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ON THE FREE BOUNDARY PROBLEM IN THE WEN-LANGMUIR SHRINKING CORE MODEL FOR NONCATALYTIC GAS-SOLID REACTIONS*

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SOMMARIO. Si dimostra un risultato locale di esistenza e unicitá della soluzione di un problema con frontiera libera per il modello del nucleo in contrazione in reazioni gas-solido non catalitiche. Le condizioni sulla frontiera libera sono del tipo

$u_x(s(t), t) = g(u(s(t), t)), \qquad 0 < t \leqslant T,$

$\dot{s}(t) = f(u(s(t), t)), \qquad 0 < t \leqslant T,$

con funzioni f e g generali soddisfacenti le ipotesi

$g < 0 \qquad g < 0, \qquad g(0) = 0,$

$f > 0 \qquad f' > 0, \qquad f(0) = 0.$

Le condizioni di Wen e di Langmuir, che sono date rispettivamente da $f(x) = -g(x) = x^n (n > 0)$ *e da* $f(x) = -g(x) = a\,x^n \,/\, (b + cx^n)$ $(a, b, c, n > 0)$, *rientrano entrambe nel presente schema.*

SUMMARY. We prove a local result in time for the existence and uniqueness of the solution of the free boundary problem in the shrinking core model for noncatalytic gas-solid reactions. We impose free boundary conditions of the type

$u_x(s(t), t) = g(u(s(t), t)), \qquad 0 < t \leqslant T,$

$\dot{s}(t) = f(u(s(t), t)), \qquad 0 < t \leqslant T,$

with general functions g and f which satisfy the assumptions

$g < 0, \qquad g' < 0, \qquad g(0) = 0,$

$f > 0, \qquad f' > 0, \qquad f(0) = 0.$

The Wen and Langmuir conditions are given by, $f(x) = -g(x) = x^n$ $(n > 0)$ *and* $f(x) = -g(x) = ax^n \,/\, (b + cx^n)$ $(a, b, c, n > 0)$ *respectively, which both fulfill the above assumptions.*

I. INTRODUCTION

In this article we shall analyze a mathematical model of an isothermal monocatalytic 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.

Since 1960, various devices and models, either phenomenological or structural, have been proposed and analyzed with the purpose of interpreting gas-solid reaction process [1-4, 7, 8, 13-16, 18-25, 27, 28].

In the present paper, 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 [28]. 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

$$\begin{aligned}
&\epsilon \frac{\partial C_A}{\partial t} = D \frac{\partial^2 C_A}{\partial y^2}, \ \sigma(\tau) < y < R, \ \tau_0 < \tau \leqslant \tau_1, \\
&C_A(R, \tau) = V_0(\tau), \ \tau_0 < \tau \leqslant \tau_1, \\
&D \frac{\partial C_A}{\partial y}(\sigma(\tau), \tau) = k_s\, a\, C_{S_0}\, C_A^{\nu}(\sigma(\tau), \tau), \ \tau_0 < \tau \leqslant \tau_1, \\
&-D \frac{\partial C_A}{\partial y}(\sigma(\tau), \tau) = a\, C_{S_0}\, \dot{\sigma}(\tau), \ \tau_0 < \tau \leqslant \tau_1, \\
&\sigma(\tau_0) = R_0 \leqslant R, \\
&C_A(y, \tau_0) = \Phi(y), \ R_0 \leqslant y \leqslant R,
\end{aligned} \tag{1}$$

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) expresses 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.

In the sequel the notation (I − n) will indicate formula (n) of Section I.

If the following dimensionless variables and parameters

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are introduced;

$$x = C_1 \frac{R-y}{R}, \quad t = C_2(\tau - \tau_0),$$

$$s(t) = C_1 \frac{R-\sigma(\tau)}{R}, \quad T = C_2(\tau_1 - \tau_0), \tag{2}$$

$$u(x,t) = C_3 C_A(y,\tau), \quad v_0(t) = C_3 V_0\left(\tau_0 + \frac{t}{C_2}\right),$$

$$\Psi(x) = C_3\, \Phi\left(R - \frac{Rx}{C_1}\right), \quad b = C_1 \frac{R-R_0}{R},$$

with

$$C_1 = \frac{\phi^\nu}{\alpha^{\nu-1}}, \quad C_3 = \frac{\alpha}{\phi C_{A_0}},$$

$$C_2 = \frac{k_s \phi^{2\nu} C^\nu_{A_0}}{R\alpha^{2\nu-1}} = \frac{k_s^2\,(a\,C_{S_0})^{2\nu}}{D\epsilon^{2\nu-1}}, \tag{3}$$

$$\phi = \frac{R\,k_s\,a\,C_{S_0}\,C^{\nu-1}_{A_0}}{D} \text{ (Thiele reaction modulus)},$$

$$\alpha = \frac{\epsilon R\,k_s\,C^\nu_{A_0}}{D} = \frac{\epsilon\,C_{A_0}\phi}{a\,C_{S_0}}.$$

where C_{A_0} denotes a reference concentration of the gas, then problem (1) is transformed into

$$\begin{aligned} &u_{xx} - u_t = 0 \text{ in } D_T, \\ &u(0,t) = v_0(t), \quad 0 < t \leqslant T, \\ &u_x(s(t),t) = -u^\nu(s(t),t), \quad 0 < t \leqslant T, \\ &u_x(s(t),t) = -\dot{s}(t), \quad 0 < t \leqslant T, \\ &s(0) = b, \\ &u(x,0) = \Psi(x), \quad 0 \leqslant x \leqslant b, \end{aligned} \tag{4}$$

where

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

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

$$\begin{aligned} &\text{i)} \quad u_{xx} - u_t = 0 \text{ in } D_T, \\ &\text{ii)} \quad u(0,t) = v_0 > 0, \; 0 < t \leqslant T, \\ &\text{iii)} \quad s(0) = 0, \\ &\text{iv)} \quad u_x(s(t),t) = g(u(s(t),t)), \quad 0 < t \leqslant T, \\ &\text{v)} \quad \dot{s}(t) = f(u(s(t),t)), \quad 0 < t \leqslant T, \end{aligned} \tag{6}$$

where f and g are real functions which satisfy

$$\begin{aligned} &\text{i)} \quad f > 0, \quad f' > 0 \text{ in } \mathbb{R}^+ \text{ and } f(0) = 0, \\ &\text{ii)} \quad g < 0, \quad g' < 0 \text{ in } \mathbb{R}^+ \text{ and } g(0) = 0. \end{aligned} \tag{7a}$$

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 $[v_0/2, v_0]$ with constants f_0 and g_0 respectively, i.e.

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

We remark here that functions f and g, defined by

$$g(x) = -x^\nu \; (= -f(x)) \quad (x \geqslant 0, \; \nu > 0) \tag{W}$$

satisfy conditions (7ai, ii).

A different choiche of g in (6iv) is considered in [8]. It is a Langmuir type condition: the chemical reaction rate is given by

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

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 [11, 12] 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

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

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

Here we exploit some techniques recently used in [6, 9, 10, 17] for sorption of swelling solvents in polymers.

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).

II. A HEAT CONDUCTION PROBLEM WITH A NON-LINEAR 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

$$\text{a) (I-6i, ii, iv),} \qquad\qquad (1)$$
$$\text{b) } v(x, 0) = \Psi(x), \quad 0 \leqslant x \leqslant b = s(0).$$

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

THEOREM II-1 : Under the hypotheses

$$\exists L > 0 \,/\, | s(t) - s(\tau) | \leqslant L \, | t - \tau | , \quad \forall t, \tau \in [0, T], \qquad (2i)$$
$$0 < a_0 \leqslant s(t) \leqslant A_0, \quad \forall t \in [0, T],$$

$$\Psi \in C^0([0, b]), \quad \Psi(0) = v_0(0), \quad \Psi > 0 \text{ in } [0, b], \qquad (2ii)$$
$$\Psi' \in C^0([b - \epsilon, b]) \quad \text{for a} \quad \epsilon > 0, \text{ with } \Psi'(b) \leqslant 0,$$

$g = g(v)$ is a strictly decreasing function in $\mathbb{R}^+$ which verifies (I-7 bii) and $g(0) = 0$, (2iii)

$$v_0 \in C^0([0, T]), v_0 > 0 \text{ in } [0, T], \qquad (2iv)$$
$$\underset{t \in [0,T]}{\text{Max}} \; v_0(t) \geqslant \underset{x \in [0,b]}{\text{Max}} \; \Psi(x)$$

there exists a unique solution of the problem

$$\text{a) (I-6i, iv), (1b),} \qquad\qquad (3)$$
$$\text{b) } v(0, t) = v_0(t), \quad 0 < t \leqslant T.$$

Proof: We follow a classical fixed point argument.

a) First, we consider an a priori estimate for the solution v of problem (3):

$$0 < v(x, t) \leqslant \underset{t \in [0,T]}{\text{Max}} \; v_0(t) \text{ in } \bar{D}_T. \qquad (4)$$

We obtain the right hand side inequality of (4) 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 (2iii).

c) *Existence*. Following the methods given in [12], and under the hypotheses (2i-iv) we have that for each given function $h = h(t) \in C^0([0, T])$ with $h \geqslant 0$ and $g(h(0)) = \Psi'(b)$, there exists a unique solution v of the associate moving boundary problem

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

This solution v is given by the following expression

$$v(x, t) = \int_0^b \Psi(\xi) \, K(x, t; \xi, 0) \, d\xi + \int_0^t \phi_1(\tau) \, K_x(x, t; 0, \tau) \, d\tau + \int_0^t \phi_2(\tau) \, K(x, t; s(\tau), \tau) \, d\tau \qquad (5)$$

where

$$K(x, t; \xi, \tau) = \frac{1}{2\sqrt{\pi(t - \tau)}} \exp \left\{ - \frac{(x - \xi)^2}{4(t - \tau)} \right\}, \quad t > \tau \qquad (6)$$

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

$$\text{i)} \quad \phi_1(t) = \int_0^t K_{12}(t, \tau) \, \phi_2(\tau) \, d\tau + f_1(t), \qquad (7)$$
$$\text{ii)} \quad \phi_2(t) = \int_0^t K_{21}(t, \tau) \, \phi_1(\tau) \, d\tau + \int_0^t K_{22}(t, \tau) \, \phi_2(\tau) \, d\tau + f_2(t)$$

where

$$\text{i)} \quad f_1(t) = -2 \, v_0(t) + 2 \int_0^b \Psi(\xi) \, K(0, t; \xi, 0) \, d\xi,$$

$$\text{ii)} \quad f_2(t) = 2 \, H(t) - 2 \int_0^b \Psi(\xi) \, K_x(s(t), t; \xi, 0) \, d\xi,$$

$$\text{iii)} \quad K_{12}(t, \tau) = 2 \, K(0, t; s(\tau), \tau), \qquad (8)$$

$$\text{iv)} \quad K_{21}(t, \tau) = -2 \, K_{xx}(s(t), t; 0, \tau),$$

$$\text{v)} \quad K_{22}(t, \tau) = -2 \, K_x(s(t), t; s(\tau), \tau).$$

The kernels $K_{ij} = K_{ij}(t, \tau)$ and the function $f_1 = f_1(t)$ are continuous in $0 \leqslant \tau \leqslant t \leqslant T$ and in $[0, T]$ respectively. The second term of the righ hand side of (8ii) has a singularity of type $t^{-1/2}$ in $t = 0$ which is transfered to $\phi_2 = \phi_2(t)$. The first term of the righ hand side of (7i) is continuous in $[0, T]$, and consequenly so is $\phi_1 = \phi_1(t)$. The third term of the righ hand side of (5) is continuous in $[0, T]$ and therefore, so is $v = v(x, t)$ in $\bar{D}_T$ (See, e.g. [12, p. 337]). Thus, for each $h \in C^0([0, T])$ we can define $\tilde{h} = \tilde{h}(t) \equiv v(s(t), t) \in C^0([0, T])$ and therefore we have the operator $F_1 : C^0([0,T]) \to C^0([0, T])$, defined in this way

$$F_1(h)(t) = \tilde{h}(t), \quad t \in [0, T]. \qquad (9)$$

Then, the fixed points of F_1 will be solutions of problem (3). 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

$$\| \tilde{h}_2 - \tilde{h}_1 \|_t \leqslant Q(T) \, \| h_2 - h_1 \|_t, \quad \forall t \in [0, T], \qquad (10)$$

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

$$\| f \|_t = \max_{\tau \in [0,t]} |f(\tau)|. \tag{11}$$

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 (3) exists and is unique for any time $T > 0$.

REMARK 1. If the hypothesis (2ii) is replaced by

$$\Psi \in C^1([0, b]), \ \Psi(0) = v_0(0), \ \Psi(b) = 0 \ \text{and} \ \Psi > 0 \text{ in } [0, b) \tag{12}$$

then by an integration by parts the function f_2, defined by (8ii), is given by

$$f_2(t) = 2\,H(t) - \frac{\Psi(0)}{\sqrt{\pi t}} \exp\left\{-\frac{s^2(t)}{4t}\right\} - \tag{13}$$

$$- 2 \int_0^b \Psi'(\xi)\, K(s(t), t; \xi, 0)\, d\xi$$

which is a continuous function in $[0, T]$. Therefore, the functions ϕ_1 and ϕ_2, solution of the integral equation system (7), and the function v, defined by (5), are also continuous functions and then we can continue as above. However, the condition $\Psi(b) = 0$ is very restrictive for our problem.

If $\Psi(b) \neq 0$, then a singular term appears in (13), namely

$$\frac{\Psi(b)}{\sqrt{\pi t}} \exp\left\{-\frac{(s(t) - b)^2}{4t}\right\}. \tag{14}$$

REMARK 2. We could use the Green function to solve problem (3) similarly to [26].

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

$$\text{(I-6i, ii, iv) with } v_0 = \text{const.} > 0 \tag{15}$$

and we obtain the following a priori estimates.

LEMMA II-2. a) If v is a solution of (15), then v verifies:

$$\begin{aligned} &\text{i)} \ \ 0 \leq v(x, t) \leq v_0 \ \text{ in } \bar{D}_T, \\ &\text{ii)} \ \ g(v_0) \leq v_x(x, t) \leq 0 \ \text{ in } \bar{D}_T. \end{aligned} \tag{16}$$

b) If the moving boundary s also satisfies the condition

$$\exists K_2 > 0 \ / \ s(t) \leq K_2 t, \ \ \forall t \in (0, t_0],$$
$$t_0 = \frac{-v_0}{2\, K_2\, g(v_0)} > 0, \tag{17}$$

then v verifies

$$\text{i)} \ \ 0 < \frac{v_0}{2} \leq v(x, t) \leq v_0 \ \text{ in } \bar{D}_{t_0}, \tag{18}$$

$$\text{ii)} \ \ g(v_0) \leq v_x(x, t) \leq g\left(\frac{v_0}{2}\right) < 0 \ \text{ in } \bar{D}_{t_0}. \tag{18}$$

Proof. (a) The proof of (16i) is similar to the one of (4). We obtain (16ii) by using $g < 0, g' < 0, v_{xx}(0, t) = 0$ in $(0, t_0]$ and the maximum principle.

(b) For $(x, t) \in D_{t_0}$, we have

$$v(x, t) = v_0 + \int_0^x v_x(y, t)\, dy \geq v_0 + g(v_0)\, s(t) \geq \frac{v_0}{2},$$

i.e. (18i). We obtain (18ii) by using (18i), $g' < 0, v_{xx}(0, t) = 0$ in $(0, t_0]$ and the maximum principle.

LEMMA II-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

$$f(y, t) \equiv y - v_0(t) - g(y)\, s(t) = 0, \ \ y > 0, \ \ t \in (0, T) \tag{19}$$

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

$$f(y_0(t), t) = 0 \ \text{ in } (0, t'), \ \ \lim_{t \to 0^+} y_0(t) = v_0(0) > 0. \tag{20}$$

Proof. It is similar to Lemma 3 of [12].

THEOREM II-4. If g verifies (I-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 (15) for a suitably small $T > 0$.

Proof. The argument for uniqueness in Theorem II-1 still holds.

To prove the existence of a solution of problem (15) we introduce a decreasing sequence (t_n) such that

$$T > t' > t_1 > t_2 > \ldots > t_n > \ldots, \ \lim_{n \to \infty} t_n = 0, \tag{21}$$

where t' is defined in Lemma II-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 $(n = 1, 2, \ldots)$:

$$\begin{aligned} &v_{n_t} - v_{n_{xx}} = 0 \ \text{ in } D_{n,T} = \{(x, t) \,/\, 0 < x < s(t), \ t_n < t \leq T\} \\ &v_n(0, t) = v_0, \ \ t_n < t \leq T, \\ &v_{n_x}(s(t), t) = g(v_n(s(t), t)), \ \ t_n < t \leq T, \\ &v_n(x, t_n) = \Psi_n(x), \ \ 0 \leq x \leq s(t_n), \end{aligned} \tag{22}$$

where

$$\Psi_n(x) = v_0 + g(\Psi_n(s(t_n)))\, x \tag{23}$$

which is justified by Lemma II-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

$$z_{n_t} - z_{n_{xx}} = 0 \text{ in } D_{n,T},$$
$$z_n(0,t) = 0, \; t_n < t \leqslant T,$$
$$z_n(x, t_n) = \Psi_n''(x) = 0, \quad 0 \leqslant x \leqslant s(t_n), \tag{24}$$
$$z_{n_x}(s(t),t) + \dot s(t)\, z_n(s(t),t) = g'(\gamma(t))\,[\dot s(t)\, g(\gamma(t)) + z_n(s(t),t)],$$

$$\gamma(t) = \int_{t_n}^{t} [\dot s(\tau)\, g(\gamma(\tau)) + z_n(s(\tau),\tau)]\, d\tau + \Psi_n(s(t_n)).$$

From [6] we can see that there exists a $T_1 > 0$ sufficiently small so that

$$\| z_n \|_{D_{n,T_1}} \leqslant \sup_{t \in [t_n, T_1)} \dot s(t) \cdot \sup_{v \in (v_0/2, v_0)} | g(v) | \leqslant \text{const.}, \tag{25}$$

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 $D_{n,T}$ $(T \leqslant T_1)$ by

$$\tilde v_n(x,t) = v_0 + x\left[g(\Psi_n(s(t_n))) + \int_{t_n}^{t} z_{n_x}(0,\tau)\, d\tau \right] + \int_0^x d\xi \int_0^{\xi} z_n(y,t)\, dy \tag{26}$$

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) $\tilde v_n(0,t) = v_0$, $0 < t \leqslant T$.

iii) $\tilde v_n(x,t_n) = v_0 + x\, g(\Psi_n(s(t_n))) = \Psi_n(x)$, $0 \leqslant x \leqslant s(t_n)$.

iv) $$\tilde v_{n_x}(s(t),t) = g(\Psi_n(s(t_n))) + \int_{t_n}^{t} z_{n_x}(0,\tau)\, d\tau + \int_0^{s(t)} z_n(x,t)\, dx = g(\Psi_n(s(t_n))) + \int_0^{t} g'(\gamma(\tau))\, \dot\gamma(\tau)\, d\tau = g(\gamma(t)), \; 0 < t \leqslant T,$$

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) $\dfrac{d}{dt}\tilde v_n(s(t),t) = \dot s(t)\, g(\gamma(t)) + z_n(s(t),t) = \dot\gamma(t)$, $t \in (t_n, T]$,

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 (22) and then we obtain that

$$\| v_{n_{xx}} \|_{D_{n,T}} \leqslant \text{const.}, \; \| v_{n_x} \|_{D_{n,T}} \leqslant \text{const.}, \quad \forall n. \tag{27}$$

Let $v = v(x,t)$ be the limit function of v_n when $n \to \infty$. Then v verifies (15i,ii); hence it remains to verify the condition (15iii) on the moving boundary $x = s(t)$. Let $t \in (0,T)$ and $x \in (0, s(t))$ be fixed and consider

$$v(s(t),t) - v(x,t) = [v(s(t),t) - v_n(s(t),t)] + [v_n(s(t),t) - v_n(x,t)] + [v_n(x,t) - v(x,t)] =$$
$$= [v(s(t),t) - v_n(s(t),t)] + [v_n(x,t) - v(x,t)] + g(v_n(s(t),t))\,(s(t)-x) - \frac{1}{2} v_{n_{xx}}(\tilde x, t)\,(s(t)-x)^2$$

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

$$| v(s(t),t) - v(x,t) - g(v_n(s(t),t))\,(s(t)-x) | \leqslant 2\| v - v_n \| + \text{const.}\,(s(t)-x)^2 \tag{28}$$

Therefore, passing to the limit $n \to \infty$ and then $x \to s(t)$, we obtain condition (15iii), because of (27).

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 (I-6), where the functions f and g verify (I-7).

Owing to $f' > 0$ and the a priori estimate (II-18) we have

$$\dot s(t) \geqslant f\left(\frac{v_0}{2}\right) > 0, \; \forall\, t \in (0, t_0] \tag{1}$$

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

$$T \leqslant \text{Min}\,(t_0, t', T_1) \tag{2}$$

where t_0, t', and T_1 are given by (II-17), Lemma II-3 and (II-25) 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 $0 < K_1 \leqslant \dot r(t) \leqslant K_2$ in $(0,T]$ we define $v = v(x,t)$ as the unique solution of the problem

$$v_t - v_{xx} = 0 \text{ in } D_{\Gamma,T} = \{(x,t) / 0 < x < r(t), \; 0 < t \leqslant T\},$$
$$v(0,t) = v_0 > 0, \; 0 < t \leqslant T, \tag{3}$$
$$v_x(r(t),t) = g(v(r(t),t)), \quad 0 < t \leqslant T.$$

Function v satisfies in $\bar D_{r,T}$ the estimates (II-17, 18), i.e.

$$\frac{v_0}{2} < v(x,t) < v_0,$$
$$|v_x(x,t)| < G \equiv \sup_{y\in[v_0/2,v_0]} |g(y)| \,(=-g(v_0)). \tag{4}$$

In a similar way to the proof of the theorem II-4 and taking into account [6], 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

$$B=\{s\in C^0[([0,T])\cap C^1((0,T])\,/\,s(0)=0, \tag{5}$$
$$0<K_1 < \dot{s}(t) < K_2,$$
$$|\dot{s}(t_2)-\dot{s}(t_1)| < K_3\,|t_2-t_1| \text{ for } 0<t_1,\,t_2<T\}$$

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

$$0<K_1<\min_{y\in[v_0/2,v_0]} f(y),\ 0<\max_{y\in[v_0/2,\,v_0]} f(y)<K_2,$$
$$K_3 > f_0[G\,K_2+z_0(G,K_2)]. \tag{6}$$

In our case, we can choose

$$K_1=f\left(\frac{v_0}{2}\right),\ K_2=f(v_0),\ K_3=f_0(G\,K_2+z_0(G,K_2)) \tag{6 bis}$$

We define the operator

$$F_2:B\to B\,/\,F_2(r)=\tilde{r}, \tag{7}$$

where $\tilde{r}$ is given by

$$\tilde{r}(t)=\int_0^t f(v(r(\tau),\tau))\,d\tau,\qquad t\in[0,T], \tag{8}$$

and $v=v(x,t)$ is the unique solution of (3) which satisfies the following estimates

$$\frac{v_0}{2}<v<v_0,\ |v_x|<G,\ |v_{xx}|<z_0 \ \text{ in } \bar{D}_{r,T}. \tag{9}$$

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

$$|\dot{\tilde{r}}(t_2)-\dot{\tilde{r}}(t_1)| < f_0\,|v(s(t_2),t_2)-v(s(t_1),t_1)| <$$
$$< f_0[\,|v(s(t_2),t_2)-v(s(t_1),t_2)|+|v(s(t_1),t_2)-v(s(t_1),t_1)|\,] <$$
$$< f_0(G\,K_2+z_0)\,|t_2-t_1| < K_3\,|t_2-t_1|,\ \text{for } t_1,t_2\in(0,T].$$

Now we define the distance between two functions in B as

$$d(s_2,s_1)=\|s_2-s_1\|_{C^\circ([0,T])}. \tag{10}$$

and we prove

THEOREM III-5. The mapping F_2 of B into itself is a contraction in the metric (10) for a suitably small $T>0$. Moreover, the free boundary problem (I-6) admits a unique solution.

Proof. Let v and u be the corresponding solution of the moving boundary problem (3) for the datum $s\in B$ and $r\in B$ respectively.

Let

$$\delta_{F_2}(t)=|\tilde{s}(t)-\tilde{r}(t)|,\ \|\delta_{F_2}\|_t=\sup_{0<\tau<t}\delta_{F_2}(\tau),$$
$$\delta(t)=|s(t)-r(t)|,\ \|\delta\|_t=\sup_{0<\tau<t}\delta(\tau), \tag{11}$$
$$\sigma_1(t)=\operatorname{Inf}(s(t),r(t)),\quad \sigma_2(t)=\operatorname{Sup}(s(t),r(t)).$$

Without loss of generality we suppose that $\sigma_1=r$ and $\sigma_2=s$. Then we have the following estimate

$$\delta_{F_2}(t)=f_0\int_0^t |v(s(\tau),\tau)-u(r(\tau),\tau)|\,d\tau < \tag{12}$$
$$< f_0\,t\,\|v|_s-u|_r\|_t$$

where (we note with $v|_s$ and $v|_r$ the restriction of v on $x=s(t)$ and $x=r(t)$ respectively)

$$\|v|_s-u|_r\|_t=\max_{0<\tau<t}|v(s(\tau),\tau)-u(r(\tau),\tau)| <$$
$$< \max_{0<\tau<t}|v(s(\tau),\tau)-v(r(\tau),\tau)|+ \tag{13}$$
$$+\max_{0<\tau<t}|v(r(\tau),\tau)-u(r(\tau),\tau)| \equiv b(t)+a(t).$$

Applying the average value theorem to the definition of $b(t)$ we deduce that

$$b(t) < G\,\|\delta\|_t. \tag{14}$$

Owing to the expressions

$$v(r(t),t)=v_0+\int_0^t v_x(x,t)\,dx, \tag{15}$$

$$u(r(t),t)=v_0+\int_0^t u_x(x,t)\,dx,$$

we obtain

$$|v(r(t),t)-u(r(t),t)| < K_2\,t\,\|v_x-u_x\|_{D_{r,t}}=$$
$$=K_2\,t\sup_{0<\tau<t} C(\tau) \tag{16}$$

where

$$C(\tau)=|v_x(r(\tau),\tau)-u_x(r(\tau),\tau)| < |v_x(r(\tau),\tau)-v_x(s(\tau),\tau)|+$$
$$+|g(v(s(\tau),\tau))-g(u(r(\tau),\tau))| < z_0\,|s(\tau)-r(\tau)|+ \tag{17}$$
$$+g_0\,|v(s(\tau),\tau)-u(r(\tau),\tau)| <$$
$$< z_0\,\|\delta\|_t+g_0\,\|v|_s-u|_r\|_t.$$

Therefore, we have

$$a(t) < K_2\,t\,[z_0\,\|\delta\|_t+g_0\,\|v|_s-u|_r\|_t]. \tag{18}$$

By using (14) and (18), we obtain

$$\|v|_s-u|_r\|_t < G\,\|\delta\|_t+K_2\,t\,[z_0\,\|\delta\|_t+ \tag{19}$$

$$+ g_0 \| v|_s - u|_r \|_t]. \tag{19}$$

i.e.

$$\| v|_s - u|_r \|_t \leqslant \frac{G + K_2 z_0 t}{1 - K_2 g_0 t} \| \delta \|_t \leqslant \alpha_0 \| \delta \|_t, \; t \leqslant t^*, \tag{20}$$

where

$$t^* = \frac{1}{2 K_2 g_0} > 0, \;\; \alpha_0 = 2G + \frac{z_0}{g_0} > 0. \tag{21}$$

From (12) and (20) we deduce that

$$\| \delta_{F_2} \|_t \leqslant f_0 \alpha_0 t \| \delta \|_t, \;\; t \leqslant t^*, \tag{22}$$

i.e. F_2 is a contraction operator for a suitably small $T > 0$. In our case, we have

$$T < \mathrm{Min} \left(t^*, \frac{1}{f_0 \alpha_0} \right). \tag{23}$$

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