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PENETRATION OF A SOLVENT INTO A NON-HOMOGENEOUS POLYMER*

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SOMMARIO. Si studia un problema unidimensionale a frontiera libera, che deriva da un modello per l'assorbimento di solventi nei polimeri vetrosi. Si suppone che il problema abbia simmetria piana e che il polimero sia non omogeneo nella direzione di avanzamento del fronte. Si prova l'esistenza e la stabilità della soluzione ed inoltre si descrive il comportamento asintotico.

SUMMARY. We consider a free boundary problem arising from a model for sorption of solvents by glassy polymers. We assume that the problem has planar symmetry, but it is non-homogeneous in the direction of the advancing front. We give an extensive mathematical analysis of the problem, proving existence and stability of the solution and describing some asymptotical behaviours.

1. INTRODUCTION

In this paper we consider a free boundary problem arising from a model for the sorption of solvents into glassy polymers.

This model was proposed in [2] by Astarita and Sarti. They assumed that the sorption process can be described using a free boundary to simulate a sharp morphological discontinuity observed in the material between a penetrated zone, with a relatively high solvent content, and a glassy region where the solvent concentration is negligibly small (and actually taken to be zero in the model).

The solvent is supposed to diffuse in the penetrated zone according to the Fick's law. Moreover the penetrating front moves into the glassy zone driven by chemical and mechanical effects that are taken into account by an empirical law relating the speed of penetration to the concentration of solvent near the front. This law must account for two main facts observed in the penetration experiences: (i) there exists a threshold value for the solvent concentration under which no penetration occurs; (ii) above such value the speed of the front increases with the concentration near the front itself. A typical form is $v = k\,|c - c^*|^n$ where v is the front speed, c is the value of the concentration at the front, c^* is the threshold value and k and n are constant ([2], [8]).

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One more condition is required in order to determine the front location together with the concentration profile inside the penetrated zone. This condition is the mass conservation across the moving free boundary (see [8] for a detailed derivation).

This model has been the objetc of a number of papers ([5], [4], [1], [8]) where the mathematics of the problem has been investigated.

Here we are interested in the case of a slab of non-homogeneous polymer, i.e. a polymer whose mechanical properties depend on the space variable. In this case the penetration law is generalized to $v = f(c, x)$, where x denotes the space variable. Denoting by $c(x, t)$ the (normalized) solvent concentration and by $x = s(t)$ the location of the front in the slab (then $0 < x < s(t)$ is the penetrated region at time t), the resulting abstract mathematical problem can be stated as follows:

Problem P: Find a triple (T, s, c) such that: $T > 0$, $s \in C^1([0, T])$, $c \in C^{2,1}(D_T) \cap C(\bar{D}_T)$, where $D_T = \{(x, t) : 0 < x < s(t), 0 < t < T\}$, and satisfying

$$c_{xx} - c_t = 0, \qquad \text{in } D_T; \tag{1.1}$$

$$s(0) = 0; \tag{1.2}$$

$$c(0, t) = c_0, \qquad 0 < t < T; \tag{1.3}$$

$$\dot{s}(t) = f(c(s(t), t), s(t)), \qquad 0 < t < T; \tag{1.4}$$

$$c_x(s(t), t) = -\dot{s}(t)c(s(t), t), \qquad 0 < t < T. \tag{1.5}$$

The function f is assumed to satisfy the following assumptions:

$$f \in C(\mathbb{R}^2); \tag{F.i}$$

there exists a non negative, continuous function $c^*(x)$ such that

$$f(c, x) > 0 \ \text{ in } \ E = \{(c, x) : c > c^*(x), \ x \geq 0\} \ \text{ and } \ f(c^*(x), x) = 0; \tag{F.ii}$$

for $x > 0$ there exist two continuous functions $L(x)$ and $\epsilon(x) > 0$ such that

$$c^*(x) - c^*(x - h) \leq L(x)h, \ \text{ for any } \ h \in (0, \epsilon(x)), \tag{F.iii}$$

$$f_c, f_x \ \text{ exist and are Lipschitz continuous in } E \tag{F.iv}$$

$$f_c(c, x) > 0, \ \text{ for any } \ (c, x) \in E \tag{F.v}$$

Here c^* represent the (normalized) threshold value for the penetration process. The function f gives the speed of penetration of the jump in concentration as an increasing function of the amount of the jump itself (condition F.v). According to the physical scheme of the process, f vanishes when the concentration equals the threshold value. Then the condition $(c(s(t), t), s(t)) \in E$ implies that the free boundary can move inward into the glassy zone. We will prove that this condition is always satisfied under our hypotheses.

The most obvious hypothesis is of course that the value c_0, i.e. the (normalized) value of the concentration on the fixed boundary, which is assumed to be constant, satisfies the condition $c_0 > c^*(0)$, i.e. the concentration on the fixed boundary excedes the threshold value there, so that the penetration of the solvent can start.

Conditions (F.iii) and (F.iv) are tecnical assumptions, in particular (F.iii) is a sort of one-side Lipschitz condition for the function c^*.

From the hypotheses (F) it follows that there exists a function $\phi \in C(\overline{f(E)} \times \mathbb{R}^+)$ such that $\phi(f(c, x), x) = c$ for any $x > 0$ and $c > c^*(x)$. Moreover ϕ satisfies:

$$\phi \in C^1(G), \qquad G = f(E) \times \mathbb{R}^+; \qquad (\Phi.\text{i})$$

$$\phi > 0, \qquad \text{in } G; \qquad (\Phi.\text{ii})$$

$$\phi(\eta, x) > c^*(x), \qquad \text{for any } \eta > 0, \ x \geq 0; \qquad (\Phi.\text{iii})$$

$$\phi_\eta(\eta, x) > 0, \qquad \text{in } G. \qquad (\Phi.\text{iv})$$

We can use the function ϕ to rewrite the penetration law (1.4) in an equivalent form:

$$c(s(t), t) = \phi(\dot{s}(t), s(t)), \qquad 0 < t < T. \qquad (1.4')$$

In the next sections we will prove existence and uniqueness of the solution of Problem P, for any $T > 0$; the continuous dependence on the datum f, and we will investigate the asymptotic behaviour of the free boundary.

2. AN AUXILIARY PROBLEM

In this section we suppose that the moving boundary is known as a function of the time, $x = r(t)$, and we study the diffusion problem for the concentration in the slab $0 < x < r(t)$.

We assume $r \in C^1[0, T] \cap C^2(0, T)$, for some fixed value of the time T. Moreover we assume

$$r(0) = 0; \qquad (2.1)$$

$$\dot{r}(0) = f(c_0, 0); \qquad (2.2)$$

$$|\ddot{r}(t)| \leq K, \qquad 0 < t < T; \qquad (2.3)$$

where K is some positive constant.

The diffusion problem we have to solve is the following: find a function $c \in C^{2,1}(D) \cap C(\overline{D})$, $D = \{(x, t) : 0 < x < r(t), 0 < t < T\}$, with c_x continuous up to the boundary $x = r(t)$ and such that

$$c_{xx} - c_t = 0, \qquad \text{in } D; \qquad (2.4)$$

$$c(0, t) = c_0, \qquad 0 < t < T; \qquad (2.5)$$

$$c_x(r(t), t) = -\dot{r}(t)\phi(\dot{r}(t), r(t)), \qquad 0 < t < T. \qquad (2.6)$$

Here condition (2.6) is reminiscent of condition (1.5), expressed in terms of the function r alone, i.e. substituting the value of the function ϕ to the value of the concentration at the boundary.

Existence and uniqueness of the solution of problem (2.4) - (2.6) have been proved in [6]. Here we give some estimates of the solution and of its derivatives.

Let us start noticing that, since the function c^* is continuous and $(c_0, 0)$ belongs to E, then we can find two positive constants, δ and x_1, such that $\overline{E(\delta, x_1)} \subset E$, where $E(\delta, x_1) = \{(c, x) : c_0 - \delta < c < c_0 + \delta, 0 < x < x_1\}$.

Now we define $A(t) = \{(x, \eta) : 0 < x < v_0 t + \frac{1}{2} Kt^2, v_0 - Kt < \eta < v_0 + Kt\}$, where $v_0 = f(c_0, 0)$. From inequality (2.3) we get

$$(r(t), \dot{r}(t)) \in A(t) \subset A(\overline{T}), \qquad 0 < t < \overline{T} < \frac{v_0}{K}. \qquad (2.7)$$

We fix a time $\overline{T}$ in such a way that the «box» $A(t)$ belongs to the set $[0, x_1] \times f(E(\delta, x_1))$ for any $t < \overline{T}$ (our assumptions grant that $\overline{T} > 0$). Then, for any time $t < \overline{T}$, we have the estimate

$$0 \leq c_0 - \delta \leq \phi(\dot{r}(t), r(t)) \leq c_0 + \delta. \qquad (2.8)$$

Since the function c_x satisfies the heat equation as well, we can apply the maximum principle to it and we obtain a first estimate:

$$-(v_0 + Kt)(c_0 + \delta) \leq c_x(x, t) \leq 0, \quad 0 < x < r(t), \quad 0 < t < \overline{T}. \qquad (2.9)$$

The last inequality, together with the condition (2.5), gives an estimate for the solution c:

$$c_0 - (v_0 + Kt)(c_0 + \delta)(v_0 + 1/2\, Kt) \leq c(x, t) \leq c_0, \quad 0 < x < r(t), \quad 0 < t < \overline{T}. \qquad (2.10)$$

Finally we can give a simple estimate, uniform w.r.t. the function r, by restricting the time $\overline{T}$.

$$c_0 - \delta < c(x, t) \leq c_0 < c_0 + \delta, \quad 0 < x < r(t), \quad 0 < t < \overline{T}. \qquad (2.11)$$

Remark 2.1. Inequality (2.11) implies that $(c(r(t), t), r(t)) \in E(\delta, x_1)$, $0 \leq t \leq \overline{T}$.

Remark 2.2. Once δ and x_1 fixed, independently of the function r in the class specified by conditions (2.1) - (2.3), the value of $\overline{T}$ depends in a nice way on K. In particular it is always positive for any finite K.

The estimate of the maximum of the time derivative c_t is obtained via the maximum principle. The complete proof, in the case ϕ not depending on the space variable, is given in [5] and it works in this case as well. In particular one can prove that $c \in C^{2,1}(\overline{D})$ and $c_{xt} \in C(\overline{D} \setminus \{0, 0\})$, and

$$|c_t(x, t)| \leq M_1(K)(1 + \sup_{(0,\overline{T})} \dot{r} / \inf_{(0,T)} \dot{r}) \sup_{(0,\overline{T})} r \leq M_1(K)(1 + 3v_0)5/4 v_0 t \leq L_1, \qquad t \leq \overline{T}; \qquad (2.12)$$

where L_1 does not depend on K, provided that the time $\overline{T}$ is less than $\frac{v_0}{2K}$.

The last inequality makes it possible to compare two solutions, c_1 and c_2, corresponding to two different boundaries $x = r_1(t)$ and $x = r_2(t)$. In fact we have

$$|c_1(r_1(t), t) - c_2(r_2(t), t)| \leqslant L_2 t \| r_1 - r_2 \|_{C^1([0, \overline{T}])}, \qquad (2.13)$$

where, again, the constant L_2 does not depend on K, if $\overline{T} \leqslant \dfrac{v_0}{2K}$. The proof is again the same as that of the spatially homeneous case in [5] and we do not repeat it.

3. LOCAL EXISTENCE, UNIQUENESS

In this section we prove the existence of a local solution using a fixed point argument. We first define an appropriate functional space. To this aim, let α be any constant with $0 < \alpha < 1$, and let $\gamma(t)$ be a positive non decreasing function defined for $t > 0$, possibly diverging for $t \to 0$. Let K and T be positive constants.

We denote by $\mathscr{X}(K, T, \gamma, \alpha)$ the [illegible] functions $r(t)$ satisfying:

$$r \in C^1([0, T]) \cap C^2((0, T]), \qquad r(0) = 0,$$

$$\dot{r}(0) = f(c_0, 0), \quad |\ddot{r}(t)| \leqslant K, \quad 0 \leqslant t \leqslant T,$$

and

$$|\ddot{r}(t_1) - \ddot{r}(t_2)| \leqslant \gamma(\tau)(t_2 - t_1)^{\alpha/2}, \quad 0 < \tau < t_1 < t_2 \leqslant T. \qquad (3.1)$$

The set $\mathscr{X}(K, T, \gamma, \alpha)$ is a closed subset of $C^1([0, T])$ w.r.t. to the C^1 norm. We define a map $\mathscr{G}$ on $\mathscr{X}$ in the following way:

for any function $r \in \mathscr{X}$ let $c(x, t)$ be the corresponding solution of (2.4) - (2.6), and let $\tilde{r}$ be defined by

$$\dot{\tilde{r}}(t) = \int_0^t f(c(r(\tau), \tau), r(\tau))\, d\tau, \qquad 0 \leqslant t \leqslant T, \qquad (3.2)$$

and define the map $\mathscr{G}$ by $\mathscr{G}r = \tilde{r}$. We want to prove that, with an appropriate choice of the constants α, K, T and of the function, γ, $\mathscr{G}$ maps the set $\mathscr{X}$ into itself and it is a contraction. This implies that there exists a unique fixed point for the operator $\mathscr{G}$ in the set $\mathscr{X}$, so that the following theorem holds:

THEOREM 3.1. Problem P admits at least a local solution, moreover the concentration c satisfies $c \in C^{2,1}(\overline{D})$ and $c_{xt} \in C(\overline{D} \setminus \{0, 0\})$.

Proof. We start proving that $\mathscr{G}$ maps $\mathscr{X}$ into itself. Conditions (2.1) and (2.2) are trivially satisfied. Moreover we have

$$\ddot{\tilde{r}}(t) = f_c(c(r(t), t), r(t))[c_x(r(t), t)\dot{r}(t) + c_t(r(t), t)] +$$
$$+ f_x(c(r(t), t), r(t))\dot{r}(t), \qquad 0 < t \leqslant T. \qquad (3.3)$$

From the estimates of sec. 2, it follows that for any constant K there exists a $T(K)$ such that the r.h.s. of (3.3) is bounded by a constant H depending only on δ, x_1 and $f(c_0, 0)$, once $T \leqslant T(K)$. Choosing $H = K$ we have $|\ddot{\tilde{r}}(t)| \leqslant K$, $0 < t \leqslant T$.

In order to prove that $\tilde{r}$ satisfies (3.1) one needs to give an estimate of the norm of $c_x(x, t)$ in the space $C^{1+\alpha}$ for some $\alpha \in (0, 1)$ (which gives an estimate of the C^α norm of c_t). To this aim, let us define $z(x, t) = c_x(x, t) + \dot{r}(t)\phi(\dot{r}(t), r(t))$, which solves

$$z_{xx} - z_t = -\ddot{r}(t)[\phi(\dot{r}(t), r(t)) + \phi_\eta(\dot{r}(t), r(t))\dot{r}(t)] -$$
$$- \dot{r}^2(t)\phi_x(\dot{r}(t), r(t)),$$
$$z_x(0, t) = 0,$$
$$z(r(t), t) = 0.$$

Now, for any $\tau \in (0, T)$ trasform the domain $\{0 < x < r(t), \tau/2 < t < T\}$ into the rectangle $(0, 1) \times (\tau/2, T)$ by the change of variables $y = x/r(t)$ and apply the Schauder estimates (see Theorem 5.2, pag. 561 of [10]) to the transformed function $\tilde{z}(y, t)$ in order to obtain the estimate

$$\|\tilde{z}\|_{C^{1+\alpha}} \leqslant \overline{\gamma}(\tau), \qquad \tau < t < T,$$

where $\overline{\gamma}(\tau)$ depends also on K, the time T, the function f, and the constant α.

Finally, inserting these estimates into (3.3) and defining $\overline{\gamma}(t)$ accordingly, we obtain that $\ddot{\tilde{r}}(t)$ satisfies (3.1).

The contractive character of $\mathscr{G}$ follows from the continuous dependence of c on the function $r(t)$, as in (2.13). Infact we have:

$$\|\tilde{r}_1 - \tilde{r}_2\|_{C^1([0,T])} \leqslant \sup_{E(\delta, x_1)} |f_c(c, x)|\, |c_1(r_1(t), t) - c_2(r_2(t), t)| +$$
$$+ \sup_{E(\delta, x_1)} |f_x(c, x)|\, \|r_1 - r_2\|_{C([0,T])} \leqslant \qquad (3.4)$$
$$\leqslant L_3 T \|r_1 - r_2\|_{C^1([0,T])}.$$

Finally we reduce T, if necessary, to have $L_3 T < 1$.

The regularity properties of the solution follow from the estimate on the solution of the auxiliary problem. To prove that $\ddot{s}(t)$ is continuous up to $t = 0$, recall (3.2) and assumption (F). □

Because of the contractive character of the transformation $\mathscr{G}$, the local solution is also unique in the set $\mathscr{X}$. Although the solution happens to be unique in a larger functional class, which is in fact the largest one for the classical solution to make sense. The proof is quite the same as in the case of f independent of x, which is given in [5], and we only state the result:

THEOREM 3.2. Problem P admits at most one solution.

4. GLOBAL EXISTENCE

Here we give some qualitative properties of the solution of Problem P.

PROPOSITION 4.1. Assume that the function f in condition (1.4) belongs to $C^\infty(E)$, then the free boundary $s(t)$ belongs to $C^\infty((0, T)) \cap C^2([0, T])$.

Proof. We define the function $u(x, t)$ by

$$u(x,t) = -\int_x^{s(t)} c(y,t)\,dy, \tag{4.1}$$

which satisfies the heat equation in $D_T = \{(x,t) : 0 < x < s(t), 0 < t < T\}$, with boundary conditions $u_x(0,t) = -c_0$, $u(s(t),t) = 0$, and the non-linear Stefan condition $f(u_x(s(t),t), s(t)) = \dot{s}(t)$. Then we can prove the regularity of the free boundary applying the iterative techniques introduced in [11] for the linear Stefan problem.

PROPOSITION 4.2. The free boundary is a strictly increasing function of t, i.e. $\dot{s}(t) > 0, 0 < t < T$.

Proof. Since $\dot{s}(0) = f(c_0, 0) > 0$, and $\dot{s}$ is continuous, then $\dot{s}(t) > 0$ for some interval $(0, t')$. Suppose that $\dot{s}(t) \leqslant 0$ somewhere, and let t_1 be the infimum of such t's. Then $t_1 > 0$, and $\dot{s}(t) > 0$ in $0 \leqslant t < t_1$, $\dot{s}(t_1) = 0$. From (1.5) $c_x(s(t_1), t_1) = 0$ and then $(s(t_1), t_1)$ is a maximum point for c_x in $D_{t_1} = \{(x,t) : 0 < x < s(t), 0 < t < t_1\}$. This implies that the space derivative of the function c_x in this point is strictly positive (see [3]), and then $c_t(s(t_1), t_1) > 0$. It follows that the total derivative w.r.t. the time of the function c evaluated along the curve $x = s(t)$ is positive in $t = t_1$ so that $c(s(t), t)$ is strictly increasing in an interval (t_2, t_1) for some $t_2 < t_1$. On the other side, since t_1 is the first zero of $\dot{s}(t)$ and $(c_0, 0) \in E$, then $(c(s(t), t), s(t)) \in E$ for any $t < t_1$, or $c(s(t), t) > c^*(s(t))$, for $t < t_1$ and $c(s(t_1), t_1) = c^*(s(t_1))$. This gives, together with assumption (F.iii)

$$\frac{c(s(t_1), t_1) - c(s(t_1 - h), t_1 - h)}{h} \leqslant \frac{c^*(s(t_1)) - c^*(s(t_1 - h))}{h} \leqslant$$

$$\leqslant L(s(t_1)) \frac{s(t_1) - s(t_1 - h)}{h}.$$

Finally we pass to the limit $h \to 0^+$, and we get the contradictory inequality

$$0 < \frac{d}{dt} c(s(t), t)\Big|_{t=t_1} \leqslant L(s(t_1))\,\dot{s}(t_1) = 0.$$

PROPOSITION 4.3. The solution of Problem P satisfies the following inequalities:

$$c(x,t) < c_0, \qquad 0 < x \leqslant s(t),\ 0 < t < T; \tag{4.2}$$

$$0 < \dot{s}(t) \leqslant \bar{s}, \qquad 0 \leqslant t \leqslant T; \tag{4.3}$$

$$-c_0 \bar{s} < c_x(x,t) < 0, \quad \text{in } D_T, \tag{4.4}$$

where $\bar{s} = \sup_{E_T} f(c,x)$, $E_T = E \cap \{(c,x) : c < c_0, x < s(T)\}$.

The proof is a strighforward application of the maximum principle to the functions c and c_x, recalling that $\dot{s}$ is strictly positive.

THEOREM 4.4. Problem P admits a solution for arbitrarily large T.

Proof. Theorem 3.2 ensures that there exists a (unique) solution of the problem up to a time determined by the estimates of the solution itself. Let T^* be the maximum time of existence and suppose that $T^* < \infty$ $(T^* > 0)$.

Now let us consider the free boundary problem for u defined by the transformation (4.1) in the region $D' = \{(x,t) : 0 < x < s(t), T^* < t < T'\}$, with initial conditions

$$s(T^*) = b = \lim_{t \to T^{*-}} s(t),$$

$$u(x, T^*) = h(t) = \lim_{t \to T^{*-}} -\int_x^{s(t)} c(y,t)\,dy, \quad 0 < x < b.$$

Notice that $\lim_{t \to T^{*-}} s(t)$ exists because of the monotonicity of the free boundary $x = s(t)$ for $t < T^*$.

In order to prove the existence of $\lim_{t \to T^{*-}} c(x,t)$, we use Green's identity in the domain $\{(\xi,\tau) : 0 < \xi < s(\tau), T'' < \tau < t - \epsilon\}$, $0 < T'' < t < T^*$, and let ϵ tend to zero. We obtain:

$$c(x,t) = \int_0^{s(T'')} G(x,t;\xi,T'')c(\xi,T'')\,d\xi + \int_{T''}^t c_0 G_\xi(x,t;0,\tau)\,d\tau -$$

$$- \int_{T''}^t G_\xi(x,t;s(\tau),\tau)c(s(\tau),\tau)\,d\tau,$$

where G is the Green's function for the first quarter: $G(x,t;\xi,\tau) = \Gamma(x,t;\xi,\tau) - \Gamma(-x,t;\xi,\tau)$, and Γ is the fondamental solution for the heat operator:

$$\Gamma(x,t;\xi,\tau) = \frac{1}{2\sqrt{\pi(t-\tau)}} \exp\left\{-\frac{(x-\xi)^2}{4\pi(t-\tau)}\right\}.$$

Using the relation $G_x = -N_\xi$ between Green's function and Neuman's function $N(x,t;\xi,\tau) = \Gamma(x,t;\xi,\tau) + \Gamma(-x,t;\xi,\tau)$, and recalling lemma 1, pag. 215 of [9], we obtain:

$$c(s(t),t) = 2\left\{\int_0^{s(T'')} G(x,t;\xi,T'')c(\xi,T'')\,d\xi + \int_{T''}^t c_0 G_\xi(x,t;0,\tau)\,d\tau + \right. \tag{4.5}$$

$$\left. + \int_{T''}^t N_x(s(t),t;s(\tau),\tau)\,c(s(\tau),\tau)\,d\tau\right\}.$$

The first two integrals in (4.5) are obviously convergent. As to the third one, it is sufficient to recall that $s(t)$ is Lipschitz-continuous (Proposition 4.3) and that $N_x(s(t), t; s(\tau), \tau) \leqslant \text{const.}/\sqrt{(t-\tau)}$.

The existence and uniqueness of the solution of the free boundary problem for u, in the region $D' = \{(x,t) : 0 < x < s(t), T^* < t < T'\}$, for a suitable $T' > T^*$, is now ensured by [7], recalling that the free boundary $s(t)$ is strictly increasing. Moreover this solution satisfies $u \in C^{1,0}(\bar{D}') \cap C^{2,1}(D')$, $s \in C^1([T^*, T'])$.

It follows that $s(t)$ and $c(x,t) = u_x(x,t)$ satisfy Problem P up to a time $T' > T^*$. □

5. CONTINUOUS DEPENDENCE AND OTHER QUALITATIVE PROPERTIES OF THE SOLUTION

First we state the continuous dependence of the solution on the function f defined in (1.4):

PROPOSITION 5.1. Assume f_1, f_2, both satisfying assumptions (F), are the data for problem (1.1) - (1.5). Let $s_i, c_i, i = 1, 2$, be the corresponding solutions in a fixed interval $(0, T)$, then:

$$\| s_1 - s_2 \|_{C^1((0,T))} \leqslant \text{const.} \sup_{E'} | f_1(c, x) - f_2(c, x) |, \qquad (5.1)$$

where $E' = E \cap \{(c, x) : c < c_0, x < \min(s_1(T), s_2(T))\}$.

Proof. The contractive character of the operator $\mathscr{G}$ defined in (3.2) does not depend on f: in fact the boundedness of $\ddot{s}$ yields a lower bound for $\dot{s}$ independent of f, in a suitable time interval $[0, T_0]$. Moreover $\overline{\mathscr{G}}$ depends continuously on $\| f_1 - f_2 \|_{C((0,T))}$.

The continuous dependence for large time can be obtained applying the results of [7] to the solution of the problem defined by (4.1).

Concerning the monotone dependence we have the following

PROPOSITION 5.2. Let $s_i, c_i, i = 1, 2$, be two solutions of problem P, corresponding to the functions f_1, f_2, both satisfying assumptions (F), and such that $f_1(c, x) < f_2(c, x)$ for any c, x. Then

$$s_1(t) < s_2(t), \qquad 0 < t < T. \qquad (5.2)$$

Proof. Let us consider the corresponding $u_i(x, t)$ defined by (4.1). Since $\dot{s}_1(0) < \dot{s}_2(0)$, suppose that a t_0 exists such that $s_1(t_0) = s_2(t_0)$ and $s_1(t) < s_2(t)$, for any $t < t_0$. Then

$$\dot{s}_1(t_0) \geqslant \dot{s}_2(t_0). \qquad (5.3)$$

Set $v = u_1 - u_2$ and $D_0 = \{(x, t) : 0 < x < s_1(t), 0 < t < t_0\}$, then v satisfies $v_{xx} = v_t$, in D_0, $v_x(0, t) = 0$, $v(s_1(t), t) > 0$, $0 < t < t_0$, and $v(s_1(t_0), t_0) = 0$. Therefore v has a minimum in the point $(s_1(t_0), t_0)$, and then $v_x(s_1(t_0), t_0) < 0$. It follows that

$$\dot{s}_1(t_0) - \dot{s}_2(t_0) = f_1(u_{1x}(s_1(t_0), t_0), s_1(t_0)) -$$
$$- f_2(u_{2x}(s_2(t_0), t_0), s_2(t_0)) \leqslant$$
$$\leqslant f_{2c}(\mu, s_1(t_0))(u_{1x}(s_1(t_0), t_0) - u_{2x}(s_2(t_0), t_0)) < 0,$$

with $u_{1x}(s_1(t_0), t_0) < \mu < u_{2x}(s_2(t_0), t_0)$, which contradicts (5.3).

Remark 5.3. Let us consider two different functions c_1^*, c_2^* with $c_1^* < c_2^*$, and corrispondently the functions f_1, f_2, such that $f_1(c, x) = f_2(c + c_2^* - c_1^*, x)$.

According to assumptions (F), we have:

$f_i > 0$ in $E_i = \{(c, x) : c > c_i^*, \ x \geqslant 0\}$, $f_i = 0$ in $\mathbb{R}^2 \setminus E_i$, $i = 1, 2$.

Then $f_1 > f_2$ for any c, x. Proposition 5.2 ensures $s_1(t) > s_2(t)$, $t > 0$.

Some more properties of the solution can be proved if we specify the behaviour of f with respect to x.

PROPOSITION 5.4. Assume f_x to be negative. Then:

$$c_t(x, t) > 0, \quad 0 < x < s(t), \quad 0 < t < T, \qquad (5.4)$$

$$c_{xt}(0, t) > 0, \quad 0 < t < T. \qquad (5.5)$$

Proof. Let $w = c_t$, then w solves the heat equation in D_T with boundary conditions $w(0, t) = 0$, $w(s(t), t)\,\alpha(t) + w_x(s(t), t) = \beta(t)$, where $\alpha(t) = 2(\dot{s} + f_c c)|_{x = s(t)}$, $\beta(t) = -\dot{s}(c_x \dot{s} + c f_c c_x + c f_x)|_{x = s(t)}$.

Since $\alpha(t)$ and $\beta(t)$ are non-negative, the maximum principle implies that w cannot assume a negative minimum nor vanish on $x = s(t)$. Then w is strictly positive inside D_T. It follows that the minimum for w is assumed on the boundary $x = 0$, that is $w_x(0, t) > 0$.

PROPOSITION 5.5. Assume f_x to be positive, then the function $a(t) = c(s(t), t)$ is decreasing in $0 < t < T$.

Proof. Set $v = (ln(c))_{xx}$. Theorem 3.2 ensures that v is continuous in $\overline{D}_T$ and that v_x is continuous in $\overline{D}_T \setminus \{0, 0\}$. Moreover v solves

$$v_{xx} + 2(ln(c))_x v_x + 2v^2 - v_t = 0, \quad \text{in } D_T, \qquad (5.6)$$

with boundary conditions

$$v(0, t) = -(c_x(0, t)/c(0, t))^2,$$

$$v(s(t), t) = (\ddot{s} - f_x \dot{s})/(f_c c)|_{x = s(t)}.$$

Since $v(0, 0) < 0$ and v is continuous at $\{0, 0\}$, $v(s(t), t)$ is negative in some interval $[0, t_0)$. The maximum principle (e.g. in the form of Thm. 5, pag. 39 of [9]) applied with some care to equation (5.6) implies that, if $v(s(t), t)$ vanishes for the first time at some $t_0 > 0$, then $(s(t_0), t_0)$ is a point of maximum for v, that is $v_x(s(t_0), t_0) > 0$. However $v_x(s(t_0), t_0) = -f_x f|_{x = s(t_0), t = t_0}$ is non-positive. Therefore $v(s(t), t)$ cannot vanish, that is $\ddot{s}(t) < f_x(c(s(t), t), s(t))\dot{s}(t)$, $0 < t < T$. The result follows recalling that $\ddot{s}(t) = f_c(c(s(t), t), s(t))\,\dot{a}(t) + f_x(c(s(t), t), s(t))\dot{s}(t)$.

6. ASYMPTOTIC BEHAVIOUR

In this section we give some Propositions describing the behaviour of the solution of Problem P when t goes to infinity.

PROPOSITION 6.1. Suppose that a finite $\bar{x}$ exists such that $c^*(\bar{x}) \geqslant c_0$, then $s(t) < \bar{x}$ for any $t > 0$.

Proof. Suppose that there exists a $\bar{t}$ such that $s(\bar{t}) = \bar{x}$, then $(c(s(\bar{t}), \bar{t}), s(\bar{t})) \in \mathbb{R}^2 \setminus E$. However Proposition 4.2 ensures that the distance of the points $(c(s(t), t), s(t))$ from the boundary of the set E is positive for any $t < T$.

PROPOSITION 6.2. Suppose that the free boundary $s(t)$ has an asymptote at $x = x_0$, then $\lim_{t\to\infty} c(s(t), t) = c_0$ and $\lim_{t\to\infty} \dot{s}(t) = 0$.

Proof. Let $u(x, t)$ be defined by (4.1), then

$$c_0(x - x_0) \leqslant u(x, t) \leqslant 0. \tag{6.1}$$

Fixed an arbitrarily large integer $\bar{n}$, for any $n > \bar{n}$ let $u_n(x, t)$ be the solution of

$$u_{n_{xx}} = u_{n_t}, \text{ in } D_n = \{(x, t) : 0 < x < x_n, \quad t > t_n\},$$

where t_n is such that $s(t_n) = x_n = x_0 - 1/n$, with initial and boundary conditions

$$u_n(x, t_n) = 0, \quad 0 < x < x_n, \quad u_{nx}(0, t) = c_0,$$

$$u_n(x_n, t) = 0, \qquad t > t_n.$$

Notice that

$$u(x, t) < u_n(x, t), \quad \text{in } D_n. \tag{6.2}$$

Letting t tend to infinity, we obtain $\lim_{t\to\infty} u_n(x, t) = c_0(x - x_n)$ for any n.

Recalling (6.1), Thm. 1 p. 158 of [9] ensures $\lim_{t\to\infty} u(x, t) = c_0(x - x_0)$ uniformly in any $\bar{D}_n$. Moreover

$$\lim_{t\to\infty} u_x(x, t) = \lim_{t\to\infty} c(x, t) = c_0,$$

uniformly in any interval $[0, x']$, for any $x' < x_0$ (see Thm. 15, p. 80 of [9]). It follows that $\lim_{t\to\infty} c(s(t), t)$ exists and is equal to c_0.

Therefore $\lim_{t\to\infty} f(c(s(t), t), s(t))$ exists and finally $\lim_{t\to\infty} \dot{s}(t) = \liminf_{t\to\infty} \dot{s}(t) = 0$.

COROLLARY 6.3. Suppose that $s(t)$ has an asymptote at $x = x_0$, then $x_0 = x^* = \inf\{x : c^* \geqslant c_0\}$.

Proof. Suppose that $x_0 < x^*$, then $(c_0, x_0) \in E$ and $f(c_0, x_0) > 0$. But, because of the continuity of f, we have $f(c_0, x_0) = \lim_{t\to\infty} f(c(s(t), t), s(t)) = \lim_{t\to\infty} \dot{s}(t) = 0$.

COROLLARY 6.4. Let $c^*(x)$ satisfy $c^*(x) < c_0$ for any x, then $\lim_{t\to\infty} s(t) = +\infty$.

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