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REPÚBLICA ARGENTINA

A Free Boundary Problem for the Diffusion of a Solvent into a Polymer with Non-Constant Conductivity Coefficient

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Abstract

We studied a one dimensional free boundary problem arising in the polymer industry. Imposing a convective boundary condition, the solution has an interesting asymptotic behavior. It is found that the free boundary is bounded by a constant which does not depend on the conductivity coefficient, which holds even if the diffusion process is nonlinear. Numerical methods are presented to compute the solutions and compare the results.

1 Introduction.

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

This model was proposed in [1] by Astarita and Sarti. They assumed that the sorption process can be described using a free boundary model 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).

Here we present a generalized version of the problem assuming that the conductivity coefficient K is a non-constant positive function which could depend on several quantities (x-coordinate, concentration, gradient, time, etc.). The solvent is supposed to diffuse in the penetrated zone according to Fick's law. Moreover, the penetrating zone 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 with the solvent concentration at the front. This law must account for two main facts observed in the penetration experiences: (a) there exists a threshold value for the solvent concentration under which no penetration occurs; (b) above such value, the speed of the front increases with the concentration at the front. A typical form for this law could be:

$$v = \alpha |u - q|^m \tag{1.1}$$

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where v is the front speed, u is the concentration at the front, q is a positive number representing the threshold value and α and m are positive constants (see [1]).

An additional condition on the free boundary is obtained imposing mass conservation, that is, equating the mass density current to the product of solvent concentration and the velocity of the free boundary.

This model has been studied for K equal to a constant. In [2], Fasano, Meyer and Primicerio studied the problem with constant concentration at the boundary. In [3], Comparini and Ricci assumed that the polymer is in perfect contact with a well-stirred bath. In [4], the authors were interested in the case of a slab of a non-homogeneous polymer. In [5], a flux condition at the fixed boundary is assumed and existence and uniqueness of the solution is proved. In [9] we studied the asymptotic behavior of the free boundary for convective boundary condition of constant thermal conductivity.

In this work, we are interested in the convective case. We suppose that there is a flux of solvent through the left side of a slab, proportional to the difference between the solvent concentration at $x = 0$ and a given function of time, which represents an external solvent concentration.

The mathematical problem can be stated as follows:

Problem PS : *Find a triple* (T, s, c) *such that:* $T > 0$, $s \in C1[0, T]$, $c \in C^{2,1}(D_T) \cap C(\bar{D}_T)$, *where* $D_T = \{(x, t) : 0 < t < T, 0 < x < s(t)\}$, *and satisfying:*

$$
\begin{aligned}
(Kc_x)_x - c_t &= 0 \qquad \text{in} \qquad D_T, && (1.2)\\
Kc_x(0, t) &= h\left[c(0, t) - g(t)\right], \qquad g(0) = 1, \quad 0 \le t \le T, && (1.3)\\
\dot{s}(t) &= f(c(s(t), t)), \qquad 0 \le t \le T, && (1.4)\\
Kc_x(s(t), t) &= -\dot{s}(t)\left[c(s(t), t) + q\right], \qquad 0 \le t \le T, && (1.5)\\
s(0) &= 0. && (1.6)
\end{aligned}
$$

where

- K is the conductivity coefficient, $K = K[c]$ is a positive operator acting on c, that is, $K[c](x, t) > 0$ for all $(x, t) \in \bar{D}_T$ with $K[c] \in C^{1,0}(\bar{D}_T)$.
- $q > 0$ is the threshold value for the solvent concentration.
- g is a positive function defined by $g(t) = \mathcal{G}(t) - q$, where $\mathcal{G}(t)$ is the external concentration at the left side of the slab. In order to assure a stable process we suppose that $g \in C^1[0, T]$ for all $T > 0$, $g\prime \le 0$ and $G = \int_0^\infty g(t)\, dt < \infty$.
- $c(x, t) = u(x, t) - q$, where $u(x, t)$ represents the concentration. The variable c is normalized such that $g(0) = 1$.
- $h > 0$ is a proportionality convective constant that relates the flux at the left side of the slab and the difference between the concentration $u(0, t)$ and $\mathcal{G}(t)$ (notice that $u(0, t) - \mathcal{G}(t) = c(0, t) - g(t)$).
- $s(t)$ is the location of the front in the slab at time t,
- f determines the evolution of the free boundary or front. Throughout this paper the function f will satisfy that $f \in C^1(0, 1]$, $f'(c) > 0$ for $c \in (0, 1]$ and $f(0) = 0$ (empirically, the function f will be a power law, like in formula (1.1)).

If $c(x,t)$ is a solution for problem **PS**, then comparing equations (1.3) and (1.5) at $t=0$, and using (1.4) and (1.6), we get the following equation:

$$h\,(c^* - 1) = -f(c^*)(q + c^*), \tag{1.7}$$

where

$$c^* = c(0,0). \tag{1.8}$$

Notice that equation (1.7) has only one solution in $(0,1)$. This can be seen because the function $\mathcal{F}(c) = h(c-1)+f(c)(q+c)$ is an increasing function of c that satisfies $\mathcal{F}(0) = -h < 0$ and $\mathcal{F}(1) = f(1)(q+1) > 0$.

For the existence and uniqueness of the problem **PS** in the particular cases $K = K(c)$ or $K = K(x)$ we can follow the ideas developed in [2] and [8].

The rest of the paper is structured as follows. In section 2 we develop numerical methods for different conductivity coefficients, namely, when the conductivity coefficient depends on x and when it depends on c.

In section 3, we study the asymptotic behavior of the free boundary. In particular, a bound can be found for s_∞: $s_\infty = \lim_{t\to\infty} s(t) \leq hG/q$. We can give a physical interpretation to this result, thinking that the slab $[0, s_\infty]$ with concentration c different from zero is bounded by the amount of solvent that has penetrated the polymer, which is bounded above by G times h, divided the minimal possible concentration within the slab, given by q. We emphasize that this bound is independent of K and f.

In section 4 we present the simulations obtained by the numerical methods for the different cases of K, showing also that this bound is optimal.

2 Numerical methods.

We will present two numerical schemes for two special types of diffusion coefficients. In both of these methods, the continuous problem is time discretized and solved at successive time levels as a sequence of free boundary problems for ordinary differential equations. For the case of constant diffusion coefficient, see [7].

Let us choose a positive number Δt, an initial time $t_0 = 0$, and define:

$$t_n = t_0 + n\Delta t, \quad n \geq 0 \tag{2.9}$$

From now on, any function $\mathcal{A}$ evaluated at time t_n will be called with a subscript $\mathcal{A}_n$, for example,

$$c_n(x) = c(x, t_n), \tag{2.10}$$
$$s_n = s(t_n), \tag{2.11}$$
$$g_n = g(t_n), \tag{2.12}$$

Each function c_n $(n \geq 0)$ is defined in $[0, s_n]$, but it can be extended (continuously up to the first derivative) to $[0, \infty)$ using a linear function, namely, $l_n(x) = c_n'(s_n)(x - s_n) + c_n(s_n)$. If we take limit as t goes to zero, then from formula (1.3) we get:

$$K[c](0,0)c_x(0,0) = h[c(0,0) - g(0)] \Longrightarrow c_x(0,0) = \frac{h}{K[c](0,0)}(c^* - 1), \tag{2.13}$$

therefore the function c_0 can be defined in $[0,\infty)$ as:

$$c_0(x) = c_x(0,0)x + c^*. \tag{2.14}$$

2.1 Non-homogeneous slab ($K = K(x)$).

Discretizing the system (1.2)-(1.6) with respect to time, we obtain:

$$\begin{aligned}
\frac{c_n - c_{n-1}(x)}{\Delta t} &= K(x)c_n'' + K'(x)c_n', \qquad 0 < x < s_n, \quad n \geq 1, && (2.15)\\
K(0)c_n'(0) &= h\left(c_n(0) - g_n\right), \qquad n \geq 1, && (2.16)\\
\frac{s_n - s_{n-1}}{\Delta t} &= f(c_n(s_n)), \qquad n \geq 1, && (2.17)\\
K(s_n)c_n'(s_n) &= -\left(\frac{s_n - s_{n-1}}{\Delta t}\right)\left[q + c_n(s_n)\right], \quad n \geq 1, && (2.18)\\
s_0 &= 0. && (2.19)
\end{aligned}$$

In system (2.15)-(2.19) the function $c_{n-1}(x)$ is supposed to be defined over $[0,\infty)$, and s_{n-1} is supposed to be known as well. In the following lemmas we will explain how to prove existence and uniqueness of c_n and s_n for all n.

Definition 2.1 *Let us assume that c_{n-1} and s_{n-1} are known. We define R and w_n as the solutions of the following system:*

$$\begin{aligned}
R' &= 1 + \left(K'(x) - \frac{R}{\Delta t}\right)\frac{R}{K(x)}, \qquad R(0) = K(0)/h, && (2.20)\\
w_n' &= \frac{R(x)}{K(x)\Delta t}\left(c_{n-1}(x) - w_n\right), \qquad w_n(0) = g_n. && (2.21)
\end{aligned}$$

Lemma 2.1 *If R and w_n are the solutions of the equations (2.20) and (2.21), then*

(a)

$$\frac{R(x)}{K(x)} \geq \frac{1}{h + x/\Delta t}, \qquad \forall\, x \geq 0. \tag{2.22}$$

(b) $R > 0$ for all $x \geq 0$.

Proof. Defining a new variable $r = R/K$ and using (2.20), we obtain that r satisfies the equation:

$$r' = \frac{1}{K(x)} - \frac{1}{\Delta t}r^2, \qquad r(0) = \frac{1}{h}, \tag{2.23}$$

From the fact that K is a positive function we deduce that $r'/r^2 \geq -1/\Delta t$. Then (a) is proved integrating the inequality between 0 y x.

To prove (b), notice that from equation (2.22) we deduce that $R > 0$ for all $x \geq 0$.

■

The functions R and w_n will be used later in order to define a Riccati transformation in order to find the solution c_n.

Lemma 2.2 *Let us assume that $n \geq 1$, s_{n-1} and c_{n-1} are known, $0 < c_{n-1} \leq 1$ in $[0, s_{n-1}]$ and $c'_{n-1} < 0$ in $[s_{n-1}, \infty)$. Then*

(a) $w_n > 0$ *in* $[0, s_{n-1}]$.

(b) $w_n \leq 1$ *for all* $x \geq 0$.

(c) If

$$\varphi(x) = \frac{K(x)w_n(x) - qR(x)(x - s_{n-1})/\Delta t}{K(x) + R(x)(x - s_{n-1})/\Delta t}, \tag{2.24}$$

then $\varphi(x) \leq w_n(x) \leq 1$ *for all* $x \geq s_{n-1}$, *and* $\varphi(s_{n-1}) > 0$.

(d) $\lim_{x\to\infty} w_n(x) = -\infty$.

(e) $\lim_{x\to\infty} \varphi(x) = -\infty$.

(f) There exists $x_0 > s_{n-1}$ *such that* x_0 *is the minimum root of* φ *in* (s_{n-1}, ∞).

Proof. (a) As (2.21) is a linear ordinary differential equation, we can compute the expression for w_n, namely,

$$w_n(x) = \exp\left(-\int_0^x \frac{R}{K\Delta t}\right)\left[g_n + \int_0^x \frac{R(y)c_{n-1}(y)}{K(y)\Delta t}\exp\left(\int_0^y \frac{R}{K\Delta t}\right)dy\right], \tag{2.25}$$

As g, R and c_{n-1} are positive functions on $[0, s_{n-1}]$, then $w_n(x)$ is positive on $[0, s_{n-1}]$.

(b) Due to the fact that $c_{n-1} \leq 1$ in $[0, s_{n-1}]$ and $c'_{n-1} < 0$ in $[s_{n-1}, \infty)$, we have that $c_{n-1} \leq 1$ for all $x \in [0, \infty)$. Replacing in equation (2.25) we obtain:

$$\begin{aligned} w_n(x) &\leq \exp\left(-\int_0^x \frac{R}{K\Delta t}\right)\left[g_n + \int_0^x \frac{R(y)}{K(y)\Delta t}\exp\left(\int_0^y \frac{R}{K\Delta t}\right)dy\right] \leq \\ &\leq \exp\left(-\int_0^x \frac{R}{K\Delta t}\right)\left[g_n + \exp\left(\int_0^x \frac{R}{K\Delta t}\right) - 1\right] \leq 1, \quad \forall\, x. \end{aligned} \tag{2.26}$$

The last inequality holds because $g' \leq 0$ and $g(0) = 1$.

(c) Clearly, if $x \geq s_{n-1}$ we can see that $\varphi(x) \leq w_n(x) \leq 1$ (the last inequality comes from (b)). Now, evaluating $\varphi(s_{n-1}) = w_n(s_{n-1}) > 0$ because of (a).

(d) From (2.22) and using that c_{n-1} is a decreasing linear function in $[s_{n-1}, \infty)$ we have that $Rc_{n-1}/(K\Delta t)$ is less than a negative constant as x goes to infinity. As $\exp\left(\int_0^x R/(K\Delta t)\right)$ is greater than 1 for all x, then the function $w_n(x) \longrightarrow -\infty$ as $x \longrightarrow \infty$.

(e) It is a consequence of (c).

(f) Notice that from the fact that $\varphi(s_{n-1}) > 0$ and (e), we deduce that there exists a number x_0 where φ vanishes. In addition, x_0 is chosen as the minimum root of φ in (s_{n-1}, ∞), therefore $s_{n-1} < x_0$.

■

We are in conditions now to define the free boundary as the root of a certain function.

Lemma 2.3 *If hypotheses of Lemma (2.2) hold, the function*

$$\sigma_n(x) = \frac{(x - s_{n-1})}{\Delta t} - f(\varphi(x)). \tag{2.27}$$

has a root in (s_{n-1}, ∞).

Proof. Evaluating the function σ_n in x_0 and s_{n-1} we obtain:

$$\begin{aligned} \sigma_n(s_{n-1}) &= -f(w_n(s_{n-1})) < 0. && (2.28)\\ \sigma_n(x_0) &= \frac{x_0 - s_{n-1}}{\Delta t} - f(0) = \frac{x_0 - s_{n-1}}{\Delta t} > 0, && (2.29)\end{aligned}$$

By continuity of σ_n the lemma is proved.

■

Let us define the number s_n as the smallest root of the function σ_n in the interval (s_{n-1}, ∞). Notice that s_n can not be equal to s_{n-1} because of (2.28). Besides that, $s_{n-1} < s_n < x_0$.

From Lemma (2.2) we know that w_n is positive in $[0, s_{n-1}]$. If there exists $y \in (s_{n-1}, s_n]$ such that $w_n(y) < 0$, then $\varphi(y) < 0$ by (c) of Lemma (2.2). Then, there exists $z \in (s_{n-1}, y)$ such that $\varphi(z) = 0$. This is a contradiction since x_0 was the minimum root of φ in (s_{n-1}, ∞). Therefore the function w_n in $[0, s_n]$. We summarize this reasoning in the following remark:

Remark 2.1 $w_n(x) > 0$ *in the interval* $[0, s_n]$.

We are on the way to define a function c_n that will be the solution of our system (2.15)-(2.19).

Definition 2.2 *Assuming that* c_{n-1} *is known, we define the function* v_n *as the solution of the following ordinary differential equation:*

$$\begin{cases} v_n' = \dfrac{1}{K}\left(\dfrac{R}{\Delta t} - K'\right) v_n + \dfrac{w_n - c_{n-1}}{K\Delta t}, \\ v_n(s_n) = -s_n'\left(\dfrac{q + w_n(s_n)}{K(s_n) + R(s_n)s_n'}\right), \qquad s_n' = \dfrac{s_n - s_{n-1}}{\Delta t}. \end{cases} \tag{2.30}$$

Also, we define the function c_n *as:*

$$c_n(x) = R(x)v_n(x) + w_n(x) \tag{2.31}$$

Lemma 2.4 *Assuming that the hypotheses of Lemma (2.2) hold, the function* c_n *has the following properties:*

(a) $c_n' = v_n$,

(b) $c_n(s_n) = \varphi(s_n) \leq 1$,

(c) $v_n' = \dfrac{(1 - R')\,v_n - w_n'}{R}$,

(d) c_n *and* s_n *satisfy equations (2.15)-(2.18).*

(e) $0 < c_n \leq 1$ *in* $[0, s_n]$.

(f) $c_n' < 0$ *in* $[s_n, \infty)$.

(g) $s_n - s_{n-1} \leq f(1)\Delta t$.

Proof. (a) Derive the function c_n, that is,

$$c_n' = R'v_n + Rv_n' + w_n'. \tag{2.32}$$

Replacing R' using (2.20), v_n' using (2.30) and w_n' using (2.21), we get the result.

(b) Evaluate $c_n(s_n) = R(s_n)v_n(s_n) + w_n(s_n)$ and replace $v_n(s_n)$ by its value, expressed in equation (2.30). The inequality is deduced from (c) of Lemma (2.2).

(c) Using (a) and equation (2.32) we get an expression for v_n. To find the value of v_n' we simply operate algebraically in the same equation.

(d) Follow these steps:

- Starting from the right-hand side of (2.15) and (a) we obtain:

$$Kc_n'' + K'c_n' = Kv_n' + K'v_n, \tag{2.33}$$

  Replacing v_n' using (c), and then replacing w_n' using (2.21), we obtain formula (2.15) through simple calculations.

- To get (2.16) we substitute $c_n'(0)$ by $v_n(0)$, and replace $v_n(0)$ using equation (2.31). Then, replace the value of w_n at zero by g_n (equation (2.21)). Finally, simple calculations allow us to demonstrate this item.

- Formula (2.17) is deduced from the definition of s_n and (b).

- If we begin with the boundary condition of (2.30), one can get $K(s_n)v_n(s_n)$. The condition (2.18) is then achieved.

(e) From (2.31) and (a), we can compute the expression of c_n, namely,

$$c_n(x) = \exp\left(-\int_x^{s_n} \frac{1}{R}\right) c_n(s_n) + \exp\left(-\int_x^{s_n} \frac{1}{R}\right) \int_x^{s_n} \frac{w_n(y)}{R(y)} \exp\left(\int_y^{s_n} \frac{1}{R}\right) dy. \tag{2.34}$$

Since $c_n(s_n) = \varphi(s_n) > 0$, R and w_n positive functions in $[0, s_n]$, we get that c_n is strictly positive in $[0, s_n]$.

In the other hand, using (b) from Lemma (2.2), we have:

$$\begin{aligned} c_n(x) &\leq \exp\left(-\int_x^{s_n} \frac{1}{R}\right) c_n(s_n) + \exp\left(-\int_x^{s_n} \frac{1}{R}\right) \int_x^{s_n} \frac{1}{R(y)} \exp\left(\int_y^{s_n} \frac{1}{R}\right) dy, \\ &\leq 1 + \exp\left(-\int_x^{s_n} \frac{1}{R}\right) [c_n(s_n) - 1] \leq 1, \qquad x \in [0, s_n]. \end{aligned} \tag{2.35}$$

The last inequality holds because of (b).

(f) If $x \geq s_n$, and using (2.18), we have:

$$c_n'(x) = c_n'(s_n) = -\frac{1}{K(s_n)}\left(\frac{s_n - s_{n-1}}{\Delta t}\right)[q + c_n(s_n)] < 0. \tag{2.36}$$

(g) As the function f is increasing, and $c_n(s_n) \leq 1$, then $s_n - s_{n-1} \leq \Delta t f(c_n(s_n)) \leq \Delta t f(1)$. ■

Now we are in conditions to formulate the following theorem of existence of the numerical solution.

Theorem 2.3 *For all $n \geq 1$ there exists a solution of the system (2.15)-(2.19) where the sequence $\{s_n\}_{n=1}^{\infty}$ is strictly increasing.*

Proof. Starting with $n = 0$ we define $s_0 = 0$ and

$$c_0(x) = \frac{h}{K(0)}(c^* - 1)x + c^*. \tag{2.37}$$

Notice that $0 < c_0 \leq 1$ in $[0, s_0]$ and $c_0' < 0$ in $[s_0, \infty)$. Using Lemma (2.3) there exists a root s_n of the function (2.27) in (s_{n-1}, ∞) (i.e. s_n is an increasing function). The function c_n is defined by formula (2.31) and holds the hypotheses of Lemma (2.2) using (e) and (f) of Lemma (2.4), then it follows the inductive step. ■

2.2 Nonlinear diffusion: ($K = K(c)$).

The second type of diffusion coefficient to be considered, is related to nonlinear diffusion processes, namely $K = K(c)$, a function of the solvent concentration. We assume that $K \in C1[0, 1]$. We present a method to compute the solution based on the same scheme that the previous section. If the system (1.2)-(1.6) is discretized in time and consider the names expressed in (2.10)-(2.12), we obtain:

$$\begin{aligned}
\frac{c_n - c_{n-1}(x)}{\Delta t} &= K(c_n)c_n'' + K'(c_n){c_n'}^2, \qquad 0 \leq x \leq s_n, && (2.38)\\
K(c_n(0))c_n'(0) &= h\left(c_n(0) - g_n\right), \qquad n \geq 1, && (2.39)\\
\frac{s_n - s_{n-1}}{\Delta t} &= f(c_n(s_n)), \qquad n \geq 1, && (2.40)\\
K(c_n(s_n))c_n'(s_n) &= -\left(\frac{s_n - s_{n-1}}{\Delta t}\right)[q + c_n(s_n)], \quad n \geq 1, && (2.41)\\
s_0 &= 0. && (2.42)
\end{aligned}$$

Starting with $s_0 = 0$ (equation (2.42)) and from (2.13) and (2.14):

$$c_0(x) = \frac{h}{K(c^*)}\left(c^* - 1\right)x + c^*, \tag{2.43}$$

the idea is to compute (s_1, c_1), (s_2, c_2), $\ldots$ and so on.

For $n \geq 1$ and $z \in [s_{n-1}, s_{n-1} + f(1)\Delta t]$, we define the function $F(z)$ as follows: (a) we solve the system

$$\begin{aligned}\frac{u-c_{n-1}(x)}{\Delta t} &= K(u)u''+K'(u)u'^2, \qquad 0\le x\le z, && (2.44)\\ u(z) &= f^{-1}\left(\frac{z-s_{n-1}}{\Delta t}\right), && (2.45)\\ u'(z) &= -\frac{1}{K(u(z))}\left(\frac{z-s_{n-1}}{\Delta t}\right)[q+u(z)], && (2.46)\end{aligned}$$

and (b) we compute:

$$F(z)=K(u(0))u'(0)-h\,[u(0)-g_n)]\,, \tag{2.47}$$

Notice that the requirement $z\in[s_{n-1},s_{n-1}+f(1)\Delta t]$ is necessary because $(z-s_{n-1})/\Delta t$ must be in $\mathrm{Dom}(f^{-1})$.

We expect that the function F has a root in $[s_{n-1},s_{n-1}+f(1)\Delta t]$, and we choose s_n as the first root in that interval. The function c_n should be defined as the solution of the system (2.44)-(2.46) taking $z=s_n$ for $0\le x\le s_n$, and c_n linear for $x>s_n$.

If this procedure can be carried out for all n, then the system (2.38)-(2.41) would have solution for all n. This can be seen in some examples shown in the next sections.

3 Asymptotic behavior.

In this section we show some results about the behavior of the free boundary $s(t)$ when t goes to infinity.

Let us $s(t)$ and $c(x,t)$ be the solution of the problem **PS**. Using Green's identity:

$$\int\int (Q_x-P_t)\,dxdt=\oint Pdx+Qdt, \tag{3.48}$$

and taking $P=c$ and $Q=Kc_x$ we have:

$$0=\oint_{\partial D_t} c(x,t)\,dx+Kc_x(x,t)\,dt, \qquad t>0, \tag{3.49}$$

which gives

$$\begin{aligned}0 &= \int_0^t c(s(\tau),\tau)\dot{s}(\tau)\,d\tau-\int_0^t \dot{s}(\tau)\left(c(s(\tau),\tau)+q\right)\,d\tau-\int_0^{s(t)} c(x,t)\,dx\\ &\quad -\int_0^t Kc_x(0,\tau)\,d\tau && (3.50)\end{aligned}$$

and then

$$\begin{aligned}qs(t) &= -\int_0^{s(t)} c(x,t)\,dx-\int_0^t Kc_x(0,\tau)\,d\tau\\ &= -\int_0^{s(t)} c(x,t)\,dx-h\int_0^t c(0,\tau)\,d\tau+h\int_0^t g(\tau)\,d\tau && (3.51)\end{aligned}$$

so

$$s(t) \leq \frac{h}{q} \int_0^t g(\tau)\, d\tau \leq \frac{h}{q} G. \tag{3.52}$$

because the function c is non-negative (this fact is deduced using the Maximum Principle).

Remark 3.1 *Notice that the inequality (3.52) is valid for all t if we define $G(t) = \int_0^t g(\tau)\, d\tau$:*

$$s(t) \leq \frac{hG(t)}{q}, \quad \forall t. \tag{3.53}$$

Since $\dot{s}(t) = f(c(s(t), t)) > 0$, the function s is increasing and there exists s_∞ such that:

$$s_\infty \doteq \lim_{t\to\infty} s(t). \tag{3.54}$$

We notice that (3.52) holds for every f and K. This fact is explained as follows.

Theorem 3.1 *We can prove that:*

$$\sup_{f,K} s_\infty = \frac{h}{q} G. \tag{3.55}$$

where the supremum is taken on the set of the functions f and operators K such that **PS** *has a non-negative solution.*

Proof. We will show that (3.52) is really an optimal bound. Let $k > 0$ be a positive real number. Let us set in the problem **PS**: h by $h/\sqrt{k}$, $f(c)$ by $\alpha c/\sqrt{k}$, where $\alpha > 0$ and K constant equal to 1. In [6] it is proved that there exists a unique solution $\{w(x,t), z(t)\}$ for this problem **PS**. Moreover, it is found that

$$\lim_{t\to\infty} z(t) = \sqrt{k\left(\frac{1}{h} + \frac{1}{\alpha q}\right)^2 + \frac{2G}{q}} - \sqrt{k}\left(\frac{1}{h} + \frac{1}{\alpha q}\right). \tag{3.56}$$

We observe that if we define $s(t) = \sqrt{k} z(t)$ and $c(x,t) = w(x/\sqrt{k}, t)$, then $\{c(x,t), s(t)\}$ is the solution of **PS** with $K = k$, and $f(c) = \alpha c$. Thus, the above equation can be rewritten as:

$$s_\infty = \sqrt{k^2\left(\frac{1}{h} + \frac{1}{\alpha q}\right)^2 + \frac{2Gk}{q}} - k\left(\frac{1}{h} + \frac{1}{\alpha q}\right), \tag{3.57}$$

Taking $\alpha = k^2$ we have:

$$s_\infty = \frac{k}{h}\left(\sqrt{1 + \frac{2Gh^2}{qk} + \frac{2h}{k^2 q} + \frac{h^2}{k^4 q^2}} - 1\right) + \frac{1}{k^2 q} \tag{3.58}$$

Using the fact that $\sqrt{1+x} = 1 + x/2 + o(x2)$, and taking:

$$x = \frac{2Gh^2}{qk} + \frac{2h}{k^2 q} + \frac{h^2}{k^4 q^2}, \tag{3.59}$$

we have that:

$$s_\infty = \frac{k}{h}\left[\frac{Gh^2}{qk} + \frac{h}{k^2 q} + \frac{h^2}{2k^4q^2} + o\left(\frac{2Gh^2}{qk} + \frac{2h}{k^2q} + \frac{h^2}{k^4q^2}\right)\right] + \frac{1}{qk^2}, \tag{3.60}$$

and taking $k \to \infty$ we get that

$$s_\infty = \frac{hG}{q}. \tag{3.61}$$

■

Given a diffusion coefficient $K = K(x)$, we will show a bound of the stationary solution s_∞ over all functions f. In order to do this, we need to find three useful equations (see (3.51), (3.65) and (3.68) below).

Similarly to the equation (3.49) and using the Green's identity (3.48) for $P = cv$ and $Q = K(x)\,(c_x v - c v_x)$ we get that:

$$\oint_{\partial D_t} cv\,dx + K(x)\,(c_x v - cv_x)\;d\tau = 0, \tag{3.62}$$

where $v(x,t)$ is any solution of the following equation:

$$(K(x)v_x)_x + v_t = 0, \qquad \text{in } D_T \tag{3.63}$$

Taking $v(x,t) = \displaystyle\int_0^x \frac{dy}{K(y)}$, the equation (3.62) would look like:

$$\begin{aligned}
0 &= \int_0^t \Bigg\{ c(s(\tau),\tau)\int_0^{s(\tau)} \frac{dx}{K(x)} s'(\tau) + \\
&+ K(s(\tau))\left[-\frac{s'(\tau)}{K(s(\tau))}\left(c(s(\tau),\tau)+q\right)\int_0^{s(\tau)}\frac{dy}{K(y)} - c(s(\tau),\tau)\frac{1}{K(s(\tau))}\right]\Bigg\}\,d\tau + \\
&+ \int_{s(t)}^0 c(x,t)\int_0^x \frac{dy}{K(y)}\,dx - \int_t^0 c(0,\tau)\,d\tau.
\end{aligned} \tag{3.64}$$

Thus we have the second equation:

$$\begin{aligned}
0 &= -q\int_0^t s'(\tau)\int_0^{s(\tau)}\frac{dy}{K(y)}\,d\tau - \int_0^t c(s(\tau),\tau)\,d\tau - \\
&- \int_0^{s(t)} c(x,t)\int_0^x\frac{dy}{K(y)}\,dx + \int_0^t c(0,\tau)\,d\tau.
\end{aligned} \tag{3.65}$$

Finally, we take $v(x,t) = t - \displaystyle\int_0^x \frac{y\,dy}{K(y)}$. The equation (3.62) becomes:

$$\begin{aligned}
0 &= \int_0^t \Bigg[c(s(\tau),\tau)\left(\tau - \int_0^{s(\tau)}\frac{y\,dy}{K(y)}\right)s'(\tau) - \\
&- s'(\tau)\left(c(s(\tau),\tau)+q\right)\left(\tau - \int_0^{s(\tau)}\frac{y\,dy}{K(y)}\right) + c(s(\tau),\tau)s(\tau)\Bigg]\,d\tau + \\
&+ \int_{s(t)}^0 c(x,t)\left(t - \int_0^x \frac{y\,dy}{K(y)}\right)dx + K(0)\int_t^0 \tau c_x(0,\tau)\,d\tau.
\end{aligned} \tag{3.66}$$

Operating algebraically in order to simplify the above expression, we get the third equation:

$$\begin{aligned}
0 &= -K(0)\int_0^t \tau c_x(0,\tau)\,d\tau - q\int_0^t \tau s'(\tau)\,d\tau + q\int_0^t s'(\tau)\int_0^{s(\tau)} \frac{y\,dy}{K(y)}\,d\tau + \\
&+ \int_0^t c(s(\tau),\tau)s(\tau)\,d\tau + \int_0^{s(t)} c(x,t)\int_0^x \frac{y\,dy}{K(y)}\,dx - \qquad (3.67)\\
&- t\int_0^{s(t)} c(x,t)\,dx. \qquad (3.68)
\end{aligned}$$

The following lemma shows that, asymptotically, the solvent concentration tends to zero (in an integral form) when t goes to infinity for non-negative bounded functions $c(x,t)$.

Remark 3.2 *Using the Maximum Principle as in [2] and [8] it follows that the function $c(x,t)$ satisfies $0 \le c(x,t) \le 1$.*

Lemma 3.1 *The following equation holds:*

$$\lim_{t\to\infty}\int_0^{s(t)} c(x,t)\,dx = 0. \qquad (3.69)$$

Proof. From expression (3.68) we have:

$$\begin{aligned}
\int_0^{s(t)} c(x,t)\,dx &= -\frac{K(0)}{t}\int_0^t \tau c_x(0,\tau)\,d\tau - \frac{q}{t}\int_0^t \tau s'(\tau)\,d\tau + \\
&+ \frac{q}{t}\int_0^t s'(\tau)\int_0^{s(\tau)} \frac{y\,dy}{K(y)}\,d\tau + \frac{1}{t}\int_0^t c(s(\tau),\tau)s(\tau)\,d\tau \\
&+ \frac{1}{t}\int_0^{s(t)} c(x,t)\int_0^x \frac{y\,dy}{K(y)}\,dx \\
&\le -\frac{K(0)}{t}\int_0^t \tau c_x(0,\tau)\,d\tau + \frac{qs_\infty^3}{6tK_0} + \\
&+ \frac{1}{t}\int_0^t c(s(\tau),\tau)s(\tau)\,d\tau + \frac{s_\infty^3}{6tK_0}. \qquad (3.70)
\end{aligned}$$

where $K_0 = \min_{x\in[0,hG/q]} K(x) > 0$. In order to prove the Lemma, it is enough that all the terms in expression (3.70) tend to zero when t goes to infinity.

From the equation (3.51) we have that:

$$\int_0^t c(0,\tau)\,d\tau \le \int_0^t g(\tau)\,d\tau \le G. \qquad (3.71)$$

Then, using the second expression (3.65) and the fact that the free boundary increases to s_∞, we can see:

$$\begin{aligned}
\int_0^t c(s(\tau),\tau)s(\tau)\,d\tau &\le s_\infty\int_0^t c(s(\tau),\tau)\,d\tau \le \\
&\le s_\infty\int_0^t c(0,\tau)\,d\tau \le s_\infty G \qquad (3.72)
\end{aligned}$$

then the third term of (3.70) tends to zero when t goes to infinity.

On the other hand, from equation (3.51):

$$-K(0)\int_0^t c_x(0,\tau)\,d\tau = \int_0^{s(t)} (q + c(x,t))\;dx > 0, \tag{3.73}$$

and

$$-K(0)\int_0^\infty c_x(0,\tau)\,d\tau = h\left(G - \int_0^\infty c(0,\tau)\,d\tau\right) < \infty \tag{3.74}$$

Then using (3.73), (3.74) and the L'Hôpital's rule:

$$\lim_{t\to\infty}\frac{1}{t}\int_0^t \tau c_x(0,\tau)\,d\tau = \lim_{t\to\infty}\left[\int_0^t c_x(0,\tau)\,d\tau - \frac{1}{t}\int_0^t\left(\int_0^\tau c_x(0,\eta)\,d\eta\right)\,d\tau\right] = 0. \tag{3.75}$$

Then the first term of (3.70) tends to zero when t goes to infinity. The proof is finished. ∎

The following Lemma is a result for a particular function f.

Lemma 3.2 *Let us suppose that $f(c) = \alpha c$ where α is a positive number. Then the following equation holds:*

$$h\int_0^{s_\infty}\int_0^x \frac{dy}{K(y)}\,dx + \left(\frac{h}{q\alpha}+1\right)s_\infty = \frac{h}{q}G. \tag{3.76}$$

Proof. Canceling $\displaystyle\int_0^t c(0,\tau)\,d\tau$ from equations (3.51) and (3.65) we obtain:

$$\begin{aligned}\frac{q}{h}s(t) + q\int_0^t\int_0^z \frac{dy}{K(y)}\,dz &= -\frac{1}{h}\int_0^t c(x,t)\,dx + \int_0^t g(\tau)\,d\tau - \\ &- \frac{1}{\alpha}s(t) - \int_0^{s(t)} c(x,t)\int_0^x \frac{dy}{K(y)}\,dx \end{aligned}\tag{3.77}$$

Taking the limit when t goes to infinity we get:

$$\frac{q}{h}s_\infty + q\int_0^{s_\infty}\int_0^x \frac{dy}{K(y)}\,dx = -\frac{1}{\alpha}s_\infty + G. \tag{3.78}$$

This concludes the proof. ∎

The next result shows a bound for s_∞.

Lemma 3.3 *The number*

$$z = \sup_f s_\infty \tag{3.79}$$

satisfies

$$h\int_0^z\int_0^x \frac{dy}{K(y)}\,dx + z = \frac{h}{q}G. \tag{3.80}$$

Proof. As in (3.77)

$$
\begin{aligned}
\frac{q}{h}s(t) + q\int_0^t \int_0^z \frac{dy}{K(y)}\,dz &= -\frac{1}{h}\int_0^t c(x,t)\,dx + \int_0^t g(\tau)\,d\tau - \\
&- \int_0^t c(s(\tau),\tau)\,d\tau - \int_0^{s(t)} c(x,t)\int_0^x \frac{dy}{K(y)}\,dx \leq \\
&\leq \int_0^t g(\tau)\,d\tau \qquad (3.81)
\end{aligned}
$$

So

$$s_\infty + h\int_0^{s_\infty}\int_0^x \frac{dy}{K(y)}\,dx \leq \frac{h}{q}G. \tag{3.82}$$

Then, the equation (3.80) is deduced from equation (3.76) taking limit when α tends to infinity. The proof is concluded.

■

4 Numerical results.

In this section we will show numerical results comparing with the theoretical results. For all the simulations we use $g(t) = e^{-2t}$, the threshold value q for the solvent concentration is set to 0.3 and the proportionality convective constant h is set to 10. For these particular cases the global bound over all functions f and K expressed in Theorem (3.1) assumes the value:

$$s_\infty = h\frac{G}{q} \approx 16.667. \tag{4.83}$$

First, we will take $K = K(x)$.

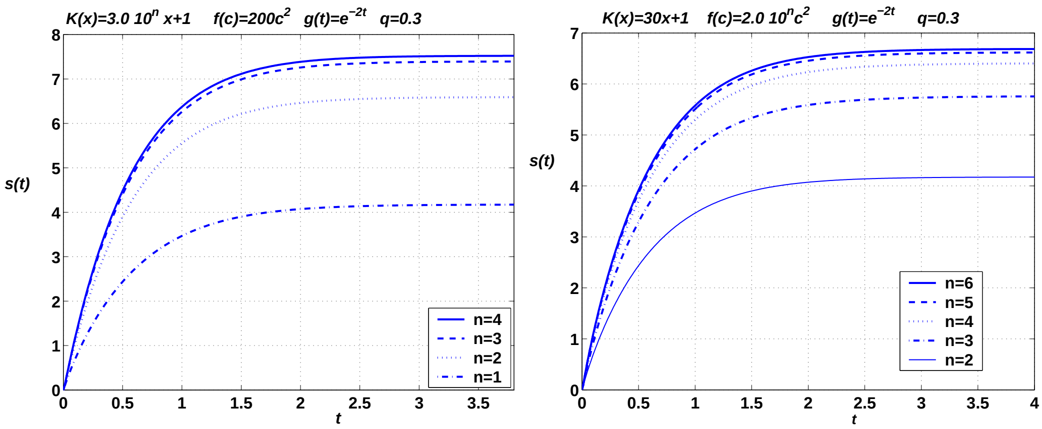

Figure 1: Case $K = K(x)$, for many functions K and many f. Left: f is fixed, K is varied. Right: K is fixed, f is varied

As we can see from the figures above, it is not possible to reach the supremum over all the functions f and K individually.

From equation (3.80) we can solve z and obtain $z \approx 6.807$. This bound is checked numerically from the picture on the right of figure (4).

If we set a function $K = K(x)$ big enough and let f go to infinity, we can reach the bound $s_\infty = hG/q \approx 16.667$ as shown in picture 2.

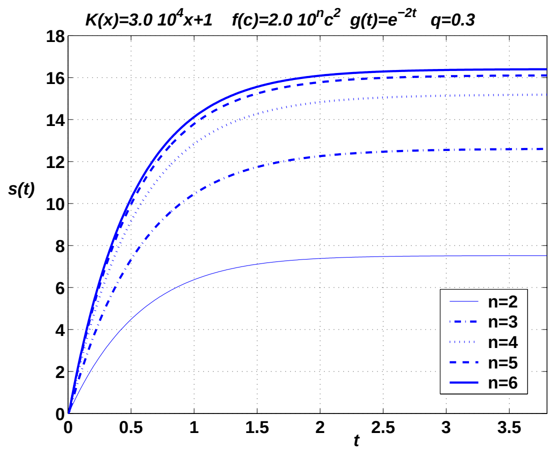

Figure 2: Case $K = K(x)$.

Clearly the numerical results agree with the theorem.

We will consider the nonlinear conductivity taking the particular case $K(c) = A/c$ with $A > 0$.

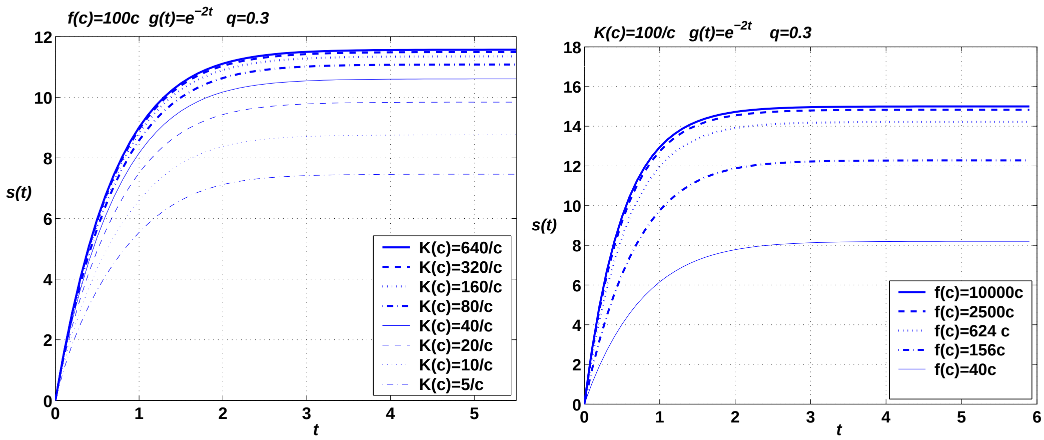

Figure 3: Case $K = K(c)$, for many functions K and many f.

As we can see in figure (3) the supremum will change if we take the supremum over all f or over all K.

In the next picture we can numerically show again that the bound expressed in equation (3.61) holds taking supremum over all K and over all f (it is enough to take a function f with a big slope).

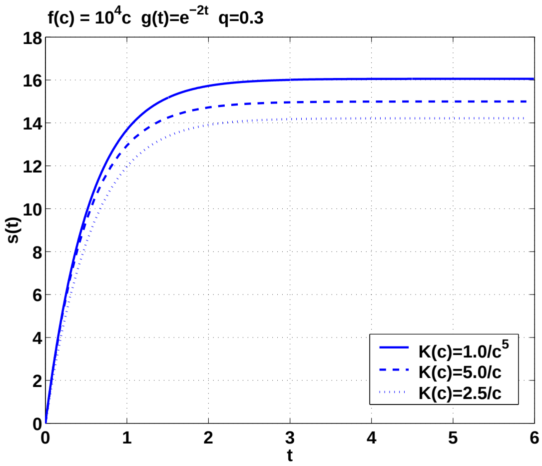

Figure 4: Case $K = K(c)$.

5 Conclusions and final comment.

In this paper we have presented a free boundary problem from the polymer industry. It has been possible to bound the free boundary with a constant which does not depend on some parameters of the problem. The most important aspect of this bound is that is independent of the diffusion processes inside the material represented by the conductivity coefficient $K[c]$ and the dynamical law of penetration f, which are often the most difficult things to describe physically. For the case $K = K(x)$ a best bound can be computed independently of f. The numerical method implemented was the straight lines method adapted to free boundary problems obtaining an ordinary differential equation system which its solution method depends strongly on the type of the operator $K[c]$. In particular, for the case of $K[c]$ depending on x, the Riccati equations are used. In both cases all the numerical experiments obey the theoretical bounds.

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