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A PHENOMENOLOGICAL MODEL FOR DESORPTION IN POLYMERS

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Abstract: A phenomenological formulation is adopted to investigate desorption in polymers. The speed of the front is studied and the well-posedeness of the general model is analyzed. Numerical simulations illustrating the dynamics of the desorption process described by the proposed model are included.

1. Introduction

Over the past decades the study of polymers behavior has received the attention of many theoretical and experimental researchers. The reasons for this large interest lies on the very challenging mathematical models underlying the phenomena but mainly on the fact that due to its designer properties polymers are used in a large number of industries as pharmaceutical, equipment, clothing and sealants.

The problems reported in the literature are essentially of two different but related kinds: sorption of penetrants by dry polymeric matrices and desorption of penetrants from polymeric saturated matrices. When a penetrant diffuses into a dry polymer, its molecules take up new configurations to accommodate incoming penetrant molecules. Consequently a swelling process is initiated which transforms the polymer to its saturated rubbery state. The behavior of the mass uptake experimentally observed, presents a great variety ([24]). We mention without being exhaustive the following properties: (i)initially mass uptake is linear in time with sharp fronts which move at constant velocity and separating glassy and the rubbery states, (ii) the velocity of the front slow down at later times;(iii) initially uptake increases like t^α with α between 0.5 and 1 (even a short times);(iv) initially increases as $\sqrt{t}$ eventually presenting sharp fronts which moves at velocity $s' \simeq 1/\sqrt{t}$. Those behaviors can not be explained only by the Fick law and are usually described as anomalous or non-Fickian.

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In recent years, several attempts have been made to model mathematically such behaviors. For sorption phenomena we found in the literature two main approaches. In the first one the mathematical models are based on Fick's law and the kinetics of the glass-rubber polymer transition is taken properly into account. We mention for instance the models presented in [1], [2], [18], [21], [22], [23], [28], [29], [30]. In the second approach Fick's law is modified by introducing in the flux a viscoelastic stress as for instance in [6], [7], [8], [9], [11], [12], [15], [19].

In the case that a polymer, in a saturated rubbery state, undergoes the process of desorption there is an overall outward solvent flux. As expected this loss of solvent triggers a change of state in the polymer which subsequently assumes a glassy crystalline configuration. The exposed surface is the first to lose solvent to the surroundings and a dry glassy skin is formed which encapsulates the rubbery saturated polymer and the desorption is significantly slowed. In what concerns the mass loss in desorption phenomena, it has been experimentally observed that the behavior tends to be less varied, less easily detectable and presenting in many cases a certain similarity with the Fick's behavior. Much less attention has been placed on the mathematical modeling of polymer desorption process. It should be pointed out that desorption is not a simple reversal of the related sorption process. In the literature we found mainly mathematical models where a viscoelastic stress has been introduced in the flux ([3], [4], [5], [13], [14], [16]). Nevertheless, the numerical simulations presented in the last papers exhibit sharp fronts which in some cases do not agree with the experimental data presented for instance in [24], [25], [26].

In the present paper we propose a mathematical model for desorption that uses Fick's law and a rate controlled motion of the moving front separating the glass and rubber regions. This motion rate is analogous to the one proposed by Qian and Taylor in [22] for sorption phenomena and depends on glass-rubber transition concentrations and their fluxes. The idea underlying our model lies on the observation of experimentalists that if one considers a system where a front separates two different states the only obvious violation of Fick's law takes place at the front ([23], [24], [22]). As a consequence, if a particular kinetics is taken into account by imposing an upper limit on the flux or on the speed of the front, there may be no need to invoke the violation of Fick's law. In [22] the definition of the velocity of the front separating the two phases is completed by introducing an analytical expression depending on the osmotic pressure. This expression generalizes the one proposed by Thomas and Windle in [28]-[30]. At the best of our knowledge there is no agreement among experimentalists concerning an analytical expression for the speed of the front in the case of desorption. In desorption a crystallization occurs requiring some organization while in sorption characterized by melting such organization doesn't occurs. Then in the two phenomena the movement of the separating front is different and more information coming from experimental data is needed to establish an accurate formula for the speed. In our approach the expression for the rubber and glassy concentrations depends on a certain parameter, which can be specified onece a particular expression for the speed is taken into account. Otherwise future improvements on such matter can be easily introduced in our model.

The paper is organized as follows. In Section 2 the model is presented. The speed of the glass-rubber front is studied in Section 3. In Section 4 the the well-posedeness of the model is analyzed. In Section 5, numerical simulations illustrating the behavior of our model are included.

2. Mathematical model

We begin by introducing $C_\star$, the characteristic solute concentration that distinguishes the glassy from the swollen state. In the swollen saturated region, the concentration C of the penetrant within the polymer is above $C_\star$, and in the glassy drier region, $C < C_\star$. We consider a one-dimensional saturated polymer which has the far end insulated, while the exposed surface through which flux is lost to the surroundings is located at $x = 0$. As a consequence of the flux lost at the exposed surface, a phase change takes place there first. As with all phenomenological models, we take as given the existence of a moving front that separates the drier glassy state of the desorbed polymer from its nearly saturated region (still in its rubbery state). The diffusion equations in the glassy core and the swollen gel have the standard Fickian form that is the flux J is defined by

$$J = -D(C)C_x \,, \tag{1}$$

where $D(C)$ is the molecular diffusion coefficient. There is a significant change in $D(C)$ as the polymer loses its solute and is transformed from the rubbery to the glassy state ([20]). The variations in magnitude of $D(C)$ within the same phase are of less consequence, so we model $D(C)$ by taking an average over each phase

$$D(C) = \begin{cases} D_g, & 0 \leq C \leq C_\star(glassy) \\ \\ D_r, & C_\star < C(rubbery)\,. \end{cases} \tag{2}$$

Combining (1) with the standard conservation law

$$C_t = -J_x \ , \tag{3}$$

where the time is represented by t, we obtain the partial differential equation for the concentration C

$$C_t = (D(C)C_x)_x\,. \tag{4}$$

Let us represent the position of the moving front separating the glassy and rubbery regions by $s(t)$. Then (4) is equivalent to

$$\begin{cases} C^g_t = D_g C^g_{xx}\,,\ x < s(t) \\ \\ C^r_t = D_r C^r_{xx}\,,\ x \geq s(t) \end{cases}\,.$$

Here C^g and C^r represent the concentrations respectively for $x < s(t)$ and $x > s(t)$.

The model is completed with a boundary condition at the front which is written as

$$C^r(s(t), t) = C_\star, t > 0. \tag{5}$$

We note that a discontinuity in the concentration is admissible because we do not impose the glassy concentration, $C^g(s(t), t)$ to be equal to $C_\star$. As the flux J and the solute concentration C are discontinuous across the front, we define the front speed by

$$s'(t)[C]_{s(t)} = [J]_{s(t)}, \tag{6}$$

where $[h]_{s(t)} = h(s(t)_+, t) - h(s(t)_-, t)$ represents the jump of h at $s(t)$. We postpone to a later section a mathematical justification for equation (6). In several models for non-Fickian polymer diffusion (see e.g. [11], [14] and [16]), the concentration is considered continuous across the front and the speed is defined by

$$s'(t)a = [J]_{s(t)}$$

where a is a constant that satisfies a certain restriction.

As our goal is the study of desorption of an initially saturated polymer, we write the initial concentration in the form

$$C(x,0) = C_{init},\ x > 0. \tag{7}$$

At $x = 0$ we consider

$$C(0,t) = C_{ext},\ t \geq 0, \tag{8}$$

where C_{ext} stands for the external concentration. The far end is insulated which translates to

$$J(\infty, t) = 0, t \geq 0. \tag{9}$$

We note that condition (8) corresponds to a model with infinite permeability at the outflow end. In fact the value of the concentration at $x = 0$ is instantaneously assigned the same value as that of the external environment.

Our model consists of the classical diffusion equation (4) with $D(C)$ defined in (2), the frontal speed $s'(t)$ given by (6), the initial concentration (7), the boundary conditions stated in (8-9), and the concentration at the front $s(t)$ defined by (5). We note that we are looking at the problem as two coupled boundary value problems defined in time depending domains, $(0, s(t))$ and $(s(t), \infty)$. As we do not impose a value on the concentration C^g at the front, a condition is missing to define completely the speed. However as in desorption phenomena there is no agrement between experimentalists concerning the form of the front speed, we didn't consider any specification for such speed. We overcome this difficulty by introducing a parameter, varying in a certain interval, that can be used to control the front speed. Once specified a definition for the speed the parameter is selected.

The model we have outlined is based on the conviction of experimentalists. We remark that in the case of sorption an analogous phenomenological formulation by Qian and Taylor [22] has been proposed.

3. On the speed of the front

In this section the speed $s'(t)$ of the front is studied. We begin by establishing expressions for the concentrations C^g and C^r. To compute $s(t)$ these expressions will be then replaced in equation (6). An integral method developed by Boyle for standard diffusion problems, and adopted by Edwards in the analysis of polymer desorption models (see e.g. [14]) is employed in this section.

3.1. The glassy and rubbery concentrations.

We assume that diffusion equation $C_t^g = D_g C_{xx}^g$, $x < s(t)$ holds in the entire domain for some fictitious unknown initial condition $f^i(x)$. Requiring then that the solution of such equation satisfies condition (6), (7) and (9) we establish a condition that f^i must satisfy.

Let

$$C^g(x,t) = C_{ext} + T^g(x,t),\ 0 < x < s(t), \tag{10}$$

where T^g is defined by

$$\begin{cases} T_t^g = D_g T_{xx}^g,\ x > 0, t > 0, \\ T^g(0,t) = 0,\ t > 0, \\ T_x^g(\infty,t) = 0,\ t > 0, \\ T^g(x,0) = f^i(x), x > 0. \end{cases} \tag{11}$$

As the solution of (11) is given by ([10])

$$T^g(x,t) = \frac{1}{\sqrt{4\pi D_g t}} \int_0^\infty f^i(y)\Big(e^{-\frac{(x-y)^2}{4D_g t}} - e^{-\frac{(x+y)^2}{4D_g t}}\Big)\,dy \tag{12}$$

it follows that

$$C^g(x,t) = C_{ext} + \frac{1}{\sqrt{4\pi D_g t}} \int_0^\infty f^i(y)\Big(e^{-\frac{(x-y)^2}{4D_g t}} - e^{-\frac{(x+y)^2}{4D_g t}}\Big)\,dy\,,\ 0 < x < s(t). \tag{13}$$

We now compute the concentration in the rubbery state C^r following an analogous procedure. We assume that the diffusion equation $C_t^r = D_r C_{xx}^r$, $x > s(t)$ holds in the semi-infinite domain along with (5), (6), (7), (9) for some fictitious boundary condition at $x = 0$ represented by $f_b(t)$.

Let

$$C^r(x,t) = C_{init} - T^r(x,t),\ x > s(t). \tag{14}$$

where

$$\begin{cases} T^r_t = D_r T^r_{xx},\ x>0, t>0, \\ T^r(0,t) = f_b(t),\ t>0, \\ T^r_x(\infty,t) = 0,\ t>0, \\ T^r(x,0) = 0, x>0. \end{cases} \tag{15}$$

Once again in (15), f_b represents a fictitious boundary term which will be computed in due course. We have

$$T^r(x,t) = f_b(t) + \int_0^t \frac{1}{\sqrt{4\pi(t-\tau)}} \int_0^\infty -f_b'(\tau)\Big(e^{-\frac{(x-y)^2}{4D_r(t-\tau)}} - e^{-\frac{(x+y)^2}{4D_r(t-\tau)}}\Big)\,dy\,d\tau, \tag{16}$$

and as

$$\int_0^t \frac{1}{\sqrt{4\pi(t-\tau)}} \int_0^\infty -f_b'(\tau)\Big(e^{-\frac{(x-y)^2}{4D_r(t-\tau)}} - e^{-\frac{(x+y)^2}{4D_r(t-\tau)}}\Big)\,dy\,d\tau = -f_b(t) + \frac{x}{\sqrt{4\pi D_r}} \int_0^t f_b(\tau) e^{-\frac{x^2}{4D_r(t-\tau)}} \frac{1}{(t-\tau)^{3/2}}\,d\tau,$$

we may conclude that

$$C^r(x,t) = C_{init} - \frac{x}{\sqrt{4\pi D_r}} \int_0^t f_b(\tau) e^{-\frac{x^2}{4D_r(t-\tau)}} \frac{1}{(t-\tau)^{3/2}}\,d\tau,\ x > s(t). \tag{17}$$

3.2. The fictitious initial and boundary conditions.

We now proceed to determine the fictitious initial and boundary terms f^i and f_b, by analyzing separately the small time and the long time behavior.

(1) Small time behavior: We make the following ansatz:

$$f^i(x) = f^i_0,\quad f_b(t) = f^b_0,\quad s(t) = 2s_0 t^n. \tag{18}$$

We compute in what follows f^i_0, f^b_0 and n. The concentration in the rubbery state (17) reduces to

$$C^r(x,t) = C_{init} - \frac{2f^b_0}{\sqrt{\pi}} \int_{\frac{x}{\sqrt{4D_r t}}}^\infty e^{-z^2}\,dz. \tag{19}$$

By making use of the erfc function, we can write (19) in the simplified form

$$C^r(x,t) = C_{init} - f_0^b \,\mathrm{erfc}\,\Big(\frac{x}{\sqrt{4D_r t}}\Big), \tag{20}$$

and at the front $s(t)$, C^r is given by

$$C_\star = C^r(s(t),t) = C_{init} - f_0^b \,\mathrm{erfc}\,\Big(\frac{s_0 t^{n-1/2}}{\sqrt{D_r}}\Big). \tag{21}$$

Let us suppose that $n < \dfrac{1}{2}$. In this case $C^r(s(t),t) \to C_{init}$ as $t \to 0$, which would imply $C_{init} = C_\star$. We must therefore take $n \geq \dfrac{1}{2}$.

The concentration in the glassy state (13) may be written as

$$C^g(x,t) = C_{ext} + \frac{f_0^i}{\sqrt{\pi}} \int_{-\frac{x}{\sqrt{4D_g t}}}^{\frac{x}{\sqrt{4D_g t}}} e^{-z^2}\, dz,$$

This may be expressed in terms of the erf function as

$$C^g(x,t) = C_{ext} + f_0^i \,\mathrm{erf}\,\Big(\frac{x}{\sqrt{4D_g t}}\Big)\,. \tag{22}$$

As at the front $s(t)$, C^g is given by

$$C^g(s(t)_-,t) = C_{ext} + f_0^i \,\mathrm{erf}\,\Big(\frac{s_0 t^{n-1/2}}{\sqrt{D_g}}\Big), \tag{23}$$

it follows that, for all $n \geq \dfrac{1}{2}$, we have $C^g(s(t)_-,t) \to C_{ext}$.

We note that if continuity was imposed to the concentration, then for $n > \dfrac{1}{2}$ we would obtain $C_\star = C_{ext}$ which is not acceptable. The lack of continuity contributes to give the front a certain non-Fickian character.

(2) Large-time behavior: Following [14],we make the following ansatz:

$$f^i(x) = f_\infty^i e^{Ax}, \quad f_b(t) = f_\infty^b e^{B^2 t}, \quad s(t) = 2s_\infty t^n. \tag{24}$$

From (11), it may be deduced that

$$C^g(x,t) = C_{ext} + \frac{f^i_\infty}{\sqrt{\pi}} e^{A^2 D_g t} \Big(e^{Ax} \int_{-\frac{x+2AD_g t}{\sqrt{4D_g t}}}^{\infty} e^{-z^2}\, dz - e^{-Ax} \int_{\frac{x-2AD_g t}{\sqrt{4D_g t}}}^{\infty} e^{-z^2}\, dz \Big),\ x < s(t)\,. \tag{25}$$

Employing the erfc function, we write (25) as

$$C^g(x,t) = C_{ext} + \frac{f^i_\infty}{2} e^{A^2 D_g t} \Big(e^{Ax} \operatorname{erfc}\big(-\frac{x+2AD_g t}{\sqrt{4D_g t}} \big) - e^{-Ax} \operatorname{erfc}\big(\frac{x-2AD_g t}{\sqrt{4D_g t}} \big) \Big)\ \ x < s(t)\,. \tag{26}$$

We determine A by taking limits in (26) as $t \to \infty$. As

$$\lim_{t\to\infty} e^{\frac{\gamma x + \gamma^2 t}{\alpha^2}} \operatorname{erfc}\big(\frac{x+2\gamma t}{2\alpha\sqrt{t}}\big) = \lim_{t\to\infty} \frac{2\alpha\sqrt{t}}{\sqrt{\pi}(x+2\gamma t)} e^{-\frac{x^2}{4\alpha^2 t}}, \tag{27}$$

and C^g can be written as

$$C^g(x,t) = C_{ext} + \frac{f^i_\infty}{2} \Big(2e^{A^2 D_g t} \big(e^{Ax} - e^{-Ax} \big) + e^{-Ax + A^2 D_g t} \operatorname{erfc}\big(\frac{-x+2AD_g t}{\sqrt{4D_g t}} \big) - e^{Ax + A^2 D_g t} \operatorname{erfc}\big(\frac{x+2AD_g t}{\sqrt{4D_g t}} \big) \Big),\ x < s(t), \tag{28}$$

we obtain, after some simplifications,

$$\lim_{t\to\infty} C^g(x,t) = \lim_{t\to\infty} \Big(C_{ext} + f^i_\infty \Big(e^{A^2 D_g t} \big(e^{Ax} - e^{-Ax} \big) + e^{-\frac{x^2}{4D_g t}} \big(\frac{\sqrt{D_g t}}{\sqrt{\pi}(-x + 2AD_g t)} - \frac{\sqrt{D_g t}}{\sqrt{\pi}(x + 2AD_g t)} \big) \Big) \Big)\,. \tag{29}$$

The limit in (29) is finite provided that $A = 0$. As a consequence, (26) reduces to

$$C^g(x,t) = C_{ext} + \frac{f^i_\infty}{2} \Big(\operatorname{erfc}\big(-\frac{x}{\sqrt{4D_g t}} \big) - \operatorname{erfc}\big(\frac{x}{\sqrt{4D_g t}} \big) \Big), \tag{30}$$

which is equivalent to

$$C^g(x,t) = C_{ext} + f^i_\infty \operatorname{erf}\big(\frac{x}{\sqrt{4D_g t}} \big). \tag{31}$$

Let us consider now the concentration in the rubbery state. Substituting $f_b(t) = f_\infty^b e^{B^2 t}$ into (17), we get

$$\begin{aligned} C^r(x,t) = C_{init} - \frac{f_\infty^b}{2} e^{B^2 t}\Big(e^{B\frac{x}{\sqrt{D_r}}} \operatorname{erfc}\big(\frac{x+2Bt\sqrt{D_r}}{\sqrt{4D_r t}}\big) \\ - e^{-B\frac{x}{\sqrt{D_r}}} \operatorname{erfc}\big(\frac{x-2Bt\sqrt{D_r}}{\sqrt{4D_r t}}\big)\Big),\ x \geq s(t) \end{aligned} \tag{32}$$

Next, we discuss B by taking limits, when $t \to \infty$, in the above expression. Substituting (27) into the large-time limit of (32), we obtain

$$\begin{aligned} \lim_{t\to\infty} C_r(x,t) = C_{init} - \frac{f_\infty^b}{2} \lim_{t\to\infty} e^{-\frac{x^2}{4D_r t}} \frac{2\sqrt{D_r t}}{\sqrt{\pi}(x+2B\sqrt{D_r}t)} \\ - \frac{f_\infty^b}{2} e^{B^2 t - \frac{Bx}{\sqrt{D_r}}} \operatorname{erfc}\big(\frac{x}{2\sqrt{D_r t}} - B\sqrt{t}\big),\ x \geq s(t). \end{aligned} \tag{33}$$

The first limit in the right side of (33) is zero. To guarantee the boundeness of $\lim_{t\to\infty} C_r(x,t)$ we must have $B = 0$ or

$$Bt - \frac{x}{\sqrt{D_r}} \leq 0,\ x \geq s(t), \tag{34}$$

which holds if

$$s(t) = \sqrt{D_r} Bt. \tag{35}$$

We next study these two cases:

(a) $B = 0$:

The large-time limit (33) is finite provided that $B = 0$. This allows us to simplify (32) to obtaining

$$C^r(x,t) = C_{init} - f_\infty^b \operatorname{erfc}\big(\frac{x}{\sqrt{4D_r t}}\big). \tag{36}$$

We analyze the large-time concentrations C^g and C^r at the front $s(t)$. Substituting $s(t)$ from (24) into (36) gives

$$C^r(s(t),t) = C_{init} - f_\infty^b \operatorname{erfc}\big(\frac{s_\infty t^{n-1/2}}{\sqrt{D_r}}\big). \tag{37}$$

For $n > \dfrac{1}{2}$ and $t \to \infty$, we get $C^r(s(t),t) \to C_{init}$. As $C^r(s(t),t) = C_\star$, this would imply that $C_\star = C_{init}$. We must therefore conclude that $n \leq \dfrac{1}{2}$.

(b) $s(t) = \sqrt{D_r} Bt$:
As $C^r(s(t), t) = C_\star$ we have

$$C_\star = C_{init} - f^b_\infty.$$

Computing now $C^r_x(s(t)_+, t)$ and $C^g_x(s(t)_-, t)$ and replacing in (6) we obtain in the large time limit

$$-D_r \frac{C_{init} - C_\star}{2} \frac{B}{\sqrt{D_r}} = \sqrt{D_r} B \big(C_\star - C_{ext} - f^i_\infty\big),$$

that is

$$f^i_\infty = C_{init} - C_{ext}. \tag{38}$$

With this value of f^i_∞ we have from (23)

$$\lim_{t \to \infty} C^g(s(t)_-, t) = C_{init}.$$

As the concentration on the glassy region, $C^g(x, t)$, must satisfy

$$C^g(x, t) \le C_\star$$

we conclude that $C_{init} \le C_\star$ which is not admissible because in a desorption problem $C_{init} > C_\star$. This means that (35) does not holds.

We must therefore conclude that the speed of the front behaves like t^{n-1} with $n \ge \frac{1}{2}$ for small time and $n \le \frac{1}{2}$ for large time.

3.3. Dependence of the moving front on the problem data. In this section we analyse the behavior of the moving front in the case $n = \frac{1}{2}$. This choice is justified from an experimental point of view because as reported in the literature, desorption phenomena presents, in same cases, great similarity with a Fickian behavior. From a mathematical point of view if $n = \frac{1}{2}$ an almost complete analytical treatment can be achieved. For this choice of n we compute f^b_0, f^b_∞ and estimates for f^i_0, f^i_∞, s_0 and for s_∞.

(1) Small time behavior:
From (18) the expression for the front position $s(t)$ is

$$s(t) = 2 s_0 \sqrt{t}, \tag{39}$$

and then (21) takes the form

$$f_0^b = \frac{C_{init} - C_\star}{\mathrm{erfc}\,\big(\frac{s_0}{\sqrt{D_r}}\big)}. \tag{40}$$

We note that as in our model the concentration in the glassy phase, C^g, is not continuous, f_0^i can not be completely computed. It assumes the role of a parameter that will be specified once a definition for the desorption speed is considered. In what follows we establish an inequality that f_0^i must satisfy.

Taking into account (20), (22), (39) and (40) in (6) we obtain after some straightforward computations

$$\sqrt{D_r}e^{-\frac{s_0^2}{D_r}}\frac{C_{init} - C_\star}{\mathrm{erfc}\,\big(\frac{s_0}{\sqrt{D_r}}\big)} - f_0^i\Big(\sqrt{D_g}e^{-\frac{s_0^2}{D_g}} + s_0\sqrt{\pi}\ \mathrm{erf}\,\big(\frac{s_0}{\sqrt{D_g}}\big)\Big)$$
$$-s_0\sqrt{\pi}\big(C_{ext} - C_\star\big) = 0. \tag{41}$$

In this equation s_0 and f_0^i are unknowns. We look at f_0^i like a parameter and we solve (41) for each value of this parameter. Let us denote the first member of (41) by $g(s_0)$. In what follows, using geometrical arguments, we establish conditions on f_0^i that guarantee the existence of solutions s_0 of (41).

(a) For

$$f_0^i \leq \sqrt{\frac{D_r}{D_g}}(C_{init} - C_\star), \tag{42}$$

it can be demonstrated that $g(0) > 0$.

On the other hand the sign of $\lim\limits_{s_0 \to +\infty} g(s)$ is the sign of $C_{init} - C_{ext} - f_0^i$, that is, when

$$f_0^i \geq C_{init} - C_{ext}, \tag{43}$$

the corresponding limit is $g(+\infty) < 0$.

From (42) and (43) we conclude that for

$$f_0^i \in [C_{init} - C_{ext}\,,\sqrt{\frac{D_r}{D_g}}(C_{init} - C_\star)]$$

when

$$C_{init} - C_{ext} \leq \sqrt{\frac{D_r}{D_g}}(C_{init} - C_\star), \tag{44}$$

holds, then equation (41) has at least one solution.
We note that if $C_{ext} = C_\star$ (44) is always satisfied. If the external environment is dry, that is $C_{ext} = 0$, we have from (44)

$$C_{init} \geq \frac{\sqrt{\frac{D_r}{D_g}} C_\star}{\sqrt{\frac{D_r}{D_g}} - 1}. \tag{45}$$

When D_r is much larger than D_g we can consider we can consider

$$\frac{\sqrt{\frac{D_r}{D_g}}}{\sqrt{\frac{D_r}{D_g}} - 1} \simeq 1,$$

and (44) is trivially verified.

(b) Given

$$f_0^i \geq \sqrt{\frac{D_r}{D_g}}(C_{init} - C_\star), \tag{46}$$

it follows that $g(0) < 0$. Furthermore, for

$$f_0^i \leq C_{init} - C_{ext}\ , \tag{47}$$

it can be shown that $g(+\infty) > 0$.
From (46), (47) we deduce that for

$$f_0^i \in [\sqrt{\frac{D_r}{D_g}}(C_{init} - C_\star)\, , C_{init} - C_{ext}]$$

when

$$C_{init} - C_{ext} > \sqrt{\frac{D_r}{D_g}}(C_{init} - C_\star), \tag{48}$$

holds, then equation (41) has at least one solution.

From the previous consideration we finally conclude that for

$$f_0^i \in \big[\min\{C_{init}-C_{ext}, \sqrt{\frac{D_r}{D_g}}(C_{init}-C_\star)\}, \max\{C_{init}-C_{ext}, \sqrt{\frac{D_r}{D_g}}(C_{init}-C_\star)\}\big],$$

(41) has always a solution. We remark that these bounds on f_0^i do not guarantee that $C^g(s(t)_-, t) \leq C_\star$. To have this upper bound satisfied we must also require that

$$f_0^i \leq \frac{C_\star - C_{ext}}{\operatorname{erf}\left(\frac{s_0}{\sqrt{D_g}}\right)}. \tag{49}$$

(2) <u>Large time behavior:</u>

From (37) we obtain $f_\infty^b = \dfrac{C_{init} - C_\star}{\operatorname{erfc}\left(\frac{s_\infty}{\sqrt{D_r}}\right)}$, which coincides with the previous result for small-time (40). Consequently, the definitions for both C^g and C^r are equal in the small and large time limits and then s_∞ satisfies (41), where f_0^i and s_0 are replaced by f_∞^i and s_∞ respectively.

We note again that if an analytical expression for the front speed was joined to (41) (with f_0^i and s_0 replaced by f_∞^i and s_∞ respectively) the values of s_∞ and f_∞^i could be computed univocally.

As before we conclude that equation (41) (with f_0^i and s_0 replaced by f_∞^i and s_∞ respectively) has a solution $s_\infty = s_0$, which will be represented by $\bar{s}$.

We recall again that due to the fact that we didn't specify a law for the speed the value of f^i is not established. Instead we estimated previously an interval of variation for f^i. Therefore s "appears" as a function of f^i and f^i can be considered as a parameter to control the front speed.

In the numerical experiments which follow $\bar{s}$ presents a very slight variation with f^i. Such numerical experiments pretend to illustrate the dependence of $\bar{s}$ on the problem data, that is $C_\star, C_{ext}, D_r$ and D_g.

Figure 1 illustrates the behavior of $\bar{s}$ with the transition concentration $C_\star$. We observe that as $C_\star$ increases an increasing of $\bar{s}$ is observed. In fact as $C_\star$ increases not as much penetrant needs to desorb in order for the solution to attain $C_\star$ and so $\bar{s}$ increases.

The velocity of the front depends also on the exterior concentration C_{ext}. In Figure 2 we plot the graphics of $\bar{s}$ for different values of C_{ext}. An increase of C_{ext} implies a decreases of the position of the front. In fact as C_{ext} increases the flux out of the front is smaller and $\bar{s}$ decreases.

The behavior of $\bar{s}$ when the rubbery coefficient D_r increases is illustrated in Figure 3. As expected the increase of D_r implies a decrease of $\bar{s}$. In fact as D_r increases the flux from the rubbery region increases so there is a greater

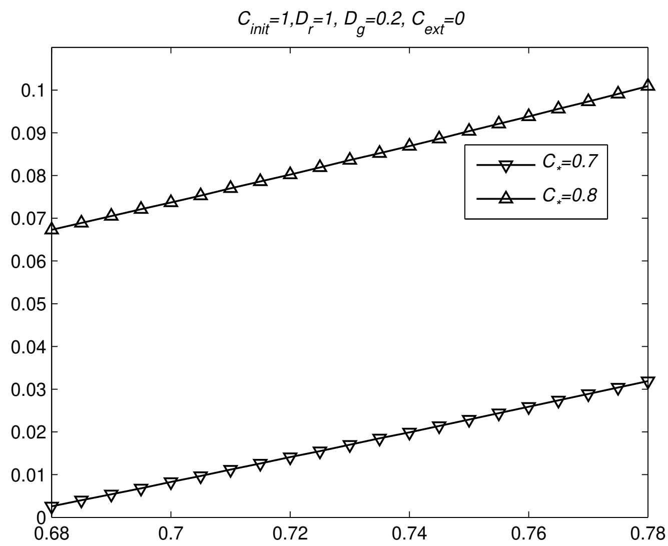

FIGURE 1. Behavior of $\bar{s}$ with $C_\star$.

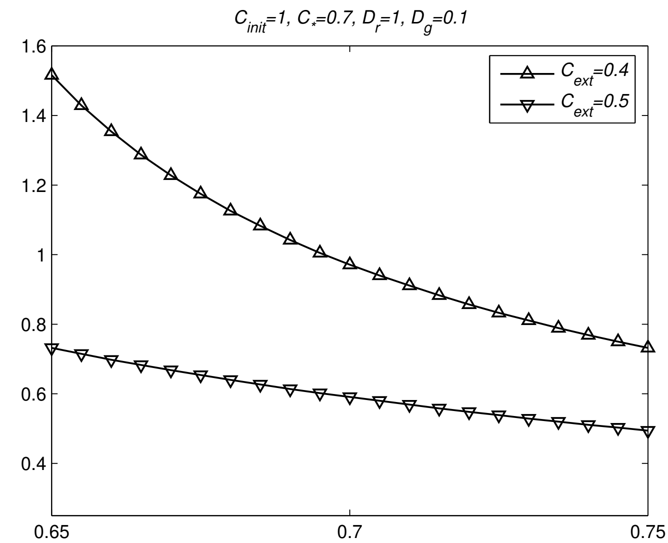

FIGURE 2. Behavior of $\bar{s}$ with C_{ext}.

barrier to surmount and consequently $\bar{s}$ decreases. The mentioned barrier decreases as D_g increases. Consequently as D_g increases $\bar{s}$ also increases. In Figure 4 we plot the graphics of $\bar{s}$ for $D_g = 0.2$ and $D_g = 0.4$.

In Figure 5 we represent the behavior of $\bar{s}$ with C_{init}. As C_{init} increases, the flux from the rubbery region increases and consequently $\bar{s}$ decreases.

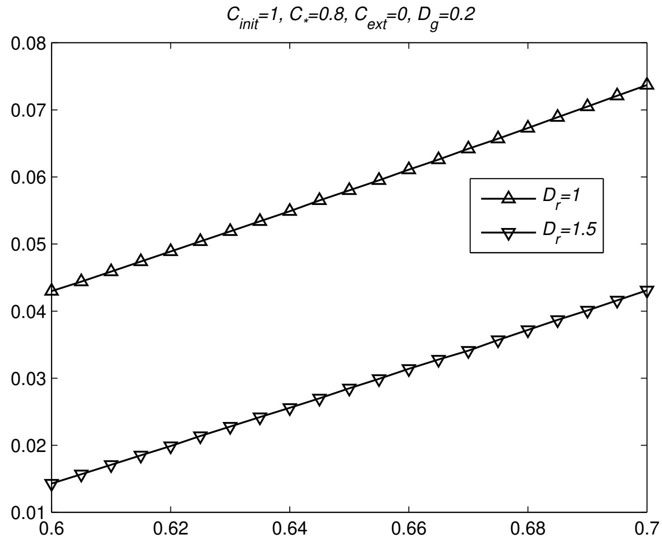

FIGURE 3. Behavior of $\bar{s}$ with D_r.

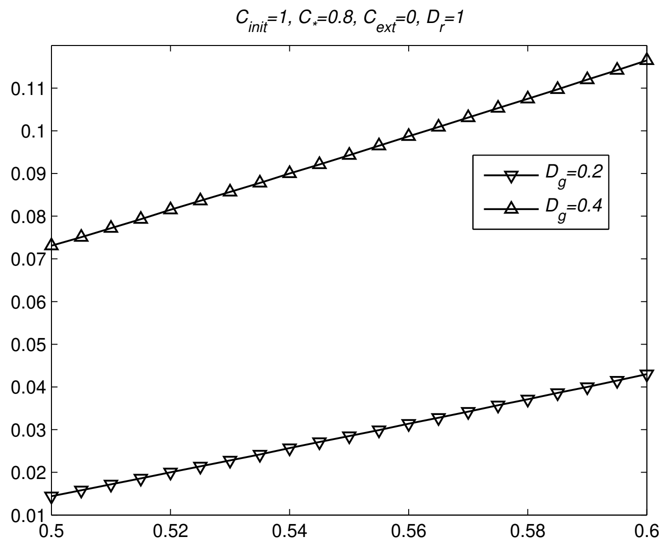

FIGURE 4. Behavior of $\bar{s}$ with D_g.

Finally, in order to study the stability behavior of $\bar{s}$ when C_{init} is perturbed we consider $\widetilde{C}(x, 0) = C_{init} - \epsilon$. Let $\bar{s}_\epsilon$ be the corresponding solution of (41). To establish heuristically the stability of $s(t)$ we plotted the error $|\bar{s} - \bar{s}_\epsilon|$ for several values of the parameters ϵ. The experiments carried on exhibit

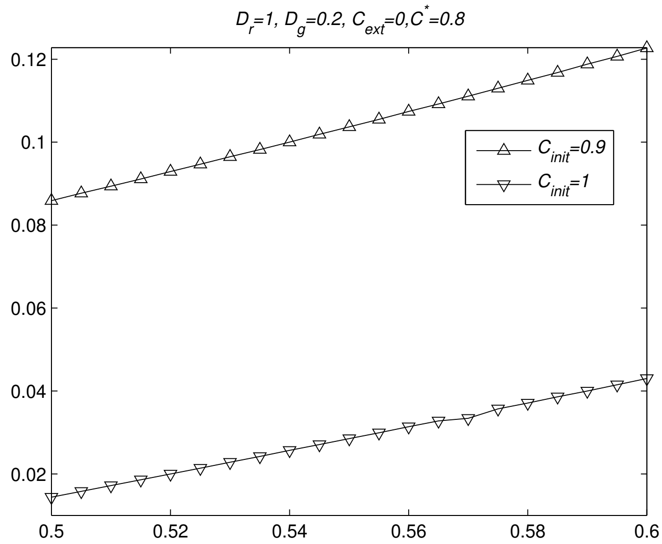

FIGURE 5. Behavior of $\bar{s}$ with C_{init}.

strong evidence of stability of the front. In Figure 6 we show a typical plot of $|\bar{s} - \bar{s}_\epsilon|$.

In Section 4 the stability behavior of $\bar{s}$ is used to establish the stability of model (4) -(9).

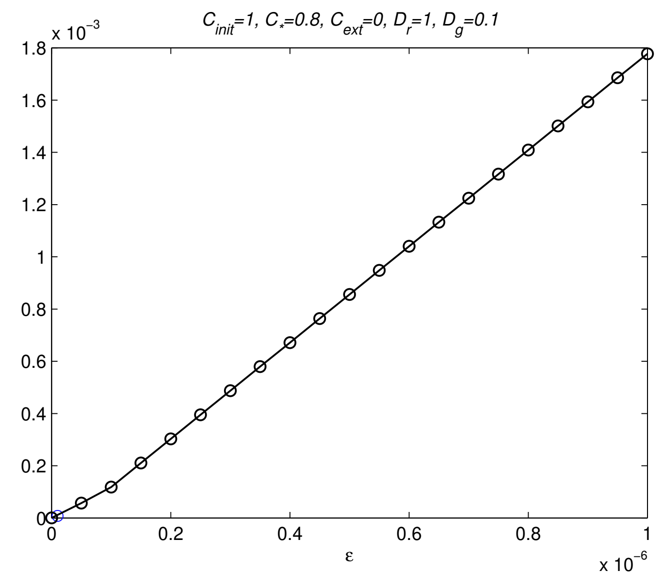

FIGURE 6. The error $|\bar{s} - \bar{s}_\epsilon|$ for $\epsilon \in [10^{-16}, 10^{-6}]$.

3.4. The large time behavior of the front revisited.

In a certain number of experimental papers is reported that the speed of the front in desorption is constant at large times. As proved in Section 3.2 when $n = 1$ is considered, that is when a constant speed is assumed in the framework of model (4) -(9), we obtain the necessary condition $C_{init} \leq C_\star$ which is not admissible. The question then arises of how to modify our present model in order that a constant speed of the front is admissible for large times. In what follows we give a answer to this question by modifying the front condition (6).

In order to understand the physical meaning of the front condition (6) we introduce $M(t)$, the total mass of the penetrant in the polymeric matrix at each time t, which defined by

$$M(t) = \int_0^\infty C(x,t)\,dx. \tag{50}$$

Taking derivatives in (50) we have

$$\begin{aligned} M'(t) = &\int_0^{s(t)} D_g C^g_{xx}(x,t)\,dx + \int_{s(t)}^\infty D_r C^r_{xx}(x,t)\,dx \\ &+ s'(t)\Big(C^g(s(t)_-,t) - C^r(s(t)_+,t)\Big)\,, \end{aligned} \tag{51}$$

and then

$$\begin{aligned} M'(t) = &\; D_g\big(C^g_x(s(t)_-,t) - C^g_x(0,t)\big) + D_r\big(C^r_x(\infty,t) - C^r_x(s(t)_+,t) \\ &+ s'(t)\Big(C^g(s(t)_-,t) - C^r(s(t)_+,t)\Big)\,. \end{aligned} \tag{52}$$

As the polymer is desorbing $M'(t) \leq 0$ and consequently from $C^r_x(\infty,t) = 0$, we establish

$$\begin{aligned} &D_g C^g_x(s(t)_-,t) - D_r C^r_x(s(t)_+,t) + s'(t)\Big(C^g(s(t)_-,t) - C^r(s(t)_+,t)\Big) \\ &\qquad\qquad \leq D_g C^g_x(0,t)\,. \end{aligned} \tag{53}$$

This last inequality can be written as

$$[J]_{s(t)} \leq s'(t)[C]_{s(t)} + D_g C^g_x(0,t)\,. \tag{54}$$

When $t \to \infty$, we deduce from (31), that $C^g_x(0,t) \to 0$ and consequently (54) assumes the form

$$[J]_{s(t)} \leq s'(t)[C]_{s(t)}\,. \tag{55}$$

We note that our previous results have been obtained under the more restrictive condition (6).

Let us consider now that $s(t)$ is defined, as before, by (35). Replacing $C_x^r(s(t)_+,t)$ and $C_x^g(s(t)_-,t)$ in new front condition (55) we obtain, instead of (38), the inequality

$$f_\infty^i \leq C_{init} - C_{ext}. \tag{56}$$

Finally replacing (56) in (23)we have

$$\lim_{t\to\infty} C^g(s(t)_-,t) \leq C_{init}$$

which is trivially verified. We can then conclude that relaxing the front condition (6) the model admits a linear speed of the front at large times.

4. On the stability of the model

In this section we investigate the overall stability of the model (4) -(9) under a perturbation of the initial condition (7). In Section 3 we presented an heuristic evidence of the stability of $s(t)$. We assume in what follows that the front is stable with respect to perturbations of the initial condition C_{init}. The usual L^2 norm is denoted by $\|.\|_{L^2}$. We shall first establish an estimate for $\|C(.,t)\|_{L^2}$ with homogeneous boundary conditions.

Multiplying (4) by C, in the sense of the L^2 inner product, we have

$$\begin{aligned}(C_t, C) &= -(DC_x, C_x) + [CJ]_{s(t)} \\ &+ C(0,t)J(0,t) - C(L,t)J(L,t).\end{aligned} \tag{57}$$

It can be easily shown that

$$\frac{d}{dt}\|C\|_{L^2}^2 = 2\int_0^L C_t C\,dx + s'(t)\left(C(s(t)_-,t)^2 - C(s(t)_+,t)^2\right). \tag{58}$$

Substituting (58) and the zero boundary condition at $x = 0$ and $x = \infty$ into (57) we obtain

$$\frac{1}{2}\frac{d}{dt}\|C\|_{L^2}^2 = -(DC_x, C_x) + \frac{1}{2}s'(t)\left(C(s(t),t)_-^2 - C(s(t)_+,t)^2\right) + [CJ]_{s(t)}. \tag{59}$$

As we are considering a desorption problem we assume that $C_x > 0$. Under this assumption we next prove that

$$\frac{1}{2}s'(t)\left(C(s(t)_-,t)^2 - C(s(t)_+,t)^2\right) + [CJ]_{s(t)} \leq 0\,. \tag{60}$$

Multiplying (6) by $C(s(t)_-,t) + C(s(t)_+,t)$, we obtain

$$\frac{1}{2}s'(t)\left(C(s(t)_+,t)^2 - C(s(t)_-,t)^2\right) = \frac{1}{2}[J]_{s(t)}\left(C(s(t)_-,t) + C(s(t)_+,t)\right).$$

Therefore, (60) follows if we prove that for $C_x > 0$ holds the inequality

$$\frac{1}{2}[J]_{s(t)}\left(C(s(t)_-,t) + C(s(t)_+,t)\right) + [CJ]_{s(t)} \leq 0. \tag{61}$$

We may express (61) in the simpler form

$$\left(J(s(t)_-,t) + J(s(t)_+,t)\right)\left(C(s(t)_-,t) - C(s(t)_+,t)\right) \geq 0\,.$$

As $C(s(t)_-,t) - C(s(t)_+,t) \leq 0$ and $C_x > 0$ we have

$$J(s(t)_-,t) + J(s(t)_+,t) \leq 0, \tag{62}$$

and consequently (61) is proved.

Finally using (60) in (59) we obtain

$$\frac{1}{2}\frac{d}{dt}\|C\|^2_{L^2} \leq -(DC_x, C_x), \tag{63}$$

from which we deduce

$$\frac{1}{2}\frac{d}{dt}\|C\|^2_{L^2} \leq 0. \tag{64}$$

This leads us to the following proposition:

Proposition 1. *Let C be the solution of (4)-(9) with initial conditions C_{init} and homogeneous boundary conditions. Then*

$$\|C(.,t)\|_{L^2} \leq \|C_{init}\|_{L^2},\ t \geq 0. \tag{65}$$

■

As a consequence of Proposition 1 we can state that the initial boundary value problem (4)-(9) has at most one solution. From Proposition 1 we can also establish the stability of the model. For the purpose of our analysis, we consider C and $\tilde{C}$ to be the solutions of problems with initial conditions respectively v_0 and $\tilde{v}_0$, where $v_0 - \tilde{v}_0 > 0$ and $v = C - \tilde{C}$.

As a corollary of Proposition 1, we establish the following result:

Corollary 1. *Let C and $\tilde{C}$ be solutions of (4)-(5) with initial conditions v_0 and $\tilde{v}_0$, where $v_0 > \tilde{v}_0$. It follows that*

$$\|v(.,t)\|_{L^2} \leq \|v_0 - \tilde{v}_0\|_{L^2},\ t \geq 0. \tag{66}$$

■

5. Numerical illustrations

In this section we illustrate the behavior of the model studied in the previous sections. Let $\{x_i = x_{i-1} + h,\ i = 1, \ldots, N\}$, with $x_0 = 0, x_N = L$, be a spatial grid in $[0, L]$ where L is large enough. In $[0, T]$, $T > 0$, we define the time grid $\{t_j = t_{j-1} + \Delta t, j = 1, \ldots, M\}$ with $t_0 = 0$ and $t_M = T$.

Each time step is decomposed in two stages. In the first stage we compute a Fickian approximation which is corrected in the second stage. We describe separately the initial step and a typical step.

(1) Initialization.
   (a) First stage:
   We discretize explicitly equation (4) obtaining

$$\frac{C_i^{j+1} - C_i^j}{\Delta t} = D_r D_{2,x} C_i^j,\ \ i = 1, \ldots, N,\ \ j \geq 0, \tag{67}$$

   with initial and boundary conditions

$$C_i^0 = C_{init}, i = 0, \ldots, N,\ C_0^j = C_{ext},\ C_{N-1}^j = C_{N+1}^j\, j \geq 1, \tag{68}$$

   where

$$D_{2,x} C_i^j = \frac{C_{i+1}^j - 2C_i^j + C_{i-1}^j}{h^2}$$

   and $x_{N+1} = L + h$.
   Let $t_{j_{1_\star}}$ be the first time level such that, at some grid point, the numerical approximation is less than the transition concentration $C_\star$. Let $x_{i_{1_\star}}$ be such that $C_i^{j_{1\star}} < C^*$, $i = 0, \ldots, i_{1_\star} - 1, C_{i_{1_\star}}^{j_{1\star}} = C_\star$. Then $x_{i_{1_\star}}$ is the first transition point determined by the Fickian behavior of the penetrant in the polymer and, in $[0, x_{i_{1_\star}})$ and $[x_{i_{1_\star}}, L]$, at this instant, the polymer presents numerical glassy and rubbery states respectively. The computed transition points is, in what follows, referred as Fikian transition points.
   (b) Second stage:
   The speed separating the rubber and glassy states is controlled by (41) which is f_0^i dependent. As remarked before, this parameter can be specified if a particular expression for the speed is taken into account. This equation is solved, for a specified f_0^i, numerically and for each time level we compute a new candidate to a transition point $s(t_{j_{1_\star}}) \simeq \bar{s}(t_{j_{1_\star}}) = 2\bar{s}\sqrt{t_{j_{1_\star}}}$. Then we define a

new transition point, $x_{i_{1_\star},new}$, as the minimum between $\bar{s}(t_j)$ and the Fickian one, that is

$$x_{i_{1_\star,new}} = \min\{\bar{s}(t_{j_{1_\star}})\,, x_{i_{1_\star}}\}.$$

(i) If the transition point is the Fickian one, that is $x_{i_{1_\star,new}} = x_{i_{1_\star}}$, then the computed numerical approximations for the concentrations $C^g(x_i, t_{j_{1_\star}})$, $C^r(x_i, t_{j_{1_\star}})$ are corrected considering the finite difference equations

$$\begin{array}{l}
\dfrac{C_i^{g,j_{1_\star}} - C_i^{g,j_{1_\star}-1}}{\Delta t} = D_g D_{2,x} C_i^{g,j_{1_\star}-1},\ i = 1, \ldots, i_{1_\star} - 1,\\
C_0^{g,j_{1_\star}} = C_{ext},\ C_{i_{1_\star}}^{g,j_{1_\star}} = C_{i_{1_\star}-1}^{j_{1_\star}},\\
C_i^{g,j_{1_\star}-1} = C_i^{j_{1_\star}}, i = 1, \ldots, i_{1_\star} - 1,\\
\dfrac{C_i^{r,j_{1_\star}} - C_i^{r,j_{1_\star}-1}}{\Delta t} = D_r D_{2,x} C_i^{r,j_{1_\star}-1},\ i = i_{1_\star} + 1,\ \ldots, N,\\
C_{i_{1_\star}}^{r,j_{1_\star}} = C_\star,\ C_{N-1}^{r,j_{1_\star}} = C_{N+1}^{r,j_{1_\star}},\\
C_i^{r,j_{1_\star}-1} = C_i^{j_{1_\star}},\ i = i_{1_\star} + 1,\ \ldots, N\,.
\end{array} \tag{69}$$

(ii) If the transition point is obtained with a non-Fickian correction, that is $x_{i_{1_\star},new} = \bar{s}(t_{j_{1_\star}})$, then we replace (69) by

$$\begin{array}{l}
\dfrac{C_i^{g,j_{1_\star}} - C_i^{g,j_{1_\star}-1}}{\Delta t} = D_g D_{2,x} C_i^{g,j_{1_\star}-1},\ i = 1, \ldots, i_{1_\star,new} - 1,\\
C_0^{g,j_{1_\star}} = C_{ext},\ C_{i_{1_\star,new}}^{g,j_{1_\star}} = C_{i_{1_\star,new}-1}^{j_{1_\star}}\,,\\
C_i^{g,j_{1_\star}-1} = C_i^{j_{1_\star}}, i = 1, \ldots, i_{1_\star,new} - 1\,,\\
\dfrac{C_i^{r,j_{1_\star}} - C_i^{r,j_{1_\star}-1}}{\Delta t} = D_r D_{2,x} C_i^{r,j_{1_\star}-1},\ i = i_{1_\star,new} + 1,\ \ldots, N,\\
C_{i_{1_\star,new}}^{r,j_{1_\star}} = C_\star,\ C_{N-1}^{r,j_{1_\star}} = C_{N+1}^{r,j_{1_\star}}\,,\\
C_i^{r,j_{1_\star}-1} = C_{init},\ i = i_{1_\star,new} + 1,\ \ldots, N\,.
\end{array} \tag{70}$$

(2) Typical steps.

(a) First stage :

Let $x_{i_\star}$ be the transition point at time level $t_{j_\star}$. The approximation to the concentrations at level $t_{j_\star+1}$ are computed using

$$\begin{array}{l}
\dfrac{C_i^{j_\star+1} - C_i^{j_\star}}{\Delta t} = D_g D_{2,x} C_i^{j_\star},\ i = 1, \ldots, i_\star - 1,\\
\dfrac{C_i^{j_\star+1} - C_i^{j_\star}}{\Delta t} = D_r D_{2,x} C_i^{j_\star},\ \ i = i_\star + 1,\ \ldots, N,
\end{array} \tag{71}$$

and

$$\frac{C_{i_\star}^{j_\star+1} - \frac{C_\star + C{i_{1_\star}}^{g,j_\star}}{2}}{\Delta t} = \frac{1}{h}\Big(D_r \frac{C_{i_\star+1}^{r,j_\star} - C_\star}{h} - D_g \frac{C_{i_\star}^{g,j_\star} - C_{i_\star-1}^{g,j_\star}}{h}\Big). \tag{72}$$

We compare the concentrations $C_i^{j_\star+1}, i = 1, \ldots, N$, with $C_\star$ and we compute $x_{\ell_\star}$ such that $C_i^{j_\star+1} < C_\star$, for $i = 1, \ldots, \ell_\star - 1$, and $C_{\ell_\star}^{j_\star+1} = C_\star$.

(b) Second stage:
Solving numerically equation (41) at time level $t_{j_\star+1}$ we compute a new candidate to a transition point $\bar{s}(t_{j_\star+1})$. Then we define the new transition point $x_{\ell_\star,new}$ by

$$x_{\ell_\star,new} = \min\{\bar{s}(t_{j_\star+1})\,, x_{\ell_\star}\}.$$

The numerical approximations computed in the first stage are then corrected using the procedure described in the second stage of the initialization with convenient adaptations.

In all numerical experiments that we present in this section we consider

$$\Delta t = 4 * 10^{-5}, h = 0.01, C_\star = 0.8, D_r = 1, D_g = 0.4, C_{ext} = 0,$$

and the plots are exhibited for different values of f_0^i.

In Figure 7 we plot the non-Fickian approximations computed with $f_0^i = 0.5, 0.55, 0.6$. As f_0^i increases the speed of the front also increases.

Approximations for the accumulated flux $F(t) = -\displaystyle\int_0^t J(0,\mu)\, d\mu, t > 0$, are plotted in Figures 8. An increase of f_0^i implies an increase of the accumulated flux.

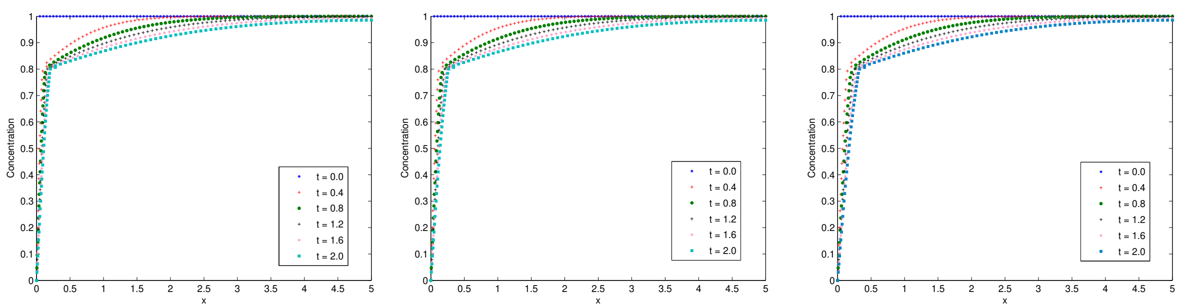

FIGURE 7. The non-Fickian approximations obtained with $f_0^i = 0.5$ (left), $f_0^i = 0.55$ (center) and $f_0^i = 0.6$ (right).

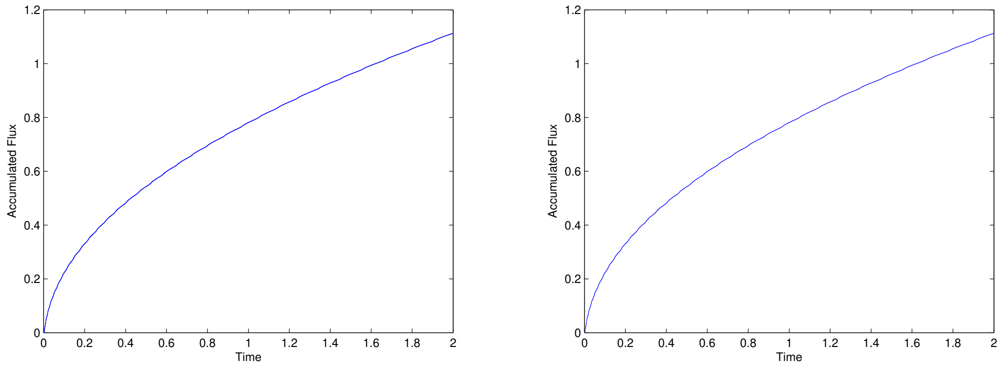

FIGURE 8. The accumulated fluxes obtained with $f_0^i = 0.5$ (left) and $f_0^i = 0.6$ (right).

In Figure 9 we plot the Fickian approximations, that is approximations computed using the method described before without the non-Fickian correction of the transition point. We observe that the transition point presents an higher speed.

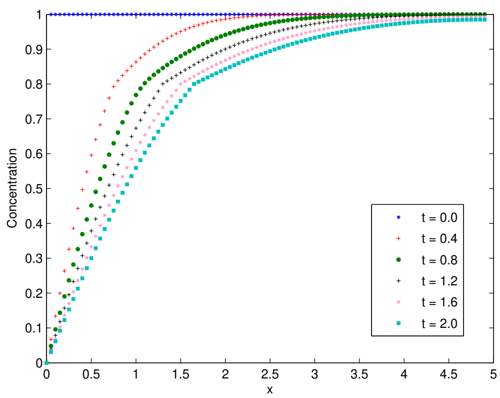

FIGURE 9. The Fickian approximations.

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