2}\right\|.$$

Since $g(u)$ is twice continuously differentiable, $g(0) = 0$, and $g'(0) = -1$, we have

$$g(U) = -U + \frac{g''(a)}{2}U^2,$$

for some $0 \le a \le U$. Thus,

$$\lim_{\varepsilon\to 0}\left\|\frac{g(U)+U}{\varepsilon^2}\right\| = \lim_{\varepsilon\to 0}\left\|\frac{g''(a)(U)^2}{2\varepsilon^2}\right\| = \frac{g''(a)}{2}(\|P_1\|+\|Q_1\|)^2 = 2g''(a).$$

Since

$$\theta^1 = \frac{2}{s + r_0 - t + \varepsilon t - \varepsilon^2 t} - 1 + \varepsilon - \varepsilon^2$$

is, for small ε, an increasing function of t, the largest value of θ^1 occurs when $t = T$. Using (4.1) we get the following limit

$$\lim_{\varepsilon\to 0}\|\theta^1\| = \lim_{\varepsilon\to 0}\frac{2}{r_0 - T + \varepsilon T - \varepsilon^2 T} - 1 + \varepsilon - \varepsilon^2 = \frac{2}{\delta} - 1.$$

Since $\|U_s\| \le 2 + 3\varepsilon$, we get

$$\lim_{\varepsilon\to 0}\|f^1\| = 2\left(\frac{2}{\delta} - 1\right) + 2g''(a). \tag{4.24}$$

Suppose that M is any fixed constant such that

$$M > 2\left(\frac{2}{\delta} - 1\right) + 2g''(a).$$

Then by continuity there exists an $\varepsilon_0 > 0$ such that $\|f^1\| \leq M$, whenever $0 < \varepsilon \leq \varepsilon_0$.

Now we assume that the induction hypothesis is true for all $i \leq j$ and show that it is true for $i = j + 1$. From (4.22), (4.23), and the induction hypothesis we get

$$\|v^{i+1}\| \leq (9 + 2M)\varepsilon^2, \qquad \|v_s^{i+1}\| = \frac{1}{2}(9 + 2M)\varepsilon^2. \tag{4.25}$$

Using (4.11), we get

$$\|\psi_t^{j+1}\| \leq \varepsilon\|P_1\| + \varepsilon^2\|P_2\| + \|v^j\| \leq \varepsilon + 2\varepsilon^2 + (9 + 2M)\varepsilon^2,$$

and

$$\|\psi^{j+1}\| \leq (\varepsilon + 2\varepsilon^2 + (9 + 2M)\varepsilon^2)T.$$

Thus,

$$\|f^{j+1}\| = \left\| \left(\frac{2}{s + \tilde{R}_2 + \psi^{j+1}} + \tilde{R}_2' + \psi_t^{j+1} \right) [v_s^{j+1} + U_s] + \frac{g(U + v^{j+1}) + U + v^{j+1}}{\varepsilon^2} \right\|$$

has the same limit as $\|f^1\|$, i.e.,

$$\lim_{\varepsilon \to 0} \|f^{j+1}\| \leq 2\left(\frac{2}{\delta} - 1\right) + 2g''(a).$$

Thus, as in the initial induction step, for any fixed M larger than this limit there exists $\varepsilon_1 > 0$ such that $\|f^{j+1}\| \leq M$, whenever $\varepsilon \leq \varepsilon_1$. Note that the same M and ε_1 will work for all j. In what follows we will need a bound on $\|\theta^i\|$ as well. Let $M^\theta > 2/\delta - 1$ be a fixed constant. Then $\|\theta^i\| > M^\theta$ for all $i > 0$, for sufficiently small ε. □

Combining Lemma 4.2 and equation (4.22) gives $\|v^i\| \leq (9 + 2M)\varepsilon^2$ for all $i \geq 0$. Using equation (4.11) we get $\|\psi^i\| \leq (\varepsilon + 11 + 2M)T\varepsilon^2$ for all $i \geq 0$.

Lemma 4.3. *For sufficiently small ε there exists a constant N such that*

$$\|\theta^i - \theta^{i-1}\| \le N\|v^{i-1} - v^{i-2}\|.$$

Proof.

$$\begin{aligned}
\|\theta^i - \theta^{i-1}\| &\le \left\| \frac{2}{s+\tilde{R}_2+\psi^i} - \frac{2}{s+\tilde{R}_2+\psi^{i-1}} \right\| + \|\psi_t^i - \psi_t^{i-1}\| \\
&\le \left\| \frac{2(\psi^{i-1}-\psi^i)}{(s+\tilde{R}_2+\psi^i)(s+\tilde{R}_2+\psi^{i-1})} \right\| + \|\psi_t^i - \psi_t^{i-1}\| \\
&\le \left\| \frac{2}{(s+\tilde{R}_2+\psi^i)(s+\tilde{R}_2+\psi^{i-1})} \right\| \\
&\quad \cdot \|\psi^{i-1}-\psi^i\| + \|\psi_t^i - \psi_t^{i-1}\| \\
&\le \left\| \frac{2}{(s+\tilde{R}_2+\psi^i)(s+\tilde{R}_2+\psi^{i-1})} \right\| \\
&\quad \cdot \|(\psi_t^{i-1}-\psi_t^i)T\| + \|\psi_t^i - \psi_t^{i-1}\| \\
&\le \left(\left\| \frac{2T}{(s+\tilde{R}_2+\psi^i)(s+\tilde{R}_2+\psi^{i-1})} \right\| + 1 \right) \|\psi_t^i - \psi_t^{i-1}\| \\
&\le \left(\left\| \frac{2T}{(s+\tilde{R}_2+\psi^i)(s+\tilde{R}_2+\psi^{i-1})} \right\| + 1 \right) \|v^{i-1} - v^{i-2}\|.
\end{aligned}$$

We can calculate the limit

$$\lim_{\varepsilon\to 0} \left\| \frac{2T}{(s+\tilde{R}_2+\psi^i)(s+\tilde{R}_2+\psi^{i-1})} + 1 \right\| \le \frac{2T}{(r_0-T)^2} + 1.$$

Fix N larger than $(2T/(r_0-T)^2)+1$. Then there exists an $\varepsilon_2 > 0$ such that for $0 < \varepsilon \le \varepsilon_2$, we have

$$\|\theta^i - \theta^{i-1}\| \le N\|v^{i-1} - v^{i-2}\|. \qquad \square$$

To show that $\{v^i\}$ is a Cauchy sequence, we need to estimate the difference between two consecutive terms:

$$v^{i+1}(s,t) - v^i(s,t) = \int_0^t \int_0^\infty G_5(s,\zeta,t-\tau)[f^i(\zeta,\tau) - f^{i-1}(\zeta,\tau)]\, d\zeta\, d\tau.$$

$$\begin{aligned}
\|v^{i+1} - v^i\| &\le \|f^i(\zeta,\tau) - f^{i-1}(\zeta,\tau)\| \int_0^t \int_0^\infty G_5(s,\zeta,t-\tau)\,d\zeta\,d\tau \\
&\le \|f^i(\zeta,\tau) - f^{i-1}(\zeta,\tau)\| 2\varepsilon^2 \\
&\le 2\varepsilon^2 \|\theta^i[v_s^i + U_s] - \theta^{i-1}[v_s^{i-1} + U_s]\| \\
&\quad + 2\|g(U+v^i) + v^i + U - g(U+v^{i-1}) - v^{i-1} - U\| \\
&\le 2\varepsilon^2 \|(\theta^i - \theta^{i-1})(U_s)\| + 2\varepsilon^2 \|\theta^i v_s^i - \theta^{i-1} v_s^{i-1}\| \\
&\quad + \|2g''(a)[(U+v^i)^2 - (U+v^{i-1})^2]\| \\
&\le 2(2+3\varepsilon)\varepsilon^2 N \|v^{i-1} - v^{i-2}\| \\
&\quad + 2\varepsilon^2 \|\theta^i(v_s^i - v_s^{i-1}) + (\theta^i - \theta^{i-1}) v_s^{i-1}\| \\
&\quad + |2g''(a)| \|(2U + v^i + v^{i-1})(v^i - v^{i-1})\| \\
&\le 2(2+3\varepsilon)\varepsilon^2 N \|v^{i-1} - v^{i-2}\| + 2\varepsilon^2 \|\theta^i\| \|v_s^i - v_s^{i-1}\| \\
&\quad + 2\varepsilon^2 N \|v^{i-1} - v^{i-2}\| \|v_s^{i-1}\| \\
&\quad + |2g''(a)| \|2U + v^i + v^{i-1}\| \|v^i - v^{i-1}\| \\
&\le 2(2+3\varepsilon)\varepsilon^2 N \|v^{i-1} - v^{i-2}\| + 2\varepsilon^2 M^\theta \|v_s^i - v_s^{i-1}\| \\
&\quad + 2\varepsilon^2 N \|v^{i-1} - v^{i-2}\| \frac{1}{2}(9+2M)\varepsilon^2 \\
&\quad + |2g''(a)| 2(2\varepsilon + 3\varepsilon^2 + (9+2M)\varepsilon^2) \|v^i - v^{i-1}\| \\
&\le 2\varepsilon^2 M^\theta \|v_s^i - v_s^{i-1}\| \\
&\quad + (2(2+3\varepsilon)\varepsilon^2 N + N(9+2M)\varepsilon^4) \|v^{i-1} - v^{i-2}\| \\
&\quad + |2g''(a)| 2(2\varepsilon + 3\varepsilon^2 + (9+2M)\varepsilon^2) \|v^i - v^{i-1}\|.
\end{aligned}$$

The bound on $\|v_s^{i+1} - v_s^i\|$ will be exactly half as large. Since all the terms in these difference inequalities are positive we can bound $\|v^{i+1} - v^i\|$ by the solution to the difference equation

$$\begin{aligned}
d_i = (\varepsilon^2 M^\theta + |2g''(a)| 2(2\varepsilon + 3\varepsilon^2 + (9+2M)\varepsilon^2))\, d_{i-1} \\
+ (2(2+3\varepsilon)\varepsilon^2 N + N(9+2M)\varepsilon^4)\, d_{i-2},
\end{aligned}$$

subject to initial conditions related to a bound on $\|v^i\|$ obtained earlier:

$$d_0 = d_1 = (9+2M)\varepsilon^2.$$

For small enough ε, the solution to this difference equation must be small. In fact, there exists a constant C such that $d_i \leq C(1/2)^{i+1}$. Thus,

$$\|v^{i+1}(s,t) - v^i(s,t)\| \leq d_i \leq C\left(\frac{1}{2}\right)^{i+1}.$$

Let us fix some integer $L > 0$ and take $m > n > L$. Then

$$v^m - v^n = (v^m - v^{m-1}) + (v^{m-1} - v^{m-2}) + \cdots + (v^{n+1} - v^n).$$

This gives

$$\|v^m - v^n\| \leq \sum_{k=n+1}^{m} \|v^k - v^{k-1}\| \leq \sum_{k=n+1}^{m} C\left(\frac{1}{2}\right)^k \leq C\sum_{k=L}^{\infty}\left(\frac{1}{2}\right)^k.$$

Thus, for any $\alpha > 0$ there exists an integer L such that for any m, n larger than L, $\|v^m - v^n\| \leq \alpha$. Hence $v^1, v^2, \ldots$ is the Cauchy sequence and therefore uniformly converges. Since each ψ^i is defined in terms of v^{i-1}, these too must converge. Thus, for sufficiently small ε, the unique solution (v, ψ) of (4.3)–(4.7) exists, and $\|v\| = \|\lim_{n\to\infty} v^n\| = O(\varepsilon^2)$, $\|\psi\| = \|\lim_{n\to\infty} \psi^n\| = O(\varepsilon^2)$. □

5. Brief discussion of the results. We have constructed an asymptotic approximation up to the terms of the first order in small parameter ε of the solution of the nondimensionalized problem (2.2)–(2.6). Dimensional representation of the approximation is given by (3.19) and (3.20). Small parameter $\varepsilon = k_2/\sqrt{-h'(0)D}$ appears due to fast reaction, i.e., the characteristic time of the reaction is much shorter than characteristic diffusion time and characteristic time of mass transfer across the bubble's boundary.

As expected, in the case of fast reaction, the mass transfer coefficient k_2 is the key factor in determining the overall rate of the process, see (3.20).

Note that the concentration of Y in the bubble, constant k_1, does not enter into our estimate for the bubble's radius. It does, however, enter into our estimate of the concentration of Y in the liquid. Since P_1 decays exponentially away from $(\xi, \eta) = (0, 0)$, our estimate of the concentration of Y in the liquid away from the initial instant of time is given by $\varepsilon k_1 Q_1$. In dimensional variables this is:

$$\varepsilon k_1 \exp\left[-\frac{(r-\rho(\tau))k_2}{D\varepsilon}\right]. \tag{5.1}$$

This exponential decay of the concentration away from the bubble's boundary distinguishes this model, derived using the boundary function method, from the film model [**2**]. In the film model the concentration is assumed to vanish at some finite distance l, the film thickness, from the bubble's boundary. For our model there is no film thickness as such. For practical purposes, however, one could say that the concentration has vanished when it reaches some small fixed percentage, e.g., 1 percent, of its maximum at the bubble's boundary. For example, solving

$$0.01\varepsilon k_1 = \varepsilon k_1 \exp\left[-\frac{lk_2}{D\varepsilon}\right]$$

for l gives the "film thickness":

$$l = \frac{D\varepsilon \ln(100)}{k_2} = \ln(100)\sqrt{\frac{D}{-h'(0)}}.$$

Thus, our method allows us to estimate the "film thickness" which, in turn, can be used to cross-validate the assumptions of corresponding film models for particular problems with fast reaction.

Equation (5.1) suggests an alternative interpretation of the small parameter ε. Our estimate predicts that concentration of Y (after the initial instant of time) in the liquid at the bubble's boundary is εk_1. Thus, ε is that factor by which the concentration of Y drops across the bubble-liquid interface.

The case of two or more species reacting, perhaps in the presence of a catalyst, can be analyzed using the methods that we applied to this problem. In fact, the linear in time decay of the bubble's radius is observed only when one gas species $Y$is contained in the bubble. If the second, nonactive, species is present, the decay will become nonlinear in time. The authors expect to publish results on these more complicated problems elsewhere.

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