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On the Limit Behavior in a Free Boundary Model for the Diffusion in a Polymer

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Summary. - *Free boundary problems arise modelling the sorption of solvents into glassy polymers. There are physical reasons to expect that a convective condition with coefficient h, behaves asymptotically as a Dirichlet condition. In this work we prove, analyzing the uniform convergence the equivalence of these problems. A condition is also derived that allows one to decide whether a specific application lies within the asymptotic regime.*

1. Introduction

In this paper, we consider a free boundary problem arising in polymer technology which models the penetration of a solvent into a glassy polymer. 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 discontinuity observed in the material between a penetrated zone (or swollen 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). We consider the one dimensional case of a slab of a

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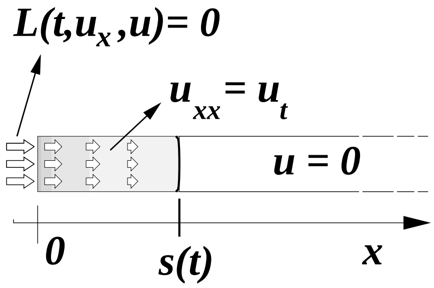

Figure 1: The solvent concentration $u(x,t)$ diffuses trough the slab. $s(t)$ is the position of the free boundary at time t.

glassy polymer in contact with a solvent. It is observed that if the solvent concentration exceeds some thereshold value, then the solvent moves into the polymer, creating a swollen layer in which the solvent diffuses according to Fick's law. The boundary between the swollen region and the glassy region obeys an empirical penetration law, relating its velocity with the (unknown) value assumed on it by the solvent concentration. A typical form is $v = \alpha|u-q|^m$ where v is the front speed, u is the value of the concentration at the front, $q > 0$ is the threshold value and α and m are positive constants ([2]). An additional condition on the free boundary is obtained imposing mass conservation, i.e., equating the mass density current to the product of solvent concentration and the velocity of the free boundary. The figure below sketches the physical problem:

Depending on the type of boundary conditions, the solvent can get into the slab in several ways represented mathematically by the operator $L(t, u_x, u)$, so they have been the object of study of a number of papers ([1, 2, 4, 5, 6, 7, 8] and [10]). Usually, all these problems were studied doing the simple change of variable $c = u - q$, where $c(x,t)$ denotes the excess of solvent concentration over the threshold value. Now, let us consider the problem studied in [8]:

Problem PS. *For* $T > 0$*, find* $s \in C^1[0,T]$ *and* $c \in C^{2,1}(D_T) \cap C(\bar{D}_T)$*, where* $D_T = \{(x,t) : 0 < t < T, 0 < x < s(t)\}$, *and satisfying*

$$
\begin{aligned}
c_{xx} - c_t &= 0 && \text{in} \quad D_T, && (1)\\
c(0,t) &= g(t), && g(0) = 1, \qquad 0 \le t \le T && (2)\\
\dot{s}(t) &= f(c(s(t),t)), && 0 \le t \le T && (3)\\
c_x(s(t),t) &= -\dot{s}(t)\left[c(s(t),t) + q\right], && 0 < t \le T && (4)\\
s(0) &= 0. && && (5)
\end{aligned}
$$

The function $g(t)$ is positive, $q + g(t)$ represents an external concentration and it satisfies $g(0) = 1$, $g \in C^1[0,\infty]$, $g'(t) \le 0$ and $\int_0^\infty g(t)\,dt < \infty$. The function f will be supposed to satisfy $f \in C[0,1] \cap C^1(\tau, 1]$, $\forall \tau > 0$, $f'(c) > 0$ for $c \in (0,1]$ and $f(0) = 0$.

Now, let us suppose $h > 0$ and consider the problem studied in [7]:

Problem PSh. *For* $T > 0$*, find* $s_h \in C^1[0,T]$ *and* $c_h \in C^{2,1}(D_{hT}) \cap C(\bar{D}_{hT})$*, where* $D_{hT} = \{(x,t) : 0 < t < T, 0 < x < s_h(t)\}$*, and satisfying*

$$
\begin{aligned}
c_{hxx} - c_{ht} &= 0 && \text{in} \quad D_T, && (6)\\
c_{hx}(0,t) &= h\left[c_h(0,t) - g(t)\right], && g(0) = 1, \quad 0 < t \le T && (7)\\
\dot{s_h}(t) &= f(c_h(s_h(t),t)), && 0 \le t \le T && (8)\\
c_{hx}(s_h(t),t) &= -\dot{s_h}(t)\left[c_h(s_h(t),t) + q\right], && 0 < t \le T && (9)\\
s_h(0) &= 0. && && (10)
\end{aligned}
$$

We note that the unique difference between **PS** and **PSh** are the boundary conditions at $x = 0$ (eqs. (1.2) and (1.7)). The aim of the paper is to show that the solution of **PSh** converges to the solution of **PS** as $h \to \infty$. The physical reason to explain this fact is that the equation (1.7) can be written as $c_{hx}(0,t) = (c_h(0,t) - g(t))/(1/h)$, representing an incremental quotient to estimate the flux of solvent at $x = 0$. Thus, when $h \to \infty$, we expect that $c_h(0,t) \to g(t)$. Actually, the convective coefficient h often is a large number, so $1/h$ models the length of a very short interval at the left side of the slab where there is a sharp difference of solvent concentration between the external and internal faces at $x = 0$.

Remark: we notice that this work is a mathematical proof of the relation between two real physical problems in the chemical industry because this convergence of the problems should be useful to decide real applications of these models.

2. Uniform Convergence

The proof of the convergence mentioned above will be accomplished by an application of the Ascoli-Arzelá theorem to the set of functions $c_h(x,t)$ and $s_h(t)$, with $h \in (0,\infty)$. In order to do it, we need to prove that this set of functions is equicontinuous (for a definition of *equicontinuous* see [9]), it is accomplished obtaining estimates that do not depend on h for c_h, c_{ht}, c_{hx}, $\dot{s}_h$ and s_h. The following estimates have been proved in [7]:

$$\left|s_h(t) - s_h(t')\right| \leq f(1)|t-t'|, \qquad t,t' \in [0,T] \tag{11}$$

$$0 < c_h(x,t) \leq 1 \qquad \text{in} \quad D_{hT}, \tag{12}$$

$$|c_{ht}(x,t)| \leq B_T \qquad \text{in} \quad D_{hT}, \tag{13}$$

with $B_T = \max\left\{\max_{[0,T]} |g'|, f(1)^2(1+q), |c_{ht}(0,0)|\right\}$. Now we prove the following result

Lemma 2.1.
$$\lim_{h\to\infty} c_{ht}(0,0) = g'(0).$$

Proof. We consider the quotient

$$\frac{c_{hx}(s_h(t),t) - c_{hx}(0,t)}{s_h(t)}$$

and take $t \to 0$. Since $c_{ht}(x,t)$ is continuous in $\bar{D}_{hT}$ (see [7]), we have from (1.7) – (1.10) that

$$c_{ht}(0,0) = \frac{hg'(0) + f(c_h^*)^2(c_h^*+q)\left(f'(c_h^*)(c_h^*+q) + f(c_h^*)\right)}{h + 2f(c_h^*) + f'(c_h^*)(c_h^*+q)},$$

where c_h^* is the unique solution of the scalar equation $f(c)(c+q) = -h(c-1)$ and it is easy to check that $c_h^* \to 1$ when $h \to \infty$. $\square$

Thus, the above lemma tell us that modifying B_T we can assume that it does not depend on h. An estimate for c_{hx} is obtained as follows:

$$\begin{aligned} |c_{hx}(x,t)| &\leq |c_{hx}(s_h(t),t)| + \int_x^{s_h(t)} |c_{hxx}(y,t)|\,dy \\ &\leq f(1)(1+q) + \int_x^{s_h(t)} |c_{ht}(y,t)|\,dy \\ &\leq f(1)(1+q) + B_T|s_h(t)-x| \\ &\leq f(1)(1+q) + 2B_T f(1)T \equiv A_T, \end{aligned} \tag{14}$$

so A_T is independent of h.

Inequality (2.11) tells us that $\{s_h : h > 0\}$ is a equicontinuous family of functions, clearly it is also equibounded, so applying Ascoli-Arzelá theorem we get a continuous function $z(t)$ defined over $[0,T]$ and a sequence $\{h_k : k \in \mathbf{N}\}$ with $h_k < h_{k+1}$ and $h_k \to \infty$ such that:

$$|z(t) - s_{h_k}(t)| \leq 2^{-k} \qquad \forall t \in [0,T]. \tag{15}$$

Now, we inductively define a sequence $\{H_n\}$, $n \geq 0$. Let $H_0 \equiv \{h_k : k \in \mathbf{N}\}$. Let us suppose $n \geq 1$ and an infinite set $H_{n-1} \subset H_0$ has been chosen. Now, we define

$$\left\{(x,t) : z^{-1}(2^{-n}) \leq t \leq T, 0 \leq x \leq z(t) - 2^{-n}\right\} \equiv D_n.$$

We remark that the origin is not included in the set D_n. We note that for h large enough, the functions $c_h(x,t)$ with $h \in H_{n-1}$ are defined on D_n. Actually, those functions constitute an equibounded and equicontinuous set on D_n, so we once again apply Ascoli-Arzelá's theorem in order to obtain an infinite set $H_n \subset H_{n-1}$ such that, $c_h(x,t)$ converges uniformly on D_n as $h \to \infty$ within H_n. Let be

$$H \equiv \left\{h'_1, h'_2, h'_3, ...\right\},$$

with $h'_n \equiv n^{th}\ \mathit{term\ of}\ H_n$. Since $H \subset H_n$ $\forall n$, we have that there exists

$$w(x,t) \equiv \lim_H c_h(x,t),$$

where $\lim_H$ denotes the limit as $h \to \infty$ within H. Moreover the convergence is uniform on each compact subset of

$$\{(x,t) : 0 < x < z(t), 0 < t < T\} \equiv D_{zT}.$$

It follows from [3, Theorem 15.1.2., p. 253] that w satisfies

$$w_{xx} - w_t = 0 \qquad \text{in } D_{zT}. \tag{16}$$

Since the gradient of $c_h(x,t)$ is bounded on its domain by a constant independent of h, we get that $w(x,t)$ has a continuous extension (still denoted by $w(x,t)$) to $\bar{D}_{zT}$, also for each $t \in (0,T]$,

$$\lim_H c_{hx}(x,t) = w_x(x,t), \qquad x \in (0, z(t)) \tag{17}$$

taking into account that $|c_{hxx}| \leq B_T$, the above argument gives that for each $t \in (0,T]$, $w_x(x,t)$ is a continuous function of x on $[0, z(t)]$.

Also we have from 1.7 and 2.14 that

$$w(0,t) = \lim_H c_h(0,t) = \lim_H \left(\frac{c_{hx}(0,t)}{h} + g(t) \right) = g(t) \quad \forall t \in [0,T] \tag{18}$$

Lemma 2.2. *The following limits hold*

$$\begin{aligned} \lim_H c_h(s_h(t),t) &= w(z(t),t), && (19)\\ \lim_H c_{hx}(s_h(t),t) &= w_x(z(t),t) && (20) \end{aligned}$$

with uniform convergence on $(0,T]$.

Proof. Let be $\epsilon > 0$ and $h \in H$ such that $|s_h(t) - z(t)| < \epsilon$ on $[0,T]$. Then,

$$\begin{aligned} |c_h(s_h(t),t) - w(z(t),t)| &\leq |c_h(s_h(t),t) - c_h(z(t)-\epsilon,t)| + \\ &\quad + |c_h(z(t)-\epsilon,t) - w(z(t)-\epsilon,t)| + \\ &\quad + |w(z(t)-\epsilon,t) - w(z(t),t)| \\ &\leq A_T\,|z(t) - s_h(t) - \epsilon| + \\ &\quad + |c_h(z(t)-\epsilon,t) - w(z(t)-\epsilon,t)| + \\ &\quad + A_T\epsilon, \end{aligned} \tag{21}$$

so we get

$$\lim_H |c_h(s_h(t),t) - w(z(t),t)| \leq 2A_T\epsilon \qquad \forall \epsilon \tag{22}$$

which proves (2.20). Finally, (2.21) follows from (1.8), (1.9) and (2.20). □

Lemma 2.3. *The function $z(t)$ belongs to $C^1[0,T]$ and it satisfies*

$$\begin{aligned} \dot{z}(t) &= f(w(z(t),t)) \qquad t \geq 0 & (23)\\ w_x(z(t),t) &= -\dot{z}(t)\,[q + w(z(t),t)] \qquad t > 0. & (24) \end{aligned}$$

Proof. From lemma 2.1 we have that

$$\begin{aligned} \int_0^t f(w(z(\tau),\tau))\,d\tau &= \lim_H \int_0^t f(c_h(s_h(\tau),\tau))\,d\tau \\ &= \lim_H s_h(t) \\ &= z(t) \qquad \forall t \geq 0, & (25) \end{aligned}$$

then

$$\begin{aligned} -\dot{z}(t)\,[q + w(z(t),t)] &= -f(w(z(t),t))\,[q + w(z(t),t)] \\ &= -\lim_H \{f(c_h(s_h(t),t))\,[q + c_h(s_h(t),t)]\} \\ &= \lim_H c_{hx}(s_h(t),t) \\ &= w_x(z(t),t) \qquad \square \end{aligned}$$

In summary, we have just obtained a sequence of $s_h(t)$ and $c_h(x,t)$ with $h \in H$ that converges to $z(t)$ and $w(x,t)$ respectively, which are really a solution of **PS** (from equations 2.17, 2.19, 2.24 and 2.25). In order to prove the whole convergence, i.e. with $h \in (0,\infty)$, it is enough to observe that the solution of equations $(1.1)-(1.5)$ is unique (from [8]), so we have $w(x,t) = c(x,t)$ and $z(t) = s(t)$. Indeed, all the above results hold for every monotone subsequence $\{h_k : k \in \mathbf{N}\} \subset (0,\infty)$. Thus we have proved the following:

Theorem 2.4.

$$\begin{aligned} \lim_{h\to\infty} c_h(x,t) &= c(x,t), \\ \lim_{h\to\infty} s_h(t) &= s(t), \end{aligned}$$

and the convergence is uniform over $\bar{D}_T$ and $[0,T]$.

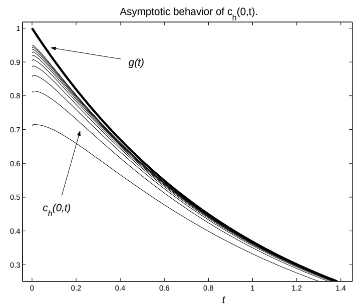

Figure 2: Plot of $g(t)$ and $c_h(0,t)$ for $h = 10, .., 100$.

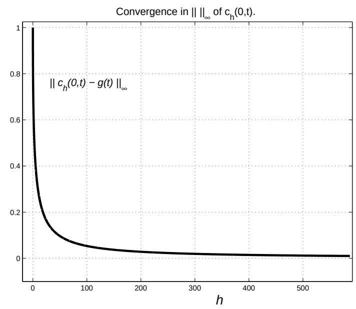

Figure 3: $c_h(0,t)$ converges to $g(t)$ as $h \to \infty$.

3. Numerical results

In this section we show some numerical calculation to illustrate the theoretical results. All the four graphics below were computed following the numerical method of [7] for $q = 5$, $f(c) = c^2$, $g(t) = e^{-t}$ and several h's. The limit free boundary $s(t)$ was computed following the numerical squeme suggested in [8] and [6].

4. A particular case

For the particular case of $f(c) = \alpha c$ ($\alpha > 0$) we can give an alternative proof of the convergence $s_h(t) \to s(t)$. We do the transformation

$$u(x,t) = -\int_x^{s(t)} [c(y,t) + q]\, dy, \tag{26}$$

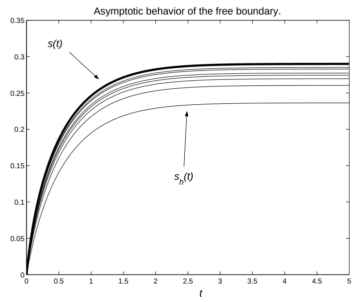

Figure 4: h=10,...,40, 130, 200 and 400.

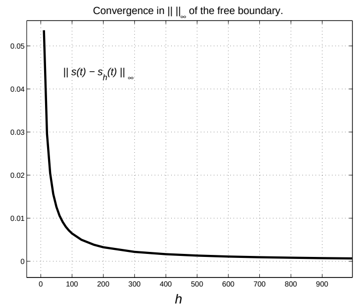

Figure 5: $s_h(t)$ converges to $s(t)$ as $h \to \infty$.

and we observe that

$$
\begin{aligned}
u_{xx} - u_t &= 0 && \text{in} \quad D_T, && (27)\\
u_x(0,t) &= g(t) + q, && 0 \leq t \leq T && (28)\\
u_x(s(t),t) &= \alpha^{-1}\dot{s}(t) + q, && 0 < t \leq T && (29)\\
u(s(t),t) &= 0, && 0 < t \leq T. && (30)
\end{aligned}
$$

Using Green's theorem we get:

$$0 = \oint_{D_t} u(x,\tau)\,dx + u_x(x,\tau)\,d\tau \tag{31}$$

and so

$$0 = \int_{s(t)}^{0} u(x,t)\,dx + \int_{t}^{0} g(\tau)\,d\tau + \alpha^{-1}s(t), \tag{32}$$

similarly, transformation (4.26) for $c_h(x,t)$ can be done obtaning

$$0 = \int_{s(t)}^{0} u_h(x,t)\,dx + \int_{t}^{0} c_h(0,\tau)\,d\tau + \alpha^{-1} s_h(t), \tag{33}$$

and differenting (4.32) and (4.33) we get

$$\begin{aligned} \alpha^{-1}\left(s(t) - s_h(t)\right) \quad = \quad & \int_0^t \left(g(\tau) - c_h(0,\tau)\right)\, d\tau \\ & + \int_0^{s(t)} u(x,t)\,dx - \int_0^{s_h(t)} u_h(x,t)\,dx. \end{aligned} \tag{34}$$

So we have to prove that the right side (4.34) goes to zero as $h \to \infty$. From (1.7) and (2.14) we have

$$|c_h(0,t) - g(t)| \leq \frac{A_T}{h}, \tag{35}$$

and we can follow [3, Theorem 18.5.1, p. 322] to show that there exists a constant k depending on q and T such that

$$\left| \int_0^{s(t)} u(x,t)\,dx - \int_0^{s_h(t)} u_h(x,t)\,dx \right| \leq \frac{k}{h}.$$

Thus we prove:

THEOREM 4.1. *Suppose that* $f(c) = \alpha c$ $(\alpha > 0)$ *in* **PSh**. *Then the free boundary* $s_h(t)$ *converges to* $s(t)$ *as* $h \to \infty$ *satisfying*

$$|s_h(t) - s(t)| \leq \frac{\bar{k}}{h}, \qquad 0 \leq t \leq T, \tag{36}$$

where $\bar{k}$ *depends on* q, α, g *and* T.

Due this theorem, we can observe fig. 5 and we can say that the order of convergence is still h^{-1}. But the generalization of Thm. 4.1 for a general function f will be the subject of future work.

5. Conclusions and final comment

The equivalence of the problems **PSh** and **PS** as $h \to \infty$ should be useful to decide real applications of these models. Numerical simulations carried out (following the numerical scheme of [7]) are often difficult to compute for very large h. Instead, we can use the numerical method for **PS**. Finally,in order to decide whether h is very large we suggest to use the inequality

$$|c_h(0,t) - g(t)| \leq \frac{A_T}{h},$$

obtained from (1.7) and (2.14).

References

[1] D. Andreucci and R. Ricci, *A free boundary problem arising from sorption of solvent in glassy polymers*, Quart. App. Math. **44** (1987), 649–657.

[2] G. Astarita G.C. Sarti, *A class of mathematical models for sorption of swelling solvents in glassy polymers*, Polymer Eng. Science **18**, no. 5 (1978) 388–395.

[3] J.R. Cannon, *The one-dimensional heat equation*, Encyclopedia of Mathematics and its applications **23**, Cambridge University Press, Cambridge, U.K. (1984).

[4] A. Comparini and R. Ricci, *On the swelling of a glassy polymer in contact with a well-stirred solvent*, Math. Meth. in the App. Sciences **7** (1985), 238–250.

[5] A. Comparini, R. Ricci and C. Turner, *Penetration of a solvent into a non-homogeneous polymer*, Meccanica **23** (1988), 75–80.

[6] A. Fasano, G.H. Meyer and M. Primicerio, *On a problem in the polymer industry: theoretical and numerical investigation of swelling*, S.I.A.M. **17**, no. 4 (1986) 945–960.

[7] M. Gaudiano, T. Godoy and C. Turner, *On a convective condition in the diffusion of a solvent into a polymer*, preprint (2006).

[8] P.H. San and N.D. Tri, *On a free boundary problem arising in the polymer industry*, Acta Math. Vietnamica **17**, no. 2 (1992) 41–52.

[9] W. Rudin, *Real and complex analysis*, McGraw-Hill Series in Higher Mathematics (1986).

[10] M. Primicerio, *Sorption of swelling solvents by glassy polymers*, Mathematics in Industry, H. Neunzert ed., Teubner, Stuttgart, (1984) 153–167.

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