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-posedness of the general model is analyzed. Numerical simulations illustrating the dynamics of the desorption process described by the proposed model are included.

Keywords: Desorption phenomena, non-Fickian behavior, speed of the glass-rubber front, well-posedness of the model.

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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 interest lie on the very challenging mathematical models underlying the phenomena but mainly on the fact that due to its 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 (Samus and Rossi (1996)). We mention without being exhaustive the following properties: (i) for small times the mass uptake increases linearly in time with sharp fronts which move at constant velocity and separating the glassy and the rubbery states, (ii) the velocity of the front slows down at later times;(iii) initially uptake

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increases like t^{α} with α between 0.5 and 1 or increases as \sqrt{t} eventually presenting sharp fronts which move at velocity $s' \simeq 1/\sqrt{t}$. These behaviors can not be completely explained by Fick's law and are usually described as anomalous or non-Fickian. In recent years, several attempts have been made to model mathematically such sorption behaviors. Two main approaches can be found in the literature. In the first one a Fickian diffusion is considered in the glassy and rubbery regions and the kinetics of the glass-rubber polymer transition is taken properly into account. Due to this kinetics these models have a locally non Fickian character. We mention for instance the models presented in Astarita and Sarti (1978), Astarita and Joshi (1978), Friedman and Rossi (1997), Peterlin (1965), Qian and Taylor (2000), Rossi et al (1995), Thomas and Windle (1980), Thomas and Windle (1981), Thomas and Windle (1982). In the second approach globally non Fickian models are considered as Fick's law is modified by introducing in the flux a viscoelastic stress as for instance in Cohen and White (1989), Cohen and White (1991), Cox and Cohen (1989), Cox (1990), Edwards and Cohen (1995), Edwards (1995), Edwards (2001), Hayes and Cohen (1992).

It should be pointed out that desorption is not a simple reversal of the related sorption process. In fact while in desorption a crystallization occurs requiring some molecular organization, in sorption, which is characterized by melting, such organization doesn't occur. In the case that a polymer, in a saturated rubbery state, undergoes the process of desorption there is an overall outward penetrant flux. As expected this loss of penetrant triggers a change of state in the polymer which subsequently assumes a glassy crystalline configuration. 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 a Fick's behavior. Much less attention has been placed on the mathematical modeling of polymer desorption process. In the literature we find mainly mathematical models where a viscoelastic stress has been introduced in the flux (Cairneross et al (1992), Cairneross et al (1996), Cairneross and Durning (1996), Edwards (1997), Edwards (1999), Edwards and Cairneross (2002)). 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 Samus and Rossi (1996), Sanopoulou and Petropoulos (2001), Sanopoulou et al (2002). Such models exhibit a global non Fickian character. However experimentalists consider that in a system where a front separates two different states the only obvious violation of Fick's law takes place at the front (Qian and Taylor (2000), Rossi et al (1995), Samus and Rossi (1996)).

Following this idea we propose in the present paper a mathematical model for desorption that uses Fick's law in the rubbery and glassy regions 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 Qian and Taylor (2000) for sorption phenomena and depends on the glass-rubber transition concentrations and their fluxes. In Qian and Taylor (2000) for the case of sorption 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 Thomas and Windle (1980)-Thomas and Windle (1982). At the best of our knowledge there is no agreement among experimentalists concerning the form of an analytical expression for the speed of the front in the case of desorption. Due to this lack of information we introduce a parameter varying in an admissible interval and which selection leads to a wide range of behaviors. Consequently the model studied in this paper is an open model. Future improvements coming from experimental studies and leading to particular forms of the front speed can be easily introduced.

The paper is organized as follows. In Section 2 the model is presented. In Section 3 the glassy and rubbery concentrations are computed. The speed of the glassrubber front is studied in Section 4. In Section 5 the well-posedness of the model is analyzed. In Section 6 numerical simulations illustrating the behavior of our model are included. A 3D extension of the model is presented in Section 7. Finally in Section 8 some conclusions are established.

2 A phenomenological model

The phenomenological model presented in this paper is based on the observation of experimentalists that the only obvious violation of Fick's law takes place at the front separating the two different states. Following this idea we consider

$$\begin{cases} C_t^g = D_g C_{xx}^g, \, x < s(t) \\ C_t^r = D_r C_{xx}^r, \, x \ge s(t) \end{cases}, \tag{1}$$

where x = s(t) represents the position of the front and D_g and D_r represent the molecular diffusion coefficients respectively in the glassy and rubbery regions. In (1) C^g and C^r denote the concentrations respectively in the glassy and rubbery regions.

The front position s(t) is defined by

$$s'(t)[C]_{s(t)} = [J]_{s(t)},$$
(2)

where $[g]_{s(t)} = g(s(t)_+, t) - g(s(t)_-, t)$ represents the jump of g at s(t) and $J = -D(C)C_x$. It is this front condition, considered for instance in Qian and Taylor

(2000), that gives a phenomenological character to the model. Condition (2) appears as a consequence of the decreasing behavior of the overall penetrant mass in the polymer and has some analogy with conditions often prescribed in the literature, as for instance in Edwards (1997),Edwards (1999). We postpone to Section 4 a rigorous explanation of (2).

Problem (1), (2) consists of two Fickian models linked by a non Fickian moving front with speed (2). The model is complemented with a boundary condition at the front which is written as

$$C^{r}(s(t),t) = C_{\star}, t > 0,$$
(3)

where C_{\star} represents the characteristic solute concentration that distinguishes the glassy from the swollen state. In the swollen saturated region, the concentration C^r of the penetrant within the polymer is greater than C_{\star} , while in the glassy drier region, $C^g < C_{\star}$. 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 it will become clear in section 4 the value of this concentration stands for the free parameter of the model.

The phenomenological model (1)-(3) cannot be confused with the Fickian model

$$C_t = -(D(C)C_x)_x, x > 0, t > 0,$$
(4)

where

$$D(C) = \begin{cases} D_g, \ x < s(t)(glassy) \\ D_r, \ x \ge s(t)(rubbery). \end{cases}$$
(5)

In fact in the framework of the theory of weak solutions, as (2) holds and the solution *C* of (4) is in $H^1(0,\infty)$ for each time *t*, we conclude

$$[J]_{s(t)}=0.$$

Furthermore, it can be established that in the case of the Fickian model described the speed satisfies

$$s'(t)[C_x]_{s(t)} = [J_x]_{s(t)}.$$

In Section 7 numerical simulations that exhibit the difference between the behavior of models (1)-(3) and the Fickian model (4), (5) are presented.

To complete the model of desorption of an initially saturated polymer we consider an initial condition

$$C(x,0) = C_{init}, x > 0.$$
 (6)

The far end is insulated which translates to

$$C_x(\infty, t) = 0, t \ge 0. \tag{7}$$

At x = 0 we consider

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

where C_{ext} stands for the external concentration. This condition 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.

The desorption problem is viewed as two coupled boundary problems defined in time depending domains (0, s(t)) and $(s(t), +\infty)$. As we do not impose a value on the glassy concentration at the glassy side of the front, $C^g(s(t)_{-},t)$, a condition is missing to define completely the speed. We already mentioned that in desorption phenomena there is no agreement among experimentalists concerning the form of the front speed. We overcome this difficulty by using the free parameter, varying in a certain interval, and depending on the characteristics of the polymer, that can be used to control the front speed.

3 The glassy and rubbery concentrations

An integral method developed by Boley for standard diffusion problems, and adopted by Edwards in the analysis of polymer desorption models (see e.g. Edwards (1999)) is employed in this section to compute the concentrations C^r and C^g .

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 (7), (8) we establish a condition that f^i must satisfy. Let

$$C^{g}(x,t) = C_{ext} + T^{g}(x,t), \ 0 < x < s(t),$$
(9)

where T^g is defined by

$$T_t^g = D_g T_{xx}^g, x > 0, t > 0,$$

$$T^g(0,t) = 0, t > 0,$$

$$T_x^g(\infty,t) = 0, t > 0,$$

$$T_x^g(\infty,t) = f^i(x), x > 0.$$

(10)

As the solution of (10) is given by (Crank (1973))

$$T^{g}(x,t) = \frac{1}{\sqrt{4\pi D_{g}t}} \int_{0}^{\infty} f^{i}(y) \left(e^{-\frac{(x-y)^{2}}{4D_{g}t}} - e^{-\frac{(x+y)^{2}}{4D_{g}t}} \right) dy, \tag{11}$$

it follows that

$$C^{g}(x,t) = C_{ext} + \frac{1}{\sqrt{4\pi D_{g}t}} \int_{0}^{\infty} f^{i}(y) \left(e^{-\frac{(x-y)^{2}}{4D_{g}t}} - e^{-\frac{(x+y)^{2}}{4D_{g}t}} \right) dy, \ 0 < x < s(t).$$
(12)

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

Let

$$C^{r}(x,t) = C_{init} - T^{r}(x,t), x \ge s(t).$$
 (13)

where

$$\begin{cases}
T_{t}^{r} = D_{r}T_{xx}^{r}, x > 0, t > 0, \\
T^{r}(0,t) = f_{b}(t), t > 0, \\
T_{x}^{r}(\infty,t) = 0, t > 0, \\
T^{r}(x,0) = 0, x > 0.
\end{cases}$$
(14)

Once again in (14), f_b represents a fictitious boundary term which will be computed in due course. We have

$$T^{r}(x,t) = f_{b}(t) + \int_{0}^{t} \frac{1}{\sqrt{4\pi(t-\tau)}} \int_{0}^{\infty} -f_{b}'(\tau) \left(e^{-\frac{(x-y)^{2}}{4D_{r}(t-\tau)}} - e^{-\frac{(x+y)^{2}}{4D_{r}(t-\tau)}} \right) dy d\tau, \quad (15)$$

and as

$$\begin{split} \int_{0}^{t} \frac{1}{\sqrt{4\pi(t-\tau)}} \int_{0}^{\infty} -f_{b}'(\tau) \Big(e^{-\frac{(x-y)^{2}}{4D_{r}(t-\tau)}} - e^{-\frac{(x+y)^{2}}{4D_{r}(t-\tau)}} \Big) dy d\tau &= -f_{b}(t) \\ + \frac{x}{\sqrt{4\pi D_{r}}} \int_{0}^{t} f_{b}(\tau) e^{-\frac{x^{2}}{4D_{r}(t-\tau)}} \frac{1}{(t-\tau)^{3/2}} d\tau, \end{split}$$

we may conclude that

$$C^{r}(x,t) = C_{init} - \frac{x}{\sqrt{4\pi D_{r}}} \int_{0}^{t} f_{b}(\tau) e^{-\frac{x^{2}}{4D_{r}(t-\tau)}} \frac{1}{(t-\tau)^{3/2}} d\tau, x > s(t).$$
(16)

The forms obtained in (12) and (16) for the concentrations C^g and C^r depend respectively on the fictitious conditions f^i and f_b .

4 On the speed of the front

4.1 The fictitious initial and boundary conditions

To study the speed of the moving front we analyse separately the small and large times behavior of C^r and C^g . Following Edwards (1999) we make some ansatz on the fictitious initial and boundary terms f^i and f_b .

1. <u>Small time behavior</u>: For small times a sound ansatz is to consider that f^i , f_b and *s* are of form

$$f^{i}(x) \sim f_{0}^{i}, \ f_{b}(t) \sim f_{0}^{b}, \ s(t) \sim 2s_{0}t^{n},$$

or more precisely

$$f^{i}(x) = f_{0}^{i} + f_{1,0}^{i}(x), \ f_{b}(t) = f_{0}^{b} + f_{1,0}^{b}(t) = 0 \ s(t) = 2s_{0}t^{n} + s_{1,0}(t),$$
(17)

where

$$\lim_{x \to 0} f_{1,0}^i(x) = 0, \ \lim_{t \to 0} f_{1,0}^b(t) = 0, \ \lim_{t \to 0} s_{1,0}(t) = 0.$$

We compute in what follows *n*. As f_0^b is constant, it can be shown that the concentration in the rubbery state (16) is given by

$$C^{r}(x,t) = C_{init} - f_0^b \operatorname{erfc}\left(\frac{x}{\sqrt{4D_r t}}\right) + \tilde{C}_0^r(x,t), \qquad (18)$$

where $\tilde{C}_0^r(x,t) \to 0, x, t \to 0$.

At the front s(t), the rubbery concentration C^r satisfies (3) and consequently

$$C_{\star} = C_{init} - f_0^b \liminf_{t \to 0} \operatorname{erfc}\left(\frac{s_0 t^{n-1/2}}{\sqrt{D_r}}\right)$$
(19)

For
$$n < \frac{1}{2}$$
, from (19) we obtain $C_{\star} = C_{init}$

As in a desorption problem $C_{init} > C_{\star}$, we must therefore conclude that $n \ge \frac{1}{2}$. From (12) it can be shown that the concentration in the glassy state may be written as

$$C^{g}(x,t) = C_{ext} + f_{0}^{i} \operatorname{erf}\left(\frac{x}{\sqrt{4D_{g}t}}\right) + \tilde{C}_{0}^{g}(x,t), \qquad (20)$$

where $\lim_{x,t\to 0} \tilde{C}_0^g(x,t) = 0.$

At the front s(t) we obtain

$$\lim_{t \to 0} C^g(s(t)_{-}, t) = C_{ext} + \lim_{t \to 0} f_0^i \operatorname{erf}\left(\frac{s_0 t^{n-1/2}}{\sqrt{D_g t}}\right).$$

and consequently, for $n > \frac{1}{2}$,

$$\lim_{t \to 0} C^g(s(t)_{-}, t) = C_{ext}.$$
(21)

We assume that

$$\lim_{t \to 0} C^g(s(t)_{-}, t) > C_{ext}$$

$$\tag{22}$$

holds. In Section 4.2 we will show that the assumption (22) is a natural restriction at least for $n = \frac{1}{2}$.

Then we conclude that for small times we must have $n = \frac{1}{2}$.

2. <u>Large-time behavior</u>: An inspection of (12) and (16) shows that $f^i(x)$ and $\overline{f^b(t)}$ can't assume an exponential form or a polynomial form. Let us analyse the exponential case by making the following ansatz:

$$f^i(x) \sim f^i_{\infty} e^{Ax}, \ f_b(t) \sim f^b_{\infty} e^{B^2 t}, \ s(t) \sim 2s_{\infty} t^n,$$

more precisely

$$f^{i}(x) = f^{i}_{\infty}e^{Ax} + f^{i}_{1,\infty}(x), \ f_{b}(t) = f^{b}_{\infty}e^{B^{2}t} + f^{b}_{1,\infty}(t), \ s(t) = 2s_{\infty}t^{n} + s_{1,\infty}(t), \ (23)$$

where

$$\lim_{x \to \infty} f_{1,\infty}^i(x) = 0 \quad \lim_{t \to \infty} f_{1,\infty}^b(t) = 0, \quad \lim_{t \to \infty} s_{1,\infty}(t) = 0.$$

From (12) and (23), it may be deduced that

$$C^{g}(x,t) = C_{ext} + \frac{f_{\infty}^{i}}{2} e^{A^{2}D_{g}t}$$

$$\left(e^{Ax} \operatorname{erfc}\left(-\frac{x + 2AD_{g}t}{\sqrt{4D_{g}t}}\right) - e^{-Ax} \operatorname{erfc}\left(\frac{x - 2AD_{g}t}{\sqrt{4D_{g}t}}\right)\right)$$

$$+ \tilde{C}^{g}_{\infty}(x,t), \ x < s(t),$$
(24)

where $\tilde{C}^g_{\infty}(x,t) \to 0, x, t \to \infty$, and then A = 0 (see Appendix 1). As a consequence C^g is given by

$$C^{g}(x,t) = C_{ext} + f^{i}_{\infty} \operatorname{erf}\left(\frac{x}{\sqrt{4D_{g}t}}\right) + \tilde{C}^{g}_{\infty}(x,t).$$
(25)

Let us analyze now the concentration in the rubbery state. Considering $f_b(t)$ into (16), we get

$$C^{r}(x,t) = C_{init} - \frac{f_{\infty}^{b}}{2} e^{B^{2}t} \left(e^{B \frac{x}{\sqrt{D_{r}}}} \operatorname{erfc}\left(\frac{x + 2Bt\sqrt{D_{r}}}{\sqrt{4D_{r}t}}\right) + e^{-B \frac{x}{\sqrt{D_{r}}}} \operatorname{erfc}\left(\frac{x - 2Bt\sqrt{D_{r}}}{\sqrt{4D_{r}t}}\right) \right) + \tilde{C}_{\infty}^{r}(x,t), \ x \ge s(t),$$

$$(26)$$

where $\tilde{C}_{\infty}^{r}(x,t) \rightarrow 0, x, t \rightarrow \infty$.

Next, we discuss *B*. If B = 0 then, from (26) we obtain

$$C^{r}(x,t) = C_{init} - f_{\infty}^{b} \operatorname{erfc}\left(\frac{x}{\sqrt{4D_{r}t}}\right) + \tilde{C}_{\infty}^{r}(x,t).$$
(27)

We analyze the large-time concentrations C^g and C^r at the front s(t). Replacing into (27) s(t) defined by (23) we get

$$\lim_{t \to \infty} C^r(s(t), t) = C_{init} - f^b_{\infty} \lim_{t \to \infty} \operatorname{erfc}\left(\frac{s_{\infty}t^{n-1/2}}{\sqrt{D_r}}\right).$$
(28)

As $C^{r}(s(t),t) = C_{\star}$, from (28), for $n > \frac{1}{2}$, we conclude $C_{\star} = C_{init}$

which is not admissible for desorption problems.

From (28), for $n < \frac{1}{2}$, we obtain

$$C_{\star} = C_{init} - f_{\infty}^b.$$

However, from (25), for $n < \frac{1}{2}$, we deduce

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

As for small times we assume that for large times

$$\lim_{t \to \infty} C^g(s(t)_{-}, t) > C_{ext}$$
⁽²⁹⁾

holds and consequently we must have $n = \frac{1}{2}$.

It can be shown that if $B \neq 0$ then $C_{init} \leq C_{\star}$ (see Appendix 2) which is not admissible because in a desorption problem $C_{init} > C_{\star}$. This means that B = 0.

We must therefore conclude that the speed of the front behaves like $t^{-\frac{1}{2}}$ for small and large times. This result justifies from a theoretical point of view several experimental data reported in the literature where desorption phenomena present some similarities with a Fickian behavior (see for instance Samus and Rossi (1996)).

4.2 Dependence of the moving front on the problem data

In this section we study the dependence of the moving front on the parameters of the models for small and large times. As the expressions of the leading terms of C^g and C^r assume the same form for small and large times we represent by f^i indifferently f_0^i, f_∞^i and by f^b the values f_0^b, f_∞^b . We note however that f^i (and f^b) can assume different values for small and large times. By \bar{s} we represent s_0 and s_∞ . Furthermore we identify in what follows and in Sections 4.3 and 4.4, C^g, C^r and s(t) with the corresponding leading terms.

From (17) the expression for the front position s(t) is

$$s(t) = 2\bar{s}\sqrt{t},\tag{30}$$

and then from (19) we have

$$f^{b} = \frac{C_{init} - C_{\star}}{\operatorname{erfc}\left(\frac{\bar{s}}{\sqrt{D_{r}}}\right)}$$
(31)

which allow us to obtain

$$C^{r}(x,t) = C_{init} - \frac{C_{init} - C_{\star}}{\operatorname{erfc}\left(\frac{\bar{s}}{\sqrt{D_{r}}}\right)} \operatorname{erfc}\left(\frac{x}{\sqrt{4D_{r}t}}\right),$$
(32)

for $x \in (0, \infty)$. Moreover, as for C^g holds the representation

$$C^{g}(x,t) = C_{ext} + f^{i} \operatorname{erf}\left(\frac{x}{\sqrt{4D_{g}t}}\right),$$
(33)

in the front we get

$$\lim_{x \to s(t)_{-}} C^g(x,t) = C_{ext} + f^i \operatorname{erf}\left(\frac{\bar{s}}{\sqrt{D_g}}\right).$$
(34)

which means that $\lim_{x\to s(t)_{-}} C^g(x,t)$ is constant for small and large times. Let us represent this constant by $C^g_{\star,j}$. We note that $C^g_{\star,j}$ can assume different values for small and large times, that is $C^g_{\star,0} \neq C^g_{\star,\infty}$. From (34) we obtain

$$f^{i} = \frac{C^{g}_{\star,j} - C_{ext}}{\operatorname{erf}\left(\frac{\bar{s}}{\sqrt{D_{g}}}\right)}$$

which allow us to establish for C^g the representation

$$C^{g}(x,t) = C_{ext} + \frac{C^{g}_{\star,j} - C_{ext}}{\operatorname{erf}\left(\frac{\bar{s}}{\sqrt{D_{g}}}\right)} \operatorname{erf}\left(\frac{x}{\sqrt{4D_{g}t}}\right).$$
(35)

Replacing (32), (35) in (2) we obtain after some straightforward computations the following equation

$$\sqrt{D_r} (C_{\star} - C_{init}) e^{-\frac{\bar{s}^2}{D_r}} \operatorname{erf} \left(\frac{\bar{s}}{\sqrt{D_g}}\right) + \sqrt{D_g} (C_{\star,j}^g - C_{ext}) e^{-\frac{\bar{s}^2}{D_g}} \operatorname{erfc} \left(\frac{\bar{s}}{\sqrt{D_r}}\right) -\bar{s} \sqrt{\pi} (C_{\star} - C_{\star,j}^g) \operatorname{erf} \left(\frac{\bar{s}}{\sqrt{D_g}}\right) \operatorname{erfc} \left(\frac{\bar{s}}{\sqrt{D_r}}\right) = 0.$$
(36)

In this equation \bar{s} and $C_{\star,j}^g$ are unknowns. We look at $C_{\star,j}^g$ as a parameter and we solve (36) for each value of this parameter. Let us denote the first member of (36)

by $g(\bar{s})$. In what follows, we establish sufficient conditions on $C^g_{\star,j}$ that guarantee the existence of solutions \bar{s} of (36).

As we have

$$g(0) = \sqrt{D_g} \left(C_{\star,j}^g - C_{ext} \right)$$

we conclude that g(0) > 0 provided that $C_{\star,j}^g > C_{ext}$. Furthermore, the signal of $g(\bar{s})$ for $\bar{s} \to \infty$ is the signal of $C_{\star,j}^g - C_{\star}$ which is not positive provided that $C_{\star,j}^g < C_{\star}$. From the previous considerations we finally conclude that for

$$C^g_{\star,j} \in (C_{ext}, C_{\star}), \ j = 0, \infty, \tag{37}$$

which is a sound physical condition and has been assumed in (22), (29), equation (36) always has a solution. This means that $C_{\star,j}^g$ does not need to assume the same value for small and large times. For instance we can have initially a certain value $C_{ext} \leq C_{\star,0}^g < C_{\star}$ and for late times a parameter $C_{\star,\infty}^g$ can be selected such that $C_{\star,\infty}^g = C_{\star}$. This corresponds to having continuous concentration at large times. We point out that once another condition for the speed is prescribed then we do not need to specify C_{\star}^g .

4.3 Qualitative behavior

In this section we present some plots to illustrate the behavior of \bar{s} , C^g and C^r for small and large times.

For \bar{s} we consider

- 1. the dependence of \bar{s} on the problem data, that is C_{\star}, C_{ext}, D_r and D_g ;
- 2. the dependence of \bar{s} on C^g_{\star} for each set C_{\star}, C_{ext}, D_r and D_g .

In what follows by C^g_{\star} we denote $C^g_{\star,i}$.

Concerning the dependence of \bar{s} with C_{\star}, C_{ext}, D_r and D_g , for each C_{\star}^g , the numerical results confirm physical evidence. Let us argue on this point.

Figure 1-I 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} . From Figure 1-II we conclude that 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.



Figure 1: Dependence of \bar{s} on C_{\star}^{g} for different values of the parameters C_{\star} and C_{ext} .



Figure 2: Dependence of \bar{s} on C^g_{\star} for different values of the parameters D_r and D_g .

The behavior of \bar{s} when the rubbery coefficient D_r increases is illustrated in Figure 2-III. 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 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. This behaviour is illustrated in Figure 2-IV.

Finally, in order to study the stability behavior of \bar{s} when C_{init} is perturbed we consider $\tilde{C}(x,0) = C_{init} - \varepsilon$. Let \bar{s}_{ε} be the corresponding solution of (36). To establish heuristically the stability of s(t) we plotted the error $|\bar{s} - \bar{s}_{\varepsilon}|$ for several values of the parameters ε . The experiments carried on exhibit strong evidence of stability of the front. In Figure 3 we show a typical plot of $|\bar{s} - \bar{s}_{\varepsilon}|$. In Section 5 the assumption on the stability behavior of \bar{s} is used to establish the stability of model (1) -(7).



Figure 3: The error $|\bar{s} - \bar{s}_{\varepsilon}|$ for $\varepsilon \in [10^{-16}, 10^{-6}]$.

In Figure 4 we present the plots of C^r and C^g defined by (32), (35) where \bar{s} is computed using (36) for two different times $t_1 = 1$ and $t_2 = 5$. The concentrations C^r and C^g for small and large times are plotted in Figure 5.

The front positions for different values of C_{\star}^{g} and the correspondent fluxes are plotted in Figure 6 and Figure 7, respectively. We remark that when C_{\star}^{g} increases an increasing on the speed and an decreasing on the flux are observed.



Figure 4: The concentrations C^r and C^g at $t_1 = 1, t_2 = 5$ defined by (32) and (33) for $C^g_* = 0.79$ and $C_{init} = 1, C_* = 0.8, C_{ext} = 0, D_r = 1, D_g = 0.4$.



Figure 5: The concentrations C^r and C^g defined by (32) and (33) for $C^g_{\star} = 0.79$ and $C_{init} = 1, C_{\star} = 0.8, C_{ext} = 0, D_r = 1, D_g = 0.4$.



Figure 6: The front position $s(t) = 2\bar{s}\sqrt{t}$ for $C_{\star}^g = 0.75, 0.79$ and $C_{init} = 1, C_{\star} = 0.8, C_{ext} = 0, D_r = 1, D_g = 0.4$ where \bar{s} is computed with (36).



Figure 7: Jump of the flux at the front s(t) for $C_{\star}^{g} = 0.75, 0.79$ and $C_{init} = 1, C_{\star} = 0.8, C_{ext} = 0, D_{r} = 1, D_{g} = 0.4$ computed with C^{r} and C^{g} defined by (32) and (33).

4.4 Revisiting the moving front

In a certain number of experimental papers it is reported that the speed of the front in some desorption problems is constant at large times. As mentioned in Section 4.1, and proved in Appendix 2, when n = 1 is considered, that is when a constant speed is assumed, 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 an answer to this question by modifying the front condition (2).

In order to understand the physical meaning of the front condition (2) we introduce M(t), the total mass of the penetrant in the polymeric matrix at each time t, which is defined by

$$M(t) = \int_0^\infty C(x,t) \, dx. \tag{38}$$

Taking derivatives in (38) we have

$$M'(t) = \int_0^{s(t)} D_g C_{xx}^g(x,t) dx + \int_{s(t)}^{\infty} D_r C_{xx}^r(x,t) dx + s'(t) \left(C^g(s(t)_{-},t) - C^r(s(t)_{+},t) \right),$$
(39)

and then

$$M'(t) = D_g \left(C_x^g(s(t)_{-}, t) - C_x^g(0, t) \right) + D_r \left(C_x^r(\infty, t) - C_x^r(s(t)_{+}, t) + s'(t) \left(C^g(s(t)_{-}, t) - C^r(s(t)_{+}, t) \right),$$

that is

$$M'(t) = J(0) - J(\infty) - s'(t)[C]_{s(t)} + [J]_{s(t)}.$$
(40)

Considering in (40) condition (2) and using the fact that the polymer has the righthand side isolated we obtain M'(t) = J(0). Finally, as we are dealing with a desorption phenomenon we conclude that $M'(t) \le 0$.

Let us consider now that M'(t) satisfies (40). As the polymer is desorbing $M'(t) \le 0$ and consequently from $C_x^r(\infty, t) = 0$, we establish

$$D_{g}C_{x}^{g}(s(t)_{-},t) - D_{r}C_{x}^{r}(s(t)_{+},t) + s'(t)\left(C^{g}(s(t)_{-},t) - C^{r}(s(t)_{+},t)\right)$$

$$\leq D_{g}C_{x}^{g}(0,t).$$
(41)

This last inequality can be written as

$$[J]_{s(t)} \le s'(t)[C]_{s(t)} + D_g C_x^g(0,t).$$
(42)

When $t \to \infty$, we deduce from (25), that $C_x^g(0,t) \to 0$ and consequently (42) assumes the form

$$[J]_{s(t)} \le s'(t)[C]_{s(t)}.$$
(43)

We note that the results in the previous subsections of Section 4 have been obtained under the more restrictive condition (2).

Let us consider n = 1 in $s(t) = 2\bar{s}t^{1/n}$. Replacing $C_x^r(s(t)_+, t)$ and $C_x^g(s(t)_-, t)$ in the new front condition (43) we obtain the inequality

$$f_{\infty}^{i} \leq C_{init} - C_{ext}. \tag{44}$$

Finally replacing (44) in (20) we have

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

which is trivially verified. We can then conclude that relaxing the front condition (2) the model admits a linear speed of the front at large times.

5 On the stability of the model

In this section we investigate the overall stability of the model (1) -(2), (6)-(8) under a perturbation of the initial condition (6). In Section 4 we presented heuristic evidence of the stability of s(t). Following this heuristic we assume 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 (1) by C, in the sense of the L^2 inner product, we have

$$(C_t, C) = -(DC_x, C_x) + [CJ]_{s(t)} + C(0, t)J(0, t) - C(L, t)J(L, t).$$
(45)

It can be easily shown that

$$\frac{d}{dt} \|C\|_{L^2}^2 = 2 \int_0^L C_t C \, dx + s'(t) \left(C(s(t)_-, t)^2 - C(s(t)_+, t)^2 \right). \tag{46}$$

Substituting (46) and the zero boundary condition at x = 0 and $x = \infty$ into (45) we obtain

$$\frac{1}{2}\frac{d}{dt}\|C\|_{L^2}^2 = -(DC_x, C_x) + \frac{1}{2}s'(t)\left(C(s(t), t)_-^2 - C(s(t)_+, t)^2\right) + [CJ]_{s(t)}.$$
(47)

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

$$\frac{1}{2}s'(t)\left(C(s(t)_{-},t)^2 - C(s(t)_{+},t)^2\right) + [CJ]_{s(t)} \le 0.$$
(48)

Multiplying (2) 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, (48) follows if we prove that for $C_x > 0$ holds the inequality

$$-\frac{1}{2}[J]_{s(t)}\left(C(s(t)_{-},t)+C(s(t)_{+},t)\right)+[CJ]_{s(t)}\leq 0.$$
(49)

We may express (49) in the simpler form

$$(J(s(t)_{-},t)+J(s(t)_{+},t))(C(s(t)_{-},t)-C(s(t)_{+},t))\geq 0.$$

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

$$J(s(t)_{-},t) + J(s(t)_{+},t) \le 0,$$
(50)

and consequently (49) is proved.

Finally using (48) in (47) we obtain

$$\frac{1}{2}\frac{d}{dt}\|C\|_{L^2}^2 \le -(DC_x, C_x),\tag{51}$$

from which we deduce

$$\frac{1}{2}\frac{d}{dt}\|C\|_{L^2}^2 \le 0.$$
(52)

The previous arguments lead us to the following proposition:

Proposition 1 Let C be the solution of (1) -(2), (6)-(8) with initial conditions C_{init} and homogeneous boundary conditions. Assuming that s(t) is stable, then

$$\|C(.,t)\|_{L^2} \le \|C_{init}\|_{L^2}, t \ge 0.$$
(53)

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As a consequence of Proposition 1 we can state that the initial boundary value problem (1), (2), (3), (6), (7) and (8) 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 (1)-(3) with initial conditions v_0 and \tilde{v}_0 , where $v_0 > \tilde{v}_0$. It follows that

 $\|v(.,t)\|_{L^2} \le \|v_0 - \tilde{v}_0\|_{L^2}, \ t \ge 0.$ (54)

6 Numerical illustrations

In the previous sections the theoretical analysis carried on leads to the conclusion that if the front position is defined by $s(t) = 2\bar{s}\sqrt{t}$ then $C^g(s(t)_-, t)$ is constant for small and large times. In what follows we illustrate the behavior of the solution of (1) -(2), (6)-(8) in two cases:

- 1. $C^{g}(s(t)_{-},t)$ is constant for all times,
- 2. $C^{g}(s(t)_{-},t)$ is function of the time with a prescribed behavior.

In this last case we assume that for small times $C^g(s(t)_-,t) = C^g_{\star,0}$ with $C^g_{\star,0} \in (C_{ext}, C_{\star})$ and $C^g(s(t), t) \to C_{\star}$ when $t \to \infty$.

The numerical results were obtained considering a standard finite standard finite difference discretization (55) of the initial boundary value problem (1) -(2), (6)-(8). Let $\{x_j = x_{j-1} + h, j = 1, ..., N\}$, 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 $\{t_n = t_{n-1} + \Delta t, n = 1, ..., M\}$ with $t_0 = 0$ and $t_M = T$. By D_2 we denote the second order centered finite difference operator and by D_- we represent the usual backward finite difference operator. Let $C_{j,n}^g$ and $C_{j,n}^r$ be the numerical approximation for $C^g(x_j, t_n)$ and $C^r(x_j, t_n)$, respectively, defined by the finite difference scheme

$$\begin{cases}
C_{j,n+1}^{g} = C_{j,n}^{g} + \Delta t D_{g} D_{2} C_{j,n+1}^{g}, \, j = 1, \dots, i_{\star}^{n+1} - 1, \\
C_{j,n+1}^{r} = C_{j,n}^{r} + \Delta t D_{r} D_{2} C_{j,n+1}^{r}, \, j = i_{\star}^{n+1} + 1, \dots, N, \\
\frac{s_{n+1} - s_{n}}{\Delta t} \left(C_{\star} - C_{i_{\star}^{n} - , n}^{g} \right) = -D_{r} D_{-} C_{i_{\star}^{n} + 1, n}^{r} + D_{g} D_{-} C_{i_{\star}^{n} - , n}^{g}
\end{cases}$$
(55)

If

$$|s_{n+1} - x_{i_{\star}^{n}}| > \frac{h}{2} \tag{56}$$

then in (55) $x_{i_{\star}^{n+1}} = x_{i_{\star}^{n+1}}$. Else $x_{i_{\star}^{n+1}} = x_{i_{\star}^{n}}$.

As initially the polymeric matrix is in the rubbery state we consider

$$i^{0}_{\star} = 0, C^{r}_{j,0} = C_{init}, j = 1, \dots, N-1, C^{r}_{0,n} = C_{ext}, C^{r}_{N-1,n} = C^{r}_{N+1,n}, n = 0, \dots, M.$$

While the polymeric matrix is in the rubbery state $C_{j,n+1}^r$ is defined by the second equation of (55). Let n_{\star} be the first time level such that $C_{2,n_{\star}}^r < C_{\star}$. Then we use (55) with

$$C_{0,n}^{g} = C_{ext}, C_{i_{\star}^{n},n}^{g} = C_{i_{\star}^{n}-,n}^{g}, C_{i_{\star}^{n},n}^{r} = C_{\star}, n \ge n_{\star}.$$

In Figure 8 we plot the numerical solution when $C^{g}(s(t)_{-},t)$ is constant for all times. In Figure 9 we plot the numerical solution with $C^{g}(s(t)_{-},t)$ defined by

$$C^{g}(s(t)_{-},t) = \begin{cases} (1-t_{0}e^{-t_{0}})C_{\star}, t \in (0,t_{0}] \\ (1-t_{0}e^{-t})C_{\star}, t \in (t_{0},+\infty). \end{cases}$$
(57)

We observe that when $C^{g}(s(t), t) = C_{\star}$ for all *t* then a Fickian model is obtained.

7 A 3D application

Let us consider now a desorption phenomenon in the 3D polymeric matrix S represented in Figure 10.

We suppose that the matrix is isolated in the top and it is soaked with a diffusing substance at initial time. We assume that the substance reaching the bottom side is immediately removed. The polymer is initially in the rubbery state and, as the diffusion substance is lost by the bottom side, a glassy front arises which propagates to the entirely polymeric matrix. As before, let C_* represents $C^r(s(t),t)$ Then the evolution in *S* of the diffusing substance can be described by the partial differential equation

$$\begin{cases} C_t^g = D_g \Delta C^g, C^g < C_* \\ C_t^r = D_r \Delta C^r, C^r \ge C_* \end{cases}, \tag{58}$$

where Δ denotes the Laplace operator

$$\Delta C(x_1, x_2, x_3, t) = \sum_{i=1}^{3} C_{x_i x_i}(x_1, x_2, x_3, t).$$



Figure 8: Numerical concentrations C^r and C^g computed with (55) for $C^g(s(t)_{-}, t) = 0.78$ and $C_{init} = 1, C_{\star} = 0.8, C_{ext} = 0, D_r = 1, D_g = 0.4$.



Figure 9: Numerical concentrations C^r and C^g computed with (55) for $C^g(s(t)_-, t)$ defined by (57) and $C_{init} = 1, C_{\star} = 0.8, C_{ext} = 0, D_r = 1, D_g = 0.4$.



Figure 10: The polymeric matrix S.

Let π represents an arbitrary horizontal section parallel to the x_1Ox_2 plan. We assume that *S* is homogeneous in the sense that the concentration at any point *P* = (x_1, x_2, x_3) of this section depends only on x_3 .

In Figure 11 we illustrate the behavior of the desorption phenomenon in the 3D polymeric matrix when $C_{\star} = 0.8$, $D_r = 1$, $D_g = 0.4$, $C_{\star}^g = 0.78$. In Figure 12 we compare non Fickian behavior with the Fickian one. As can be observed, in the Fickian case the drug release is faster.

8 Conclusions

The main contribution of this paper is the explanation provided for the slowing of the front speed and the qualitative behavior of penetrant loss in polymeric matrices. At the best of our knowledge these two characteristics of polymer desorption have been explained in the mathematical literature by the introduction of the viscoelastic effect. The phenomenological model presented here avoids the global viscoelastic effect and is based on the observation by experimentalists that the only obvious violation of Fick's law arises in the front.

We show that the slowing of the front and the behavior of penetrant loss can be achieved with a local non Fickian model obtained with a natural condition. This



Figure 11: Evolution in time of the diffusing substance in the polymer vehicle S computed with (55).



Figure 12: Fickian and non Fickian evolution in time of the diffusing substance in *S* computed with (55).

front condition is based on the physics of desorption and is related to the decreasing behavior of the overall mass of the penetrant within the polymeric matrix. The analytical results established and the numerical results presented agree with the experimentalists observations.

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Appendices

Appendix 1

We compute *A* by taking limits in (24) as $t \to \infty$. As

$$\lim_{t \to \infty} e^{\frac{\gamma x + \gamma^2 t}{\alpha^2}} \operatorname{erfc}\left(\frac{x + 2\gamma t}{2\alpha\sqrt{t}}\right) = \lim_{t \to \infty} \frac{2\alpha\sqrt{t}}{\sqrt{\pi}(x + 2\gamma t)} e^{-\frac{x^2}{4\alpha^2 t}},\tag{59}$$

and C^g can be written as

$$C^{g}(x,t) = C_{ext} + \frac{f_{\infty}^{i}}{2} \left(2e^{A^{2}D_{g}t} \left(e^{Ax} - e^{-Ax} \right) + e^{-Ax + A^{2}D_{g}t} \operatorname{erfc} \left(\frac{-x + 2AD_{g}t}{\sqrt{4D_{g}t}} \right) - e^{Ax + A^{2}D_{g}t} \operatorname{erfc} \left(\frac{x + 2AD_{g}t}{\sqrt{4D_{g}t}} \right) \right), \ x < s(t),$$
(60)

we obtain, after some simplifications,

$$\lim_{t \to \infty} C^{g}(x,t) = \lim_{t \to \infty} \left(C_{ext} + f_{\infty}^{i} \left(e^{A^{2}D_{g}t} \left(e^{Ax} - e^{-Ax} \right) + e^{-\frac{x^{2}}{4D_{g}t}} \left(\frac{\sqrt{D_{g}t}}{\sqrt{\pi}(-x + 2AD_{g}t)} - \frac{\sqrt{D_{g}t}}{\sqrt{\pi}(x + 2AD_{g}t)} \right) \right) \right).$$
(61)

The limit in (61) is finite provided that A = 0.

Appendix 2

Let us suppose that in (26) $B \neq 0$. Substituting (59) into the large-time limit of (26), we obtain

$$\lim_{t \to \infty} C^{r}(x,t) = C_{init} - \frac{f_{\infty}^{b}}{2} \lim_{t \to \infty} e^{-\frac{x^{2}}{4D_{r}t}} \frac{2\sqrt{D_{r}t}}{\sqrt{\pi}(x+2B\sqrt{D_{r}t})}$$

$$-\frac{f_{\infty}^{b}}{2} \lim_{t \to +\infty} e^{B^{2}t - \frac{Bx}{\sqrt{D_{r}}}} \operatorname{erfc}\left(\frac{x}{2\sqrt{D_{r}t}} - B\sqrt{t}\right), \ x \ge s(t).$$
(62)

The first limit in the right side of (62) is zero. To guarantee the boundness of $\lim_{t \to 0} C^r(x,t)$ for $x \ge s(t)$ we must have

$$Bt - \frac{x}{\sqrt{D_r}} \le 0, x \ge s(t), \tag{63}$$

which holds if

$$s(t) = \sqrt{D_r}Bt. \tag{64}$$

As $C^r(s(t), t) = C_{\star}$ from (62) we have

$$C_{\star} = C_{init} - f_{\infty}^b.$$

Computing now $C_x^r(s(t)_+,t)$ and $C_x^g(s(t)_-,t)$ and replacing in (2) we obtain in the large time limit

$$-D_r(C_{init}-C_{\star})\frac{B}{\sqrt{D_r}}=\sqrt{D_r}B(C_{\star}-C_{ext}-f_{\infty}^i),$$

that is

$$f_{\infty}^{i} = C_{init} - C_{ext}.$$
(65)

With this value of f_{∞}^{i} we have from (25)

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

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

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

we conclude that $C_{init} \leq C_{\star}$ which is not admissible because in a desorption problem $C_{init} > C_{\star}$. This means that (64) does not hold and then B = 0.

Appendix 3	
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Symbol	Definition
D_r	Diffusion coefficient in the rubbery state
D_g	Diffusion coefficient in the glassy state
$C^{\ddot{g}}$	Concentration in the glassy region
C^r	Concentration in the rubbery region
s(t)	Position of the front at time <i>t</i>
s'(t)	Time derivative of $s(t)$
C_t^g	First order partial derivative of C^g with respect to time variable t of C^g
C^g_{xx}	Second order partial derivative with respect to the spatial variable x of C^g
C_{xx}^r	Second order partial derivative with respect to the spatial variable x of C^r
$[C]_{s(t)}$	Jump of the concentration at $s(t)$
J(x,t)	Flux at (x,t)
$[J]_{s(t)}$	Jump of the flux at the front $s(t)$
C_{\star}	Characteristic solute concentration
Cinit	Initial concentration in the polymeric matrix
C_{ext}	External concentration
f^i	Fictitious initial glassy concentration
f_b	Fictitious left boundary rubbery concentration
erf(v)	$\frac{2}{2}\int_{-\infty}^{y}e^{-s^2}ds$
	$\sqrt{\pi} \int_0^\infty dx$
$\operatorname{erfc}(y)$	$1 - \operatorname{erf}(y)$
f_0^i	f^i for small times
f^l_{∞}	f^{i} for large times
f_0^{ν}	f_b for small times
f^{p}_{∞}	f_b for large times
$C^g(s(t),t)$	$\lim_{x \to s(t)^{-}} C^{g}(x,t)$
$C^g_{\star 0}$	$C^{g}(s(t)_{-},t)$ for small times
$C^{\widehat{g},\circ}_{\star,\infty}$	$C^{g}(s(t)_{-},t)$ for large times
M(t)	Total mass of the penetrant in the polymeric matrix
C_{in}^{g}	Numerical approximation for $C^{g}(x_{i},t_{n})$
$C_{j,n}^{r}$	Numerical approximation for $C^r(x_i, t_n)$
D_2	Second order centered finite difference operator
D_{-}	Backward finite difference operator
<i>s</i> _n	Numerical approximation for $s(t_n)$

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