ON A FREE BOUNDARY PROBLEM FOR NONCATALYTIC GAS-SOLID REACTIONS

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I. INTRODUCTION.

In this talk, which show some results obtained jointly with L.T. Villa, we shall analyze a mathematical model of an isothermal noncatalytic diffusion-reaction process of a gas A with a solid slab S. The solid has a very low permeability and semi-thickness R along the gas diffusion direction.

Various devices and models, either phenomenological or structural, have been proposed and analyzed with the purpose of interpreting gas-solid reaction process [BeLeWa, Bi, CaCu1, CaCu2, CoRi2, Do, FaPrRi, FrBi, IsWe, LeCaCu, Le, RaDo, SaHu, SoSz1, SoSz2, St, SzEvSo, SzEv1, SzEv2, TaVi1, TaVi2, ViQu1, ViQu2, We]. We assume the solid is chemically attacked from the surface $y = R$ with a quick and irreversible reaction of order $\nu > 0$ with respect to the gas A and zero order with respect to the solid S. We also assume that the solid has uniform and constant composition. As a result of the chemical reaction an inert layer is formed which is permeable to the gas and the process will exhibit a free boundary (the reaction front) as described in [We]. The corresponding mathematical scheme (Wen's model) is formulated as follows : Find the gas concentration $C_A = C_A(y,\tau)$ and the free boundary $y = \sigma(\tau)$ such that

$$
(1)\qquad \left|\begin{array}{l}
\epsilon \dfrac{\partial C_A}{\partial t} = D \dfrac{\partial^2 C_A}{\partial y^2} \ , \ \sigma(\tau) < y < R \ , \ \tau_0 < \tau < \tau_1 \ , \\
C_A(R,\tau) = V_0(\tau) \ , \quad \tau_0 < \tau < \tau_1 \ , \\
D \dfrac{\partial C_A}{\partial y}\Big(\sigma(\tau),\tau\Big) = k_S \, a \, C_{S_0} \, C_A^{\nu}(\sigma(\tau),\tau) \ , \quad \tau_0 < \tau < \tau_1 \ , \\
- D \dfrac{\partial C_A}{\partial y}\Big(\sigma(\tau),\tau\Big) = a \, C_{S_0} \, \dot\sigma(\tau) \ , \quad \tau_0 < \tau < \tau_1 \ , \\
\sigma(\tau_0) = R_0 \le R \ , \\
C_A(y,\tau_0) = \Phi(y) \ , \quad R_0 \le y \le R \ ,
\end{array}\right.
$$

where a, C_{S_0} , D, k_S and ϵ are positive constants denoting the stoichiometric coefficient, the reactant solid concentration, the effective gas diffusion coefficient in the porous layer, the chemical reaction velocity, and the porosity of the inert layer, respectively. We are assuming that at the time τ_0 a porous layer of nonzero thickness $R - R_0$ is already formed and this explains the initial conditions (1_5), (1_6). The gas concentration is prescribed at the outer surface by condition (1_2). On the free boundary $y = \sigma(\tau)$ (1_3) express the equality of the rate of mass consumption of the component A in the reaction (r.h.s.) and the incoming mass flux of the same component (l.h.s.). Equation (1_4) states the same balance in terms of the free boundary velocity, since $-a C_{S_0} \dot\sigma(\tau)$ is again the rate of mass consumption of the gas.

We remark that in general, in gas-solid system for reaction-diffusion process, the gas surface concentration $C_A(\sigma(\tau),\tau)$ is supposed to be much smaller than C_{S_0}, the concentration of the reactant solid. So that, in the right hand side of the fourth condition in (1), the term $a C_A(\sigma(\tau),\tau)\dot\sigma(t)$ has been considered to be negligible with respect to $a C_{S_0} \dot\sigma(\tau)$. The preceding consideration does not apply, in general, to processes such as sorption of swelling solvents in polymers and this fact leads to a principal difference between the latter problem and one we are concerned with (Wen's model).

If the following dimensionless variables and parameters are introduced :

$$(2) \quad \begin{aligned} & x = C_1 \frac{R - y}{R} \ , \quad t = C_2(\tau - \tau_0) \ , \ s(t) = C_1 \frac{R - \sigma(\tau)}{R} \ , \\ & T = C_2(\tau_1 - \tau_0) \ , \quad u(x,t) = C_3\, C_A(y,\tau) \ , \ v_0(t) = C_3\, V_0\Big(\tau_0 + \frac{t}{C_2}\Big) \ , \\ & \Psi(x) = C_3\, \Phi\Big(R - \frac{R\,x}{C_1}\Big) \ , \ b = C_1 \frac{R - R_0}{R} \ , \end{aligned}$$

with

$$(3) \quad \begin{aligned} & C_1 = \frac{\phi^\nu}{\alpha^{\nu-1}} \ , \quad C_3 = \frac{\alpha}{\phi\, C_{A_0}} \ , \ \alpha = \frac{\epsilon\, R\, k_s\, C_{A_0}^\nu}{D} = \frac{\epsilon\, C_{A_0}\, \phi}{a\, C_{S_0}} \\ & C_2 = \frac{k_s\, \phi^{2\nu}\, C_{A_0}^\nu}{R\, \alpha^{2\nu-1}} = \frac{k_s^2 \left(a\, C_{S_0}\right)^{2\nu}}{D\, \epsilon^{2\nu-1}} \ , \\ & \phi = \frac{R\, k_s\, a\, C_{S_0}\, C_{A_0}^{\nu-1}}{D} \quad \text{(Thiele reaction modulus)} \ , \end{aligned}$$

where C_{A_0} denotes a reference concentration of the gas, then problem (1) is transformed into the following free boundary problem [Ta] :

$$
(4) \quad \left| \begin{array}{l}
u_{xx} - u_t = 0 \quad \text{in } D_T \ , \\
u(0,t) = v_0(t) \ , \quad 0 < t < T \ , \\
u_x(s(t),t) = -\, u^{\nu}(s(t),t) \ , \quad 0 < t < T \ , \\
u_x(s(t),t) = -\, \dot{s}(t) \ , \quad 0 < t < T \ , \\
s(0) = b \ , \\
u(x,0) = \Psi(x) \ , \quad 0 \le x \le b \ ,
\end{array} \right.
$$

where

$$
(5) \qquad D_T = \{ (x,t) \, / \, 0 < x < s(t) \, , \, 0 < t < T \} \, .
$$

From now on we shall consider $b=0$ and $v_0(t) = v_0 > 0$ and more general free boundary conditions on $x = s(t)$ are introduced. Then, the mathematical formulation of the problem consists in finding the functions $u = u(x,t)$ and $x = s(t)$ defined in D_T and $(0,T)$ respectively, such that they satisfy the following conditions

$$
(6) \quad \left| \begin{array}{l}
\text{i) } u_{xx} - u_t = 0 \quad \text{in } D_T \ , \\
\text{ii) } u(0,t) = v_0 > 0 \ , \quad 0 < t < T \ , \\
\text{iii) } s(0) = 0 \ , \\
\text{iv) } u_x(s(t),t) = g(u(s(t),t)) \ , \quad 0 < t < T \ , \\
\text{v) } \dot{s}(t) = f(u(s(t),t)) \ , \quad 0 < t < T \ ,
\end{array} \right.
$$

where f and g are real functions which satisfy

$$
(7a) \quad \left| \begin{array}{l}
\text{i) } f > 0 \ , \ f' > 0 \ \text{in } \mathbb{R}^+ \text{ and } f(0) = 0 \ , \\[2ex]
\text{ii) } g < 0 \ , \ g' < 0 \ \text{in } \mathbb{R}^+ \text{ and } g(0) = 0 \ .
\end{array} \right.
$$

Functions f and g may be defined in $\mathbb{R}$ but we are only interested in positive arguments of them as it will be seen below. Moreover, we shall assume that f and g are Lipschitz functions in $[\frac{v_0}{2}, v_0]$ with constants f_0 and g_0 respectively, i.e.

$$
(7b) \quad \left| \begin{array}{l}
\text{i) } \exists \, f_0 > 0 \, / \, | f(v_2) - f(v_1) | \le f_0 \, | v_2 - v_1 | \, , \ \forall v_1 \, , v_2 \in [\frac{v_0}{2}, v_0] \ , \\[2ex]
\text{ii) } \exists \, g_0 > 0 \, / \, | g(v_2) - g(v_1) | \le g_0 \, | v_2 - v_1 | \, , \ \forall v_1 \, , v_2 \in [\frac{v_0}{2}, v_0] \ .
\end{array} \right.
$$

We remark here that functions f and g , defined by

$$
(W) \qquad g(x) = -\, x^{\nu} \quad (= -\, f(x) \,) \quad (x \ge 0 \, , \nu > 0)
$$

satisfy conditions (7ai,ii). A different choice of g in (6iv) is considered in [Do] ; It is a Langmuir type condition : the chemical reaction rate is given by

$$\text{(L)} \qquad g(x) = -\frac{a\,x^n}{b + c\,x^n} \quad (= -f(x))\ ,\ a, b, c = \text{const.} > 0\ ,\ n > 0$$

which also verifies conditions (7aii) for all constants a, b, c, n > 0 . We remark here that the (L) condition reduces to a (W) condition when c = 0 .

In §II. we study an auxiliary moving boundary problem which will be used in §III. We generalize the results obtained in [FaPr1, FaPr2] changing the nonlinear condition on the fixed face $x=0$ by other one on the moving boundary $x = s(t)$, given by (6iv).

In §III. we study the Wen-Langmuir free boundary model for noncatalytic gas-solid reactions that consists in finding $T>0$, $x=s(t)$ and $u = u(x,t)$ such that they satisfy conditions (6). We prove that there exists a unique solution for a sufficiently small $T > 0$. Moreover, the solution is given through the unique fixed point, in an adequate Banach space, of the following contraction operator F_2 : For $s=s(t) \in C^0([0,T])$ we define

$$\text{(8)} \qquad F_2(s)\,(t) = \int_0^t f(v(s(\tau),\tau))\ d\tau$$

where v is the solution of problem (6i-iv).

Here we exploit some techniques recently used in [CoRi1, Fa, FaMePr, Pr] for sorption of swelling solvents in polymers. Another approach is to use the general theory for free boundary for the heat equation [Co, FaPr3]. In [BoTaTwVi], the condition $u(0,t)=v_0(t)$, $0<t<T$ is considered by using a method developed in [BoTw].

Remark 1. Taking into account the transformation

$$\text{(9)} \qquad v(x,t) = \int_x^{s(t)} u(\xi,t)\ d\xi$$

the problem (4), with conditions $u_x(s(t),t)=g(u(s(t),t))$ and $\dot{s}(t)=f(u(s(t),t))$, $0<t<T$, for the triple (v,s,T) becomes :

$$\text{(10)} \quad \left| \begin{array}{l} \text{(a)}\ \ v_t - v_{xx} = q(\dot{s}) \ \text{ in } D_T\ , \\ \text{(b)}\ \ v_x(0,t) = -\,v_0(t)\ ,\ 0<t<T\ , \qquad \text{(c)}\ \ s(0)=b\ ,\ b>0\ , \\ \text{(d)}\ \ v(s(t),t)=0\ , \quad \text{(e)}\ \ \dot{s}(t) = f(-\,v_x(s(t),t))\ ,\ 0<t<T\ , \\ \text{(f)}\ \ v(x,0) = \displaystyle\int_x^b \psi(\xi)\,d\xi\ \ ,\ 0\le x\le b\ , \end{array} \right.$$

where

(11) $$q(\dot{s}) = g(f^{-1}(\dot{s})) + \dot{s}\ f^{-1}(\dot{s}) .$$

Such a problem is of type of the free boundary problems analysed in [Co, FaPr3]. Moreover, in [BoTaTwVi], the same problem is studied through a system of two integral equations for the unknown functions Φ_1 and Φ_2 defined by

(12) $$\Phi_1(t) = u(s(t),t), \qquad \Phi_2(t) = \frac{d}{dt}\left[\frac{u(s(t),t)}{\dot{s}(t)} \right] , \quad 0 < t < T.$$

The free boundary is then given by the expression

(13) $$s(t) = b + \int_0^t f(\Phi_1(\tau))\, d\tau .$$

Now, we show the approach given in [TaVi1] by using a result obtained in [CoRi1].

II. A HEAT CONDUCTION PROBLEM WITH A NONLINEAR CONDITION ON THE MOVING BOUNDARY.

For each Lipschitz continuous function $s = s(t)$, defined in $[0,T]$ with $s(0) = b > 0$, we consider the following moving boundary problem : Find the function $v = v(x,t)$ such that it satisfies

(14) a) (6i, ii, iv) , b) $v(x,0) = \Psi(x) \ , \ 0 \le x \le b = s(0)$.

For a solution of this problem we mean a function $v = v(x,t)$, continuous in $\overline{D}_T$ with the derivatives v_{xx} and v_t continuous in D_T that satisfies conditions (1) for a given $T > 0$.

Theorem 1 . Under the hypotheses

(15i) $$\left| \begin{array}{l} \exists\, L > 0 \ / \ | s(t) - s(\tau) | \le L \, | t - \tau | \ , \quad \forall t, \tau \in [0,T] \ , \\ 0 < a_0 \le s(t) \le A_0 \ , \quad \forall t \in [0,T] \ , \end{array} \right.$$

(15ii) $$\left| \begin{array}{l} \Psi \in C^0([0,b]) \ , \quad \Psi(0) = v_0(0) \ , \ \Psi > 0 \ \text{in} \ [0,b] \ , \\ \Psi' \in C^0([b-\epsilon, b]) \quad \text{for a} \ \ \epsilon > 0 \ , \text{with} \ \Psi'(b) \le 0 \ , \end{array} \right.$$

(15iii) $g = g(v)$ is a strictly decreasing function in $\mathbb{R}^+$ which verifies (7bii) and $g(0) = 0$,

$$\text{(15iv)} \quad \left| \begin{array}{l} v_0 \in C^0([0,T]) \quad , \quad v_0 > 0 \ \text{ in } \ [0,T] \ , \\[2ex] \underset{t \in [0,T]}{\text{Max}} \ v_0(t) \ \geq \ \underset{x \in [0,b]}{\text{Max}} \ \Psi(x) \end{array} \right.$$

there exists a unique solution of the problem

$$\text{(16)} \qquad \text{a) (6i, iv) , (14b) ,} \qquad \text{b) } v(0,t) = v_0(t) \ , \quad 0 < t < T \ .$$

Proof. We follow a classical fixed point argument.

a) First, we consider an a priori estimate for the solution v of problem (16) :

$$\text{(17)} \qquad 0 < v(x,t) \ \leq \ \underset{t \in [0,T]}{\text{Max}} \ v_0(t) \quad \text{in } \bar{D}_T \ .$$

We obtain the right hand side inequality of (17) because of the maximum principle and $g < 0$. We prove $v > 0$ in $\bar{D}_T$ by absurd. Let $T_0 > 0$ be the first time such that $v(s(T_0),T_0) = 0$. Therefore, we have $v_x(s(T_0),T_0) < 0$ by the maximum principle which is a contradiction because $v_x(s(T_0),T_0) = g(v(s(T_0),T_0)) = g(0) = 0$.

b) Uniqueness. It follows from the maximum principle and from (15iii).

c) Existence. Following the methods given in [FaPr1], and under the hypotheses (15i-iv) we have that for each given function $h = h(t) \in C^0([0,T])$ with $h \geq 0$ and $g(h(0)) = \Psi'(b)$, there exists a unique solution v of the associate moving boundary problem

$$\text{(6i, 1b, 3b)} \ , \quad v_x(s(t), t) = g(h(t)) \equiv H(t) \ , \quad 0 < t < T \ .$$

This solution v is given by the following expression

$$\text{(18)} \qquad v(x,t) = \int_0^b \Psi(\xi) \ K(x,t;\xi,0) \ d\xi \ + \int_0^t \phi_1(\tau) \ K_x(x,t;0,\tau) \ d\tau \ + $$

$$+ \int_0^t \phi_2(\tau) \ K(x,t;s(\tau),\tau) \ d\tau$$

where

$$\text{(19)} \qquad K(x,t;\xi,\tau) = \frac{1}{2\sqrt{\pi(t-\tau)}} \ \exp\left\{-\frac{(x-\xi)^2}{4(t-\tau)}\right\} \ , \quad t > \tau$$

is the fundamental solution of the heat equation, and ϕ_1 and ϕ_2 satisfy the following system of two second kind Volterra integral equations

$$(20)\quad \begin{cases} \text{i)} & \phi_1(t) = \int_0^t K_{12}(t,\tau)\ \phi_2(\tau)\ d\tau + f_1(t) \quad , \\ \text{ii)} & \phi_2(t) = \int_0^t K_{21}(t,\tau)\ \phi_1(\tau)\ d\tau + \int_0^t K_{22}(t,\tau)\ \phi_2(\tau)\ d\tau + f_2(t) \end{cases}$$

where

$$(21)\quad \begin{cases} \text{i)} & f_1(t) = -\,2\ v_0(t) + 2\int_0^b \Psi(\xi)\ K(0,t;\xi,0)\ d\xi \ , \\ \text{ii)} & f_2(t) = 2\ H(t) - 2\int_0^b \Psi(\xi)\ K_x(s(t),t;\xi,0)\ d\xi \ , \\ \text{iii)} & K_{12}(t,\tau) = 2\ K(0,t;s(\tau),\tau) \quad , \quad \text{iv)} \quad K_{21}(t,\tau) = -\,2\ K_{xx}(s(t),t;0,\tau) \ , \\ \text{v)} & K_{22}(t,\tau) = -\,2\ K_x(s(t),t;s(\tau),\tau) \quad . \end{cases}$$

Thus, for each $h \in C^0([0,T])$ we can define $\tilde{h} = \tilde{h}(t) \equiv v(s(t),t) \in C^0([0,T])$ [FaPr2, TaVi1] and therefore we have the operator $F_1 : C^0([0,T] \rightarrow C^0([0,T])$, defined in this way

$$(22)\qquad F_1(h)(t) = \tilde{h}(t) \quad , \quad t \in [0,T] \ .$$

Then, the fixed points of F_1 will be solutions of problem (16). We can prove that F_1 is a contraction operator from a classical argument, that is, there exists an increasing continuous function $Q = Q(T)$ of the variable T, vanishing for $T = 0$ and depending continuously upon the parameters a_0 , A_0 , L, g_0 , such that

$$(23)\qquad \| \tilde{h}_2 - \tilde{h}_1 \|_t \ \leq\ Q(T)\ \| h_2 - h_1 \|_t \quad , \quad \forall t \in [0,T] \ ,$$

where $\| f \|_t$ is defined by

$$(24)\qquad \| f \|_t = \max_{\tau \in [0,t]} |\, f(\tau)\, | \ .$$

Therefore, there exists $T_0 = T_0(\ a_0 , A_0 , L , g_0) > 0$ such that $Q(T) \leq Q(T_0) < 1$ for all $T \leq T_0$ and then F_1 is a contraction operator on $C^0([0,T])$. Moreover, Q(T) does not depend upon the data

$\Psi = \Psi(x)$ and $v_0 = v_0(t)$, so that the same method can be repeated without any change and consequently, the solution of problem (16) exists and is unique for any time $T > 0$.

We shall consider now the case $b = 0$, i.e. for a given $s \in C^0([0,T]) \cap C^1((0,T])$ with $s(0) = 0$ and $s(t) \geq K_1 t$ $(K_1 > 0)$ in $[0,T]$ we pose the moving boundary problem

(25) (6i, ii, iv) with $v_0 = \text{const.} > 0$

and we obtain the following a priori estimates.

Lemma 2. a) If v is a solution of (25), then v verifies :

(26) i) $0 \leq v(x,t) \leq v_0$ in $\bar{D}_T$, ii) $g(v_0) \leq v_x(x,t) \leq 0$ in $\bar{D}_T$.

b) If the moving boundary s also satisfies the condition

(27) $\exists\, K_2 > 0 \,/\, s(t) \leq K_2 t$, $\forall\, t \in (0, t_0]$, with $t_0 = \dfrac{-v_0}{2 K_2\, g(v_0)} > 0$,

then v verifies

(28) i) $0 < \frac{v_0}{2} \leq v(x,t) \leq v_0$ in $\bar{D}_{t_0}$, ii) $g(v_0) \leq v_x(x,t) \leq g\left(\frac{v_0}{2}\right) < 0$ in $\bar{D}_{t_0}$.

Lemma 3. If $g \in C^0(\mathbb{R}^+)$, $s \in C^0([0,T])$ with $s(0) = 0$ and $v_0 \in C^0([0,T])$ with $v_0 > 0$ in $[0,T]$ then there exists $t' \in (0,T)$ such that the equation

(29) $f(y,t) \equiv y - v_0(t) - g(y)\, s(t) = 0$, $y > 0$, $t \in (0,T)$

has at least one solution y for each $t \in (0,t')$. Moreover, we can define $y_0 = y_0(t) > 0$ in $(0,t')$ such that

(30) $f(y_0(t),t) = 0$ in $(0,t')$, $\lim_{t \to 0^+} y_0(t) = v_0(0) > 0$.

Theorem 4. If g verifies (7aii) and $s \in C^0([0,T]) \cap C^1((0,T])$ with $s(0) = 0$ and $s(t) \geq K_1 t$ $(K_1 > 0)$ in $[0,T]$, then there exists a unique solution of the moving boundary problem (25) for a suitably small $T > 0$.

Proof. The argument for uniqueness in Theorem 1 still holds. To prove the existence of a solution of problem (25) we introduce a decreasing sequence (t_n) such that

$$(31) \qquad T > t' > t_1 > t_2 > \ldots\ldots > t_n > \ldots\ldots, \quad \lim_{n\to\infty} t_n = 0 ,$$

where t' is defined in Lemma 3 (in the present case we have $v_0(t) = v_0 > 0$ in $(0,T]$). We define the sequence (v_n) such that $v_n = v_n(x,t)$ is the solution of the following problem $(n = 1, 2, \ldots)$:

$$(32) \qquad \left|\begin{array}{l} v_{n_t} - v_{n_{xx}} = 0 \quad \text{in} \quad D_{n,T} = \left\{(x,t) \ / \ 0 < x < s(t) \ , \ t_n < t < T\right\} , \\ v_n(0,t) = v_0 \ , \ t_n < t < T , \\ v_{n_x}(s(t),t) = g\Big(v_n(s(t),t)\Big) \ , \quad t_n < t < T \ , \\ v_n(x,t_n) = \Psi_n(x) \ , \quad 0 \le x \le s(t_n) \ , \end{array}\right.$$

where

$$(33) \qquad \Psi_n(x) = v_0 + g\Big(\Psi_n(s(t_n))\Big)\, x$$

which is justified by Lemma 3 choosing $\Psi_n(s(t_n)) = y_0(t_n) > 0$ for each n that verifies $\lim_{n\to\infty} \Psi_n(s(t_n)) = v_0 > 0$.

We define $z_n = v_{n_{xx}}$ which satisfies the following problem

$$(34) \qquad \left|\begin{array}{l} z_{n_t} - z_{n_{xx}} = 0 \quad \text{in} \quad D_{n,T} \ , \\ z_n(0,t) = 0 \quad , \quad t_n < t < T \ , \\ z_n(x,t_n) = \Psi_n''(x) = 0 \ , \quad 0 \le x \le s(t_n) \ , \\ z_{n_x}(s(t),t) + \dot{s}(t) \ z_n(s(t),t) = g'(\gamma(t)) \ [\ \dot{s}(t) \ g(\gamma(t)) + z_n(s(t),t) \ ] \ , \\ \gamma(t) = \displaystyle\int_{t_n}^{t} [\ \dot{s}(\tau) \ g(\gamma(\tau)) + z_n(s(\tau),\tau) \ ] \ d\tau \ + \ \Psi_n(s(t_n)) \quad . \end{array}\right.$$

From [CoRi1] we can see that there exists a $T_1 > 0$ sufficiently small so that

$$(35) \qquad \| z_n \|_{D_{n,T_1}} \le \sup_{t \in [t_n, T_1)} \dot{s}(t) \ . \ \sup_{v \in \left(\frac{v_0}{2}, v_0\right)} | g(v) | \le \text{const.} ,$$

where we note with $\| \cdot \|_D$ the norm in the Banach space $C^0(\bar{D})$. If we define $\tilde{v}_n = \tilde{v}_n(x,t)$ in $D_{n,T}$ $(T \le T_1)$ by

$$(36) \qquad \tilde{v}_n(x,t) = v_0 + x \left[g(\Psi_n(s(t_n))) + \int_{t_n}^{t} z_{n_x}(0,\tau)\, d\tau\right] + \int_0^x d\xi \int_0^{\xi} z_n(y,t)\ dy$$

we obtain the following properties :

i) $\tilde v_{n_{xx}}(x,t) = \tilde v_{n_t}(x,t) = z_n(x,t)$ in $D_{n,T}$;

ii) $\tilde v_n(0,t) = v_0$, $0 < t < T$;

iii) $\tilde v_n(x,t_n) = v_0 + x\, g\big(\Psi_n(s(t_n))\big) = \Psi_n(x)$, $0 \le x \le s(t_n)$;

iv) $$\tilde v_{n_x}(s(t),t) = g\big(\Psi_n(s(t_n))\big) + \int_{t_n}^{t} z_{n_x}(0,\tau)\ d\tau + \int_0^{s(t)} z_n(x,t)\ dx =$$

$$= g\big(\Psi_n(s(t_n))\big) + \int_0^{t} g'(\gamma(\tau))\ \dot\gamma(\tau)\ d\tau = g(\gamma(t)) \ ,\ 0 < t < T \,,$$

because, for $t \in (t_n\ ,T]$, we have

$$0 = \iint_{D_n,t} (\, z_{n_{xx}} - z_{n_t}\,)\ dx\, d\tau = \int_{\partial D_n,t} z_n\ dx + z_{n_x}\ d\tau =$$

$$= \int_{t_n}^{t} [\, z_n(s(\tau),\tau)\ \dot s(\tau) + z_{n_x}(s(\tau),\tau)\,]\ d\tau - \int_0^{s(t)} z_n(x,t)\ dx - \int_{t_n}^{t} z_{n_x}(0,\tau)\ d\tau \ ;$$

v) $\frac{d}{dt}\ \tilde v_n(s(t),t) = \dot s(t)\ \ g(\gamma(t)) + z_n(s(t),t) = \dot\gamma(t)$, $t \in (t_n\ ,T]$, and by integration, we obtain $\tilde v_n(s(t),t) = \gamma(t)$ for $t \in (t_n\ ,T]$.

Therefore, we deduce $\tilde v_n = v_n$ because of the uniqueness of the solution of (32) and then we obtain that

(37) $$\| v_{n_{xx}} \|_{D_{n,T}} \le \text{const.} \quad , \quad \| v_{n_x} \|_{D_{n,T}} \le \text{const.} \quad , \quad \forall n \,.$$

Let $v = v(x,t)$ be the limit function of v_n when $n \to \infty$. Then v verifies (25i,ii) ; hence it remains to verify the condition (25iii) on the moving boundary $x = s(t)$. Let $t \in (0,T)$ and $x \in (0,s(t))$ be fixed and consider

$$v(s(t),t) - v(x,t) = [\, v(s(t),t) - v_n(s(t),t)\,] + [\, v_n(s(t),t) - v_n(x,t)\,] +$$

$$+ [\, v_n(x,t) - v(x,t)\,] = [\, v(s(t),t) - v_n(s(t),t)\,] + [\, v_n(x,t) - v(x,t)\,] +$$

$$+ g(v_n(s(t),t))\ (s(t) - x) - \tfrac{1}{2}\ v_{n_{xx}}(\tilde x,t)\ (s(t) - x)^2$$

for some $\tilde x \in (x,s(t))$, so we deduce that

(38) $$|\, v(s(t),t) - v(x,t) - g(v_n(s(t),t))\ (s(t) - x)\,| \le$$
$$\le\ 2\, \| v - v_n \| + \text{const.}\ (s(t) - x)^2 \ .$$

Therefore, passing to the limit $n \to \infty$ and then $x \to s(t)$, we obtain condition (25iii), because of (37).

III. THE WEN - LANGMUIR - LIKE FREE BOUNDARY MODEL.

The Wen-Langmuir free boundary model for noncatalytic gas-solid reactions consists in finding (in dimensionless variables) a time $T > 0$, the free boundary $s = s(t) \in C^0([0,T]) \cap C^1((0,T])$ with $s(0) = 0$ and the concentration $u = u(x,t) \in C(\bar{D}_T) \cap C^{2,1}(D_T)$ with u_x continuous on $x = s(t)$, such that they satisfy conditions (6), where the functions f and g verify (7). Owing to $f' > 0$ and the a priori estimate (28) we have

(39) $$\dot{s}(t) \geq f\left(\frac{v_0}{2}\right) > 0 \ , \quad \forall t \in (0, t_0]$$

and therefore we obtain $s(t) > 0$ for all $t \in (0, t_0]$.

From now on we suppose that T is a suitably small time; in particular, we have

(40) $$T \leq \mathrm{Min}\ (t_0 \ , t', T_1)$$

where t_0, t', and T_1 are given by (27), Lemma 3 and (35) respectively. We consider the following auxiliary moving boundary problem : Given $r = r(t) \in C^0([0,T]) \cap C^1((0,T])$ with $r(0) = 0$ and $0 < K_1 \leq \dot{r}(t) \leq K_2$ in $(0,T]$ we define $v = v(x,t)$ as the unique solution of the problem

(41) $$\left| \begin{array}{l} v_t - v_{xx} = 0 \quad \text{in} \quad D_{r,T} = \left\{(x,t) \ / \ 0 < x < r(t) \ , \ 0 < t < T \right\} \ , \\ v(0,t) = v_0 > 0 \ , \ 0 < t < T \ , \\ v_x(r(t),t) = g\big(v(r(t),t)\big) \ , \quad 0 < t < T \ . \end{array} \right.$$

Function v satisfies in $\bar{D}_{r,T}$ the estimates (27, 28), i.e.

(42) $$\frac{v_0}{2} \leq v(x,t) \leq v_0 \ , \qquad | v_x(x,t) | \leq G \equiv \sup_{y \in [\frac{v_0}{2}, v_0]} | g(y) | \ \ (= - g(v_0)) \ .$$

In a similar way to the proof of the theorem 4 and taking into account [CoRi1], we have that v_{xx} is bounded in $D_{r,T}$ by a constant z_0 which depends upon K_2 and G for a $T > 0$ small enough.

Let B be the set

(43) $$B = \Big\{ s \in C^0([0,T]) \cap C^1((0,T]) \ / \ s(0) = 0 \ , \ 0 < K_1 \leq \dot{s}(t) \leq K_2 \ , \\ | \dot{s}(t_2) - \dot{s}(t_1) | \leq K_3 \ | t_2 - t_1 | \ \text{for} \ 0 < t_1 \ , t_2 \leq T \Big\}$$

which is a closed subset of $C^0([0,T])$ and the coefficients K_1, K_2 and K_3 satisfy the conditions

(44) $$\left| \begin{array}{l} 0 < K_1 \leq \min_{y \in [\frac{v_0}{2}, v_0]} f(y) \ , \quad 0 < \max_{y \in [\frac{v_0}{2}, v_0]} f(y) \leq K_2 \ , \\ K_3 \geq f_0 [\, G\, K_2 + z_0(G, K_2) \,] \ . \end{array} \right.$$

In our case, we can choose

(44 bis) $$K_1 = f\left(\frac{v_0}{2}\right), \quad K_2 = f(v_0) \quad , \quad K_3 = f_0(\, G\, K_2 + z_0(G, K_2)\,) \quad .$$

We define the operator

(45) $$F_2 : B \to B \;\; / \;\; F_2(r) = \tilde{r} \quad ,$$

where $\tilde{r}$ is given by

(46) $$\tilde{r}(t) = \int_0^t f(v(r(\tau),\tau))\; d\tau \quad , \quad t \in [0,T] \quad ,$$

and $v = v(x,t)$ is the unique solution of (41) which satisfies the following estimates

(47) $$\frac{v_0}{2} \le v \le v_0 \;\; , \;\; |\, v_x \,| \le G \;\; , \;\; |\, v_{xx} \,| \le z_0 \;\; \text{in} \;\; \overline{D}_{r,T} \;\; .$$

We have $\tilde{r} \in B$ because

$$|\, \dot{\tilde{r}}(t_2) - \dot{\tilde{r}}(t_1) \,| \;\le\; f_0 \;|\, v(s(t_2),t_2) - v(s(t_1),t_1) \,| \;\le$$

(48) $$\le\; f_0 \,[\, |\, v(s(t_2),t_2) - v(s(t_1),t_2) \,| \;+\; |\, v(s(t_1),t_2) - v(s(t_1),t_1) \,|\,] \;\le$$

$$\le\; f_0 \;(\, G\, K_2 + z_0 \,)\; |\, t_2 - t_1 \,| \;\le\; K_3 \;|\, t_2 - t_1 \,| \;\; , \;\; \text{for} \;\; t_1 \,, t_2 \in (0,T] \;.$$

Now we define the distance between two functions in B as

(49) $$d(s_2 \,, s_1) = \|\, s_2 - s_1 \,\|_{C^0([0,T)]}$$

and we can prove [TaVi1].

Theorem 5. The mapping F_2 of B into itself is a contraction in the metric (49) for a suitably small $T > 0$. Moreover, the free boundary problem (6) admits a unique solution.

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