A Mathematical Model For Spaghetti Cooking with Free Boundaries

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Abstract

We propose a mathematical model for the process of dry pasta cooking with specific reference to spaghetti. Pasta cooking is a two-stage process: water penetration followed by starch gelatinization. Differently from the approach adopted so far in the technical literature, our model includes free boundaries: the water penetration front and the gelatinization onset front representing a fast stage of the corresponding process. Behind the respective fronts water sorption and gelatinization proceed according to some kinetics. The outer boundary is also moving and unknown as a consequence of swelling. Existence and uniqueness are proved and numerical simulations are presented.

1 Introduction.

The aim of cooking starch rich products (pasta, cereals, potatoes, etc.) is to convert starch to a digestible form through the so-called gelatinization process. Starch is a polymer $(C_6H_{10}O_5)_n$ whose chains come in two forms: amylose and amylopectin. Gelatinization involves the breakage of intermolecular bonds and the aggregation of water molecules. Such a process requires a sufficiently high temperature and also a sufficiently large moisture content. It is believed that the threshold temperature for gelatinization is a linear function of the moisture content (see e.g. [4]). Of course this can be true only within some moisture range, because the process does not take place at all if not enough water is available. Therefore dry pasta has to be penetrated by water before gelatinization starts. Water penetration occurs even at room temperature (although very slowly and with no gelatinization) and is greatly facilitated in boiling water. Cereals are even more compact and need longer soaking times ([7], [4]). In the technical literature water soaking has been described on the basis of a supposed similarity with the process of the penetration of solvents into glassy polymers. Accordingly, the governing equation for the water motion has been assumed to be a nonlinear diffusion equation with a diffusivity depending exponentially on the moisture concentration [6]. An alternative approach, still based on diffusion, has been proposed in [1], where water diffusivity D is taken piecewise constant, with two different values: D_0 in the non-gelatinized region, and γD_0, $\gamma > 1$, in the gelatinized region. Our model for dry pasta cooking adopts a Darcyan mechanism for water transport and is based on the following observations:

1. Room temperature soaking leads to moderate volume increase.

2. In the normal cooking process the following stages can be observed:

   i) A few seconds after immersion in boiling water spaghetti acquire enough flexibility to be slightly bent, so to be fully immersed in the water. No visible volume change takes place in this early stage. Since dry spaghetti are rather brittle, it means either that some penetration has occurred, in the sense that capillarity has driven water to saturate the material without modifying its very low original porosity or the sudden raise of temperature has modified the mechanical properties.

   ii) During the following few minutes flexibility increases at a slow rate. Spaghetti are still breakable beyond some curvature. More precisely, a relatively stiff unpenetrated core can be seen, which is responsible for breaking. The core radius reduces progressively, until very good flexibility is reached more or less after half of the suggested cooking time. This means that massive soaking has progressed significantly.

   iii) During the cooking process cross sections exhibit the following structure: a whitish core, surrounded by a region of neutral colour, and an external annulus which looks softer and slightly yellow. The three regions are separated by visible interfaces. They can be identified with the not yet soaked region (the core), the intermediate region, with a moisture content below the gelatinization threshold (at the temperature of the boiling water, since the process is basically isothermal), and an external region in which gelatinization is taking place. Such a structure is still visible at the end of the cooking time, meaning that spaghetti "al dente" are still far from full gelatinization.

3. Boiling potatoes is a different process, because the water utilized in the gelatinization is the one already present in the raw tuber. Therefore no soaking is needed and gelatinization is triggered by the propagation of an isotherm (e.g. 75°C).

4. Cooking fresh pasta is a different and much quicker process, which is achieved in just a couple of minutes. For instance, the cooking time corresponds approximately (not differently from potatoes) to the propagation time of the 75°C isotherm, meaning that the original water content is large enough for gelatinization to take place.

We may conclude that
A) in spaghetti cooking there is a significant delay between the onset of soaking and the onset of gelatinization,
B) a model including free boundaries is legitimate.

For this reason we will describe water penetration introducing a soaking front, triggering some imbibitions kinetics. Air contained in dry pasta (less then 1% in volume) is not considered to affect any stage of the process. As we said, while the study of the thermal field is essential in the cooking of larger bodies, as potatoes or gnocchi, temperature can be considered uniform in spaghetti and equal to the boiling temperature, since the propagation time of the 75°C isotherm for spaghetti of $1 \div 2$ mm diameter and heat conductivity of $1.5\,10^{-3}\text{cm}^2/\text{sec}$ is of the order of a few seconds.

Isotherm (°C)	Lasagna	Spaghetti	Gnocchi	Potatoes
60	4.2 sec	2.2 sec	151 sec	604 sec
70	5.7 sec	2.9 sec	197 sec	790 sec
80	7.6 sec	3.7 sec	232 sec	930 sec
90	11 sec	5.0 sec	337 sec	1349 sec

Table 1: Isotherm penetration time for different geometries: plane (lasagna, half thickness 1 mm), cylindrical (spaghetti, radius 1 mm), spherical (gnocchi, radius 1 cm) and small potatoes (radius 2 cm).

Experimental evidence of a progressive gelatinization interface has been reported in [5]. More references on penetration and gelatinization are [9], [3]. In the next section we describe a mathematical model for soaking and gelatinization, characterized by the presence of two interfaces: the water penetration front (carrying a discontinuity of the water content) and the surface at which moisture reaches the threshold for gelatinization to occur. Since in our setting both imbibitions and gelatinization are seen as processes evolving along the trajectories of the solid starch particles, the introduction of a Lagrangian coordinate is very convenient. This is the aim of Section 3. In Section 4 we will determine the behaviour of the soaking front at the beginning of the process. The soaking process before the onset of gelatinization is studied in Section 5, where existence and uniqueness of the solution is proved. The continuation of the solution in the presence of gelatinization is studied in Section 6. A numerical scheme for the computation of the penetration front is illustrated in Sect. 7. In Section 8 some numerical simulations are presented and compared with the experimental data of [1] for spaghetti and for flat forms. The very good agreement with experimental data confirms that the validity of our approach, which exhibits several differences with respect to the previous literature, trying to be closer to the physics of the phenomenon. The aim of the Appendix is to summarize the process in plane geometry, for which it is possible to perform an analysis of the soaking kinetics, leading to the choice of some basic parameters that has been adopted also in the case of spaghetti. The plane case has an interest in itself, since it refers not only to pasta in the form of sheets (lasagna), but also to other shapes (e.g. hollow cylinders) in which the thickness of the sample is much smaller than its radius of curvature.

2 The mathematical model.

According to the discussion in the previous section, we start at time $t = 0$ with a fully saturated domain $0 < r < R$ with porosity $\phi_0 << 1$; this pristine porosity is introduced for the sake of generality, in view of what said under 2(ii), but it could be safely neglected, for practical purposes in the case of dry pasta. The onset of the soaking process is immediate, while gelatinization will start only after the porosity has reached some critical value ϕ_M. Correspondingly, we have a soaking region S and a gelatinization region G. We consider just a cross section far enough from the ends, exploiting the fact that the ratio radius/length is very small for spaghetti.

2.1 The soaking process.

If we denote by ϕ the liquid volume fraction and by ϕ_S the solid volume fraction, we have that in the region S in which $\phi \in (\phi_0, \phi_M)$

$$\phi + \phi_S = 1. \tag{1}$$

We describe soaking to be very fast during a first stage, accordingly described as a penetration front accompanied by a jump of ϕ, then followed by a slower process.

Before the onset of gelatinization, the region S is bounded between two unknown radii: the penetration front $r = s(t)$, and the outer boundary, $x = \sigma(t)$. The latter will be replaced by the S/G interface $r = h(t)$, from the moment it appears (see Fig. 1).

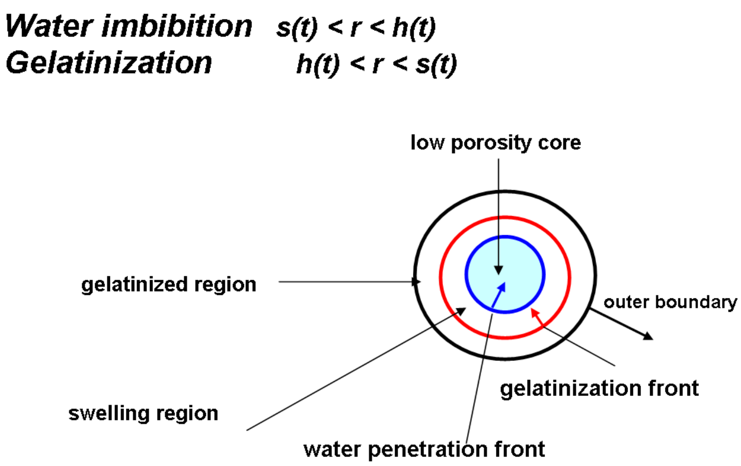

Figure 1: Sketch of the geometry of the problem

Instead of using the nonlinear diffusion equation which in the literature has been mutuated from the penetration of solvents into glassy polymers, here we describe the residual soaking as a relaxation process, following the kinetics

$$\dot{\phi} = F(\phi), \tag{2}$$

where $\dot{\phi}$ is the Lagrangian derivative along the motion of the solid particles (the region S moves due to the swelling) and F is positive continuous in $[0,1]$ and smooth for $\phi < \phi_M$, such that $F'(\phi) < 0$ for $\phi \in [0, \phi_M]$. Of course F depends on the temperature but this is not important here. The selection of the function F is very delicate. We will discuss some aspects related to it in the Appendix with reference to the problem in a plane geometry.

Denoting by $u(r,t)$ the velocity of the solid particles and by $v(r,t)$ the velocity of the water, we write the mass balance equation for the two species in the region S:

$$\frac{\partial \phi_S}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r}(ru\phi_S) = 0, \tag{3}$$

$$\frac{\partial \phi}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r}(rv\phi) = 0. \tag{4}$$

Remembering (1) we deduce the global incompressibility condition

$$\frac{\partial}{\partial r}[r(u\phi_S + v\phi)] = 0. \tag{5}$$

Now we rewrite (2) in the form

$$\frac{\partial \phi}{\partial t} + u\frac{\partial}{\partial r}(\phi) = F(\phi), \tag{6}$$

which, together with (1), (3) yields

$$\phi_S \frac{1}{r}\frac{\partial}{\partial r}(ru) = F(\phi). \tag{7}$$

Similarly we deduce

$$\phi \frac{1}{r}\frac{\partial}{\partial r}(rv) = -F(\phi). \tag{8}$$

Finally, Darcy's law provides the equation for the motion of the water relative to the solid:

$$\phi(v-u) = -\kappa(\phi)\frac{\partial p}{\partial r}, \tag{9}$$

where $\kappa(\phi)$ is he hydraulic conductivity (also depending on the temperature), and p is pressure. We set the atmospheric pressure equal to zero, and we impose the conditions

$$p(\sigma(t), t) = 0, \tag{10}$$

$$p(s(t), t) = -p_0, \tag{11}$$

where p_0 is the (temperature dependent) capillary pressure.

At the penetration front we suppose that ϕ jumps from ϕ_0 to a larger value ϕ_W:

$$\phi(s(t)^+, t) = \phi_W. \tag{12}$$

Consistently with the experimental observation that gelatinization seems to be substantially delayed with respect to soaking, we must assume that ϕ_W is still well below the threshold ϕ_M making the onset of gelatinization.

The Rankine-Hugoniot condition associated to (3) reads

$$[\phi_S]\dot{s} = [u\phi_S] \Rightarrow (\phi_W - \phi_0)\dot{s}(t) = -(1-\phi_W)u(s(t)^+, t), \tag{13}$$

relating the swelling velocity at the front with the front speed:

$$u(s(t), t) = -\frac{\phi_W - \phi_0}{1-\phi_W}\dot{s}(t). \tag{14}$$

The analogous balance for the liquid gives

$$[\phi]\dot{s} = [v\phi] \Rightarrow (\phi_W - \phi_0)\dot{s}(t) = \phi_W v(s(t)^+, t), \tag{15}$$

or

$$v(s(t),t) = \frac{\phi_W - \phi_0}{\phi_W} \dot{s}(t) \tag{16}$$

(of course, if the pristine porosity ϕ_0 is neglected, then the front is a material surface, i.e. it moves with the same speed as the water molecules).

We can now observe that the compound velocity $\phi_S u + \phi v$ evaluated at the penetration front is zero. Thus (5) implies that it has to vanish everywhere:

$$(1-\phi)u + \phi v = 0. \tag{17}$$

The initial conditions for the fronts $x = \sigma(t)$, $x = s(t)$ are obviously

$$\sigma(0) = s(0) = R. \tag{18}$$

Another obvious feature of the soaking model is that $\dot{s} < 0$ (the converse would require water desorption).

As we shall see in the next section (remark 2), the global mass balance of the solid implies that the external surface moves with the speed u of the solid particles.

2.2 Gelatinization

It is convenient to model gelatinization as a two-step process, like we have done for soaking. A first stage fast enough to be considered concentrated at the boundary $r = h(t)$, followed by a second stage evolving according to some kinetics.

We neglect the possible volume change accompanying the water molecules rearrangement, since the absence of swelling in boiled potatoes suggests that gelatinization does not produce any appreciable density change. Since water is partly immobilized in the gelatinization process, we have to split the water volume fraction into the sum $\phi + \eta$ of the free and bound components, respectively.

We must impose that

$$\phi + \eta + \phi_S = 1. \tag{19}$$

We can write down the balance equation for free and bound water respectively

$$\frac{\partial \phi}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r}(r\phi v) = -\delta \phi_S, \tag{20}$$

$$\frac{\partial \eta}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r}(r\eta u) = \delta \phi_S, \tag{21}$$

where δ represents the transfer rate $\phi \to \eta$ per unit volume of the solid. We may assume that the process is governed by a known kinetics:

$$\delta = G(\eta) \tag{22}$$

with $G(\eta)$ defined for $\eta \in [\eta_0, \eta_M]$, positive and smooth for $\eta < \eta_M$, and decreasing to zero as $\eta \to \eta_M$. In our setting η_0 is the jump experienced by η at the interface $r = h(t)$. Of course the model is flexible enough to exclude either the first stage ($\eta_0 = 0$) or the second stage ($\eta = \eta_M$). The ratio η/η_M can be considered as an index of gelatinization.

The interface $r = h(t)$ is identified with the level set $\phi = \phi_M$. We remark that the continuity of ϕ_S across $r = h(t)$ implies the continuity of u:

$$[\phi_S] = [u] = 0. \tag{23}$$

From (19) we have

$$[\phi] = -[\eta] = -\eta_0, \tag{24}$$

so the Rankine-Hugoniot condition for (20), gives[1]

$$-\eta_0 \dot{h} = (\phi_M - \eta_0)v^+ - \phi_M v^-. \tag{25}$$

The r.h.s. of (25) is the difference between the free water fluxes on the right and on the left of the front, while the l.h.s. is the free water loss rate accompanying the front displacement.

Having neglected any further swelling, we write $\dot{\phi}_S = 0$ in the gelatinization region, implying

$$\phi_S = 1 - \phi_M, \quad h(t) \le r \le \sigma(t) \tag{26}$$

and $\nabla \cdot u = 0$, i.e.

$$ru(r,t) = h(t)u(h(t),t), \quad h(t) \le r \le \sigma(t). \tag{27}$$

Clearly (26) is equivalent to $\phi + \eta = \phi_M$ and therefore the field $\phi v + \eta u$ is divergence free:

$$\begin{aligned} r(\phi v + \eta u) &= h(t)\{(\phi_M - \eta_0)v^+ + \eta_0 u^+\} \\ &= h(t)\{\phi_M v^- - \eta_0(\dot{h} - u^+)\}, \quad h < r < \sigma, \end{aligned} \tag{28}$$

where we have used (25). Of course $(\phi_M - \eta_0)v^+ + \eta_0 u^+$ is the total water flux.

Darcy's law has still the form (9) and continuity of pressure is imposed across $r = h(t)$.

Combining Darcy's law with (28) (or (25)), we see that across $r = h(t)$

[1] From now on we use the obvious notation $v^\pm = v(s(t)^\pm, t)$, $u^\pm = u(s(t)^\pm, t)$

$$\left[-\kappa \frac{\partial p}{\partial r} \right] = \eta_0 (u^+ - \dot{h}). \tag{29}$$

Using the fact that $\phi v + (\eta + \phi_S)u$ is divergence free, we easily get, in addition to (28):

$$r(\phi v + (\eta + \phi_S)u) = -h\eta_0 \{\dot{h} - u^+\}, \tag{30}$$

owing to the fact that $\phi_M v^- + (1 - \phi_M)u$ vanishes.

Remark 1. *The problem with $\eta_0 = 0$ is greatly simplified , since not only ϕ_S and u are continous across $r = h(t)$, but also ϕ and v (and consequently also the pressure gradient). In particular (30) provides*

$$\phi v + (\eta + \phi_S - 1)u = 0 \Rightarrow \phi(v - u) + u = 0.$$

3 Describing the motion of solid particles: a Lagrangian coordinate

Let us denote by ξ the radial coordinate of the solid particles at time $t = 0$, i.e. prior to water penetration with swelling (soaking). This quantity plays the role of a Lagrangian coordinate during the entire motion. The mass conservation of the solid implies that for any (r, t) in the region S

$$\int_{s(t)}^{r} r' \phi_S(r', t) dr' = \frac{1}{2}(1 - \phi_0)(\xi^2 - s^2(t)), \quad s(t) < r < h(t). \tag{31}$$

Remark 2. *Setting $r = \sigma(t)$ and $\xi = R$, (31) is shown to be equivalent to $u|_{r=\sigma} = \dot{\sigma}$.*

We can differentiate w.r.t. r and t, obtaining:

$$(1 - \phi_0)\xi \frac{\partial \xi}{\partial r} = r\phi_S, \tag{32}$$

$$(1 - \phi_0)\xi \frac{\partial \xi}{\partial t} = -r\phi_S u, \tag{33}$$

compatible with $\dot{\xi} = 0$.

To the Lagrangian coordinate ξ we may also associate the time variable τ (Fig. 2), corresponding to the time instant at wich the soaking front reaches the location ξ:

$$s(\tau) = \xi. \tag{34}$$

We may transform the unknowns $\phi(r, t)$, $\phi_S(r, t)$ to $\Phi(\xi, t)$, $\Phi_S(\xi, t)$, and this facilitates the integration of equation (2).

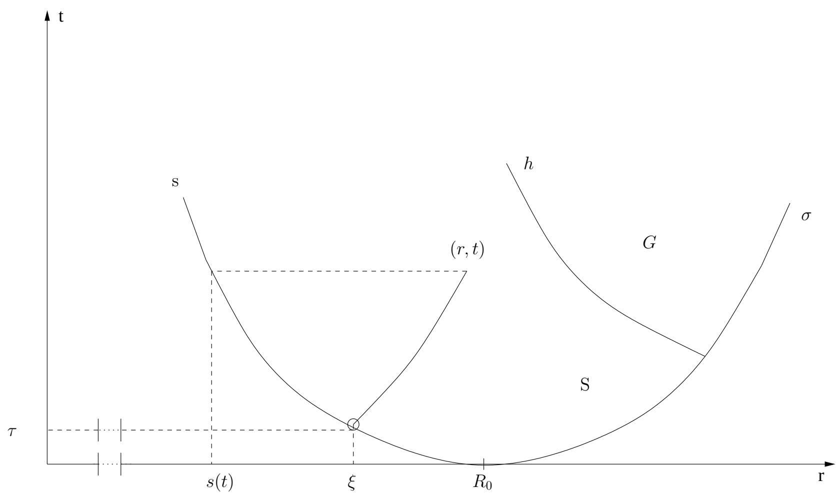

Figure 2: Scheme of the soaking region (S), gelatinization region (G), showing the free boundaries (s, h, σ) and the Lagrangian coordinate ξ.

For instance, we may select

$$F(\Phi) = A(\Phi^* - \Phi)^n, \text{ with } \phi^* > \phi_M, \quad n \geq 2, \quad A > 0. \tag{35}$$

This choice of F is justified on the basis of the analysis of the one-dimensional plane geometry (illustrated in the appendix). Indeed

$$\Phi(\xi, t) = \phi^* - \{(\phi^* - \phi_W)^{-n+1} + (n-1)A(t-\tau)\}^{-\frac{1}{n-1}} \tag{36}$$

so that the time t_g needed for gelatinization is

$$t_g = \frac{1}{(n-1)A}\{(\phi^* - \phi_M)^{-n+1} - (\phi^* - \phi_W)^{-n+1}\}. \tag{37}$$

To be specific, if we take $n = 2$, $\phi^* = 0.8$, $\phi_M = 0.75$, $\phi_W = 0.6$ and we want $t_g = 300$ sec, we need $A = 5 \cdot 10^{-2}$ sec^{-1}.

In the region G the global balance of the solid takes the form

$$\int_{s(t)}^{h(t)} r\phi_S(r,t)dr + (1-\phi_M)\frac{1}{2}(r^2 - h^2) = \frac{1}{2}(1-\phi_0)(\xi^2 - s^2(t)), \tag{38}$$

so that (32), (33) become

$$(1-\phi_0)\xi\frac{\partial \xi}{\partial r} = (1-\phi_M)r, \tag{39}$$

$$(1-\phi_0)\xi\frac{\partial \xi}{\partial t} = (1-\phi_0-\phi_W)s\dot{s} \tag{40}$$

We remark that, from (27)

$$\sigma(t)\dot{\sigma}(t) = h(t)u(h(t),t). \tag{41}$$

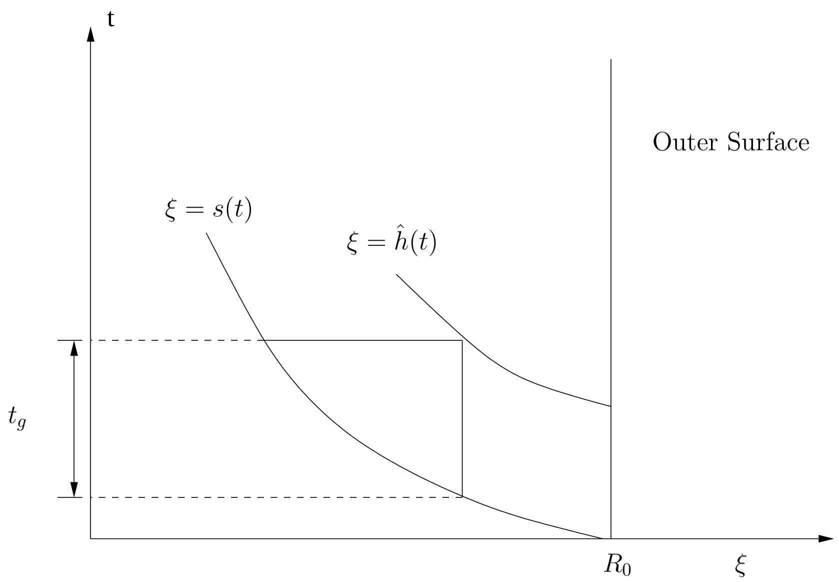

Figure 3: In the (ξ, t)plane the gelatinization front is just a translation of the water penetration front.

The time taken to complete the transition $\phi_W \to \phi_M$ is independent of ξ. Thus in the (ξ, t) plane the S/G interface $\xi = \hat{h}(t)$ is simply obtained by means of a time translation of $\xi = s(t)$ by the amount t_g (Fig.3):

$$\xi = \hat{h}(t) = s(t - t_g), \quad t > t_g. \tag{42}$$

The velocity fields in the region S can be found once the function $\Phi(\xi, t)$ is known. Note that (32) guarantees that the mapping $\xi \to r$ is $1:1$ for each t. To find its inverse we can use (32), defining the function

$$\Psi(\xi, t) = \int_{\xi}^{R} \frac{1-\phi_0}{1-\Phi(\xi', t)} \xi' d\xi', \tag{43}$$

which allows to derive from (32) that

$$r^2 = \sigma^2(t) - 2\Psi(\xi, t), \quad t \leq t_g. \tag{44}$$

At this point, we introduce the transforms $U(\xi,t)$, $V(\xi,t)$, $P(\xi,t)$ of $u(r,t)$, $v(r,t)$, $p(r,t)$, respectively. Combining (9), (17) and (32), we deduce

$$U(\xi, t) = k(\Phi) \frac{r(\xi, t)}{\xi} \frac{1-\Phi}{1-\phi_0} \frac{\partial P}{\partial \xi}. \tag{45}$$

The expression of $U(\xi,t)$ can be found by integrating (7) and recalling (14):

$$U(\xi,t) = \frac{1}{r(\xi,t)}\left\{-\frac{\phi_W-\phi_0}{1-\phi_W}s\dot{s} + \int_{s(t)}^{\xi}\frac{(1-\phi_0)\xi'}{[1-\Phi(\xi',t)]^2}F[\Phi(\xi',t)]d\xi'\right\}, \quad (46)$$

so that (42) can be used to obtain the pressure field $P(\xi,t)$, exploiting the boundary condition (11).

The fluid velocity field is simply

$$V(\xi,t) = -\frac{1-\Phi}{\Phi}U. \quad (47)$$

It is interesting to remark that the setting of the soaking model suggests that the velocity fields can be found without using Darcy's law, whose role seems to be reduced to the determination of the pressure field. In other words, pressure looks like to be automatically adjusted to fit the prescribed soaking kinetics. Nevertheless, pressure is not just an optional quantity. Indeed the motion of the soaking front has still to be determined and to this aim it is necessary to use the boundary condition (11), so that Darcy's law fully comes into play.

Returning to the original variables, the velocity field $u(r,t)$ becomes

$$u(r,t) = \frac{1}{r}\left\{-\frac{\phi_W-\phi_0}{\phi_W}s\dot{s} + \int_s^r \frac{r'}{1-\phi(r',t)}F[\phi(r',t)]dr'\right\} \quad (48)$$

and we may write

$$p_0 = \int_{s(t)}^{\sigma(t)}\frac{u(r,t)}{k[\phi(r,t)]}dr, \quad (49)$$

to be interpreted as a functional equation for $s(t)$, since in turn the boundary $\sigma(t)$ is implicitly defined putting $\xi = R$ in (31):

$$\int_{s(t)}^{\sigma(t)} r[1-\phi(\xi,t)]dr = \frac{1}{2}(1-\phi_0)(R^2-s^2(t)). \quad (50)$$

Since $1-\phi < 1-\phi_0$, (50) has a unique solution $\sigma(t) > R$, $\forall t > 0$. The system (49), (50) is more complicated than it looks, since we must remember that ϕ depends explicitly on the time τ, and through it on s. We remind that it has to be used in the stage preceding gelatinization.

After the appearence of the region G, as we have seen, the relationship between r and ξ is more complicated. On the basis of (38) and (31) we deduce that in G the inverse mapping $\xi \to r$ can be expressed as

$$\sigma^2 - r^2 = \frac{1-\phi_0}{1-\phi_M}(R^2-\xi^2), \quad \hat{h}(t) \le \xi \le R, \quad (51)$$

where $\xi = \hat{h}(t)$ corresponds to $r = h(t)$, namely

$$\hat{h}(t)^2 = R^2 - \frac{1-\phi_M}{1-\phi_0}(\sigma^2 - h^2). \tag{52}$$

For $\xi < \hat{h}$, we have instead

$$h^2 - r^2 = 2\int_{\xi}^{\hat{h}(t)} \frac{1-\phi_0}{1-\Phi(\xi', t)}\xi' d\xi', \quad t > t_g. \tag{53}$$

As we have pointed out, the curve $\xi = \hat{h}(t)$ is nothing but $\xi = s(t - t_g)$ for $t > t_g$. Thus (52) can be used as the formula giving $h(t)$ in terms of $\sigma(t)$ and of $s(t - t_g)$, for $t > t_g$.

4 A-priori properties of the water penetration front

We can easily deduce the behaviour of $s(t)$ and $\sigma(t)$ for small t, taking the approximation $\phi \sim \phi_W$ in (49) and (50). First of all we deduce the asymptotic relationship:

$$\sigma^2(t) \approx \frac{1}{1-\phi_W}[(1-\phi_0)R^2 - (\phi_W - \phi_0)s(t)^2], \tag{54}$$

or, to the first order in $\sigma - R$ or $R - s$,

$$\sigma - R \approx \frac{\phi_W - \phi_0}{1-\phi_W}(R - s). \tag{55}$$

Clearly, since $\sigma - s \approx \frac{1-\phi_0}{1-\phi_W}(R-s)$, in order to satisfy (49), u must exhibit a singularity of the order $\frac{1}{R-s}$, which in (48) can only be attributed to $\dot{s}$. Hence, if we want $-\dot{s} = \frac{d}{dt}(R-s)$ to behave as $(R-s)^{-1}$, we must take the ansatz:

$$s(t) \simeq R(1 - \alpha\sqrt{t}) \Rightarrow \sigma(t) \simeq R\left(1 + \frac{\phi_W - \phi_0}{1-\phi_W}\alpha\sqrt{t}\right) \tag{56}$$

and we can keep just the singular term of u to perform the calculation in (49), obtaining the coefficient α:

$$\alpha = \left[\frac{2k(\phi_W)p_0}{(\phi_W - \phi_0)(1-\phi_0)}\right]^{1/2} \frac{1-\phi_W}{R}. \tag{57}$$

The soaking processes is related to the efficiency of water transport, besides the intensity of the capillarity (expressed by p_0). Indeed, coupling the equations $u = k\nabla p$ and $div(u) = F/\phi_S$, we see that pressure satisfies the elliptic equation

$$div(k(\phi)\nabla p) = \frac{F(\phi)}{1-\phi}, \quad s(t) < r < \sigma(t). \tag{58}$$

Using the expression (14) of u on the soaking front, we get the Stefan condition

$$-\frac{\phi_W - \phi_0}{1-\phi_S}\dot{s} = k(\phi_W)\frac{\partial p}{\partial r}|_{r=s(t)}. \tag{59}$$

The quantity

$$\beta = k(\phi_W)\frac{\partial p}{\partial r}|_{r=s(t)} \tag{60}$$

can be calculated integrating twice (58) and imposing the two boundary conditions for pressure:

$$\beta \int_s^\sigma \frac{dr}{k(\phi)} = p_0 - \int_s^\sigma \frac{1}{k(\phi)}\left(\int_s^r \frac{r'F}{1-\phi}dr'\right) dr, \tag{61}$$

leading to the estimate

$$\beta < \frac{p_0 k_{max}}{\sigma - s} - \frac{F_{min}}{1-\phi_W}\frac{\sigma^2 - s^2 + s(\sigma - s)}{6} \tag{62}$$

Using the inequalities (see (50))

$$(\sigma^2 - s^2)(1-\phi_M) < (1-\phi_0)(R^2 - s^2) < (\sigma^2 - s^2)(1-\phi_W), \tag{63}$$

it is possible to derive from (60), (62) a differential inequality for s.

5 Study of the water penetration stage

Going back to equation (2), we immediately realize that, introducing the function

$$Q(y) = \int_{\phi_W}^y \frac{dz}{F(z)} \tag{64}$$

we obtain the integral

$$\Phi(\xi, t) = Z(t - \tau(\xi)), \tag{65}$$

with $Z = Q^{-1}$, emphasising the dependence on the difference $t - \tau(\xi)$. The use of the Lagrangian variable ξ seems more natural if we want to study equation (49). Once more, from (32)

$$dr = \frac{1-\phi_0}{1-\phi}\frac{\xi}{r(\xi,t)}d\xi \quad \text{for fixed } t,$$

and we can write (46) as

$$p_0 = \int_{s(t)}^{R} \frac{U(\xi,t)}{k(\Phi(\xi,t))} \frac{1-\phi_0}{1-\Phi(\xi,t)} \frac{\xi}{r(\xi,t)} d\xi, \tag{66}$$

where $U(\xi,t)$ is given by (46), Φ by (65) and $r(\xi,t)$ by (43) and (44).

Hence

$$p_0 = -\frac{(1-\phi_0)(\phi_W-\phi_0)}{1-\phi_W} s(t)\dot{s}(t) \int_{s(t)}^{R} \frac{\xi d\xi}{r^2 k(\Phi)(1-\Phi)} + \\ +(1-\phi_0)^2 \int_{s(t)}^{R} \frac{\xi d\xi}{r^2 k(\Phi)(1-\Phi)} \int_{s(t)}^{\xi} \frac{\xi'}{[1-\Phi(\xi',t)]^2} F[\Phi(\xi',t)] d\xi'. \tag{67}$$

It is now convenient to use the transformation $\xi = s(\tau)$, $\xi' = s(\tau')$:

$$\begin{aligned} p_0 &= \frac{(1-\phi_0)(\phi_W-\phi_0)}{1-\phi_W} s(t)\dot{s}(t) \int_0^t \frac{s(\tau)\dot{s}(\tau)d\tau}{r^2 k[Z(t-\tau)][1-Z(t-\tau)]} + \\ &+ (1-\phi_0)^2 \int_0^t \left\{ \frac{s(\tau)\dot{s}(\tau)d\tau}{r^2 k[Z(t-\tau)][1-Z(t-\tau)]} \cdot \right. \\ &\cdot \left. \int_\tau^t \frac{s(\tau')\dot{s}(\tau')}{[1-Z(t-\tau')]^2} F[Z(t-\tau')] d\tau' \right\} d\tau \end{aligned} \tag{68}$$

where (after the usual transformation in (44))

$$r^2(s(\tau),t) = \sigma^2(t) + 2\int_0^\tau \frac{1-\phi_0}{1-Z(t-\tau')} s(\tau')\dot{s}(\tau') d\tau' \tag{69}$$

and $\sigma(t)$ is expressed through $s(t)$ by means of

$$\sigma(t) = R + \int_0^t U(R,\tau) d\tau, \tag{70}$$

namely (see 46)

$$\begin{aligned} \sigma(t) &= R + \int_0^t \frac{1}{\sigma(\tau)} \left\{ -\frac{\phi_W-\phi_0}{1-\phi_W} s(\tau)\dot{s}(\tau) - \right. \\ &- \left. \int_0^\tau \frac{(1-\phi_0)s(\tau')\dot{s}(\tau')}{[1-Z(t-\tau')]^2} F[Z(t-\tau')] d\tau' \right\} d\tau, \end{aligned} \tag{71}$$

i.e. a nonlinear Volterra integral equation, with the product $s\dot{s}$ entering the kernel (which is weakly singular).

Therefore the r.h.s. of (68) can be regarded as an operator applied to the product $s\dot{s}$.

Now we prove the following

Theorem 5.1. *The functional equation (68) has a unique solution $s(t)$, continuously differentiable for $t > 0$ and continuous for $t = 0$.*

Proof. Let us define

$$-s\dot{s}\sqrt{t} = \Sigma(t), \tag{72}$$

and

$$B(t,\tau;\Sigma) = \int_\tau^t \frac{\Sigma(\tau')}{\sqrt{\tau'}} \frac{d\tau'}{r^2(s(\tau'),t)k[Z(t-\tau')][1-Z(t-\tau')]}, \tag{73}$$

where r^2 is defined in terms of Σ via (69), (71), (72).

We may rewrite equation (68), using the quantities above and interchanging the order of integration in the double integral:

$$\begin{aligned} p_0 &= \frac{(1-\phi_0)(\phi_W-\phi_0)}{1-\phi_W}\Sigma(t)\frac{1}{\sqrt{t}}B(t,0;\Sigma) + \\ &+ (1-\phi_0)^2 \int_0^t \frac{\Sigma(\tau)}{\sqrt{\tau}} \frac{F[Z(t-\tau)]}{[1-Z(t-\tau)]^2} B(t,\tau;\Sigma)d\tau \end{aligned} \tag{74}$$

We consider the set

$$S = \left\{ \Xi \in C[0,T] |\ \Xi(0) = \frac{1}{2}\alpha R^2,\ 0 < \mu_0 \le \Xi \le \mu_1 \right\}, \tag{75}$$

where T, μ_0, μ_1 are parameters to be chosen (more restrictions will be imposed in the course of the proof).

Taken $\Xi \in S$, we use it to compute $B(t,\tau;\Xi)$, according to (73), with Ξ replacing Σ also in (69), (71), and we define the mapping $\mathcal{M} : \Xi \longmapsto \Sigma$ by means of the Volterra equation

$$\begin{aligned} p_0 &= \frac{(1-\phi_0)(\phi_W-\phi_0)}{1-\phi_W}\Sigma(t)\frac{1}{\sqrt{t}}B(t,0;\Xi) + \\ &+ (1-\phi_0)^2 \int_0^t \frac{\Sigma(\tau)}{\sqrt{\tau}} \frac{F[Z(t-\tau)]}{[1-Z(t-\tau)]^2} B(t,\tau;\Xi)d\tau \end{aligned} \tag{76}$$

(whose solvability is immediately established by means of a contractive mapping argument). Note that $t^{-1/2}B(t,0;\Xi)$ is uniformly bounded for $\xi \in S$ if we restrict T in such a way that r, as given by (69), is greater than a given fraction of R, i.e. R/N with $N > 1$. For instance, a rough estimate of such time T_N can be

$$\frac{R^2}{N^2} \le R^2 - 2\int_0^{T_N} \frac{1-\phi_0}{1-\phi_M}\frac{\mu_1}{\sqrt{\tau}}d\tau,$$

hence

$$T_N \le \left[\frac{R^2}{4\mu_1} \left(1 - \frac{1}{N^2} \right) \frac{1-\phi_M}{1-\phi_0} \right]^2, \tag{77}$$

implying that, for $t \in (0, T_N)$,

$$\frac{1}{\sqrt{t}} B(t, 0; \Xi) < \frac{2\mu N^2}{R^2 k_{min}(1-\phi_M)} =: B_M. \tag{78}$$

We can also say that $t^{-1/2} B(t, 0; \Xi)$ is uniformly bounded away from zero, since

$$\frac{1}{\sqrt{t}} B(t, 0; \Xi) > \frac{\mu_0}{\sqrt{t}} \int_0^t \frac{1}{R^2 k_{max}} \frac{1}{\sqrt{\tau}} d\tau = \frac{2\mu_0}{R^2 k_{max}} =: B_m. \tag{79}$$

Coming back to equation (76), since both terms on the r.h.s. are positive, we can derive the following estimates:

$$\Sigma(t) < \frac{p_0(1-\phi_W)}{(1-\phi_0)(\phi_W - \phi_0)} \frac{R^2 k_{max}}{2\mu_0}, \tag{80}$$

$$\Sigma(t) > \frac{p_0(1-\phi_W)}{(1-\phi_0)(\phi_W - \phi_0)} \frac{R^2 k_{min}(1-\phi_M)}{2\mu_1 N^2} - \frac{(1-\phi_0)^2}{1-\phi_M} F_{max} 2t \sup_{[0.T]} \Sigma(t) \tag{81}$$

so we can possibly reduce T so to guarantee that $\Sigma(t)$ is greater than a given fraction of $\Sigma(0)$.

Unfortunately, (80), (81) just say that Σ is bounded, but they are unsuitable to show that $\mathcal{M}$ maps S into itself.

Therefore, let us take the subset $\hat{S} \subset S$ in which we impose the further requirement that Ξ is Lipschitz continuous in any interval $[\varepsilon, T]$, with $\varepsilon > 0$ and Lipschitz constant $L(\varepsilon)$, unbounded for $\varepsilon \to 0$ and decreasing in ε.

Since we will prove that the limit $\Sigma(t) \to \Sigma(0)$ as $t \to 0^+$ is uniform for Ξ in $\hat{S}$, the structure we have given to S guarantees the existence of a fixed point of the mapping $\mathcal{M}$, using Schauder's theorem in a suitable way, provided we prove that $\mathcal{M}\hat{S} \subset \hat{S}$ and that $\mathcal{M}$ is continuous in $\hat{S}$ w.r.t. the sup norm.

With this aim, and keeping in mind all the restrictions we have imposed on T, let us compute the difference $\Sigma(t_1) - \Sigma(t_2)$, e.g. with $t_1 > t_2$. From (76), setting:

$a = \frac{(1-\phi_0)(1-\phi_W)}{\phi_W - \phi_0}$, $\quad \mathcal{F}(Z) = \frac{F(Z)}{(1-Z)^2}$, $\quad \|\Sigma\| = \sup_{(0,T)} \Sigma(\tau)$

$\mathcal{K}(Z) = [k(Z)(1-Z)]^{-1}$, $\quad \mathcal{F}^* = \sup_{Z \in (0,\phi_M)} |\mathcal{F}'|$, $\quad \mathcal{K}^* = \sup_{Z \in (0,\phi_M)} |\mathcal{K}'|$,

$F_M = \sup_{y \in (0,\phi_M)} F(y)$, $\quad 0 < B_m = \inf \frac{B}{\sqrt{t}}$ for any $\Xi \in S$, we get

$$
\begin{aligned}
|\Sigma(t_1)-\Sigma(t_2)| \leq \|\Sigma\| & \left\| \frac{1}{\sqrt{t_1}} B(t_2,0;\Xi) - \frac{1}{\sqrt{t_2}} B(t_2,0;\Xi) \right\| + \\
& + \frac{a}{B_m} \left\| \int_0^{t_2} \frac{\Sigma(\tau)}{\sqrt{\tau}} \mathcal{F}'(\bar{Z})[Z(t_1-\tau)-Z(t_2-\tau)]B(t_1,\tau;\Xi)d\tau \right. \\
& \left. + \int_0^{t_2} \mathcal{F}(Z(t_2-\tau))[B(t_1,\tau;\Xi)-B(t_2,\tau;\Xi)]d\tau \right\| + \\
& + \frac{a}{B_m} \int_{t_1}^{t_2} \frac{\Sigma(\tau)}{\sqrt{\tau}} \mathcal{F}(Z(t_1-\tau))B(t_1,\tau;\Xi)d\tau,
\end{aligned}
\tag{82}
$$

with $t_1 > t_2 > \varepsilon$.

Using the estimates

$$
|\sigma(t_1)-\sigma(t_2)| \leq \frac{\mu_1}{R} \frac{\phi_W-\phi_0}{1-\phi_W} \frac{1}{2\sqrt{t_2}}(t_1-t_2) \tag{83}
$$

(deducible from (71), for T sufficiently small)

$$
\begin{aligned}
|r^2(s(\tau),t_1)-r^2(s(\tau),t_2)| \leq \mu_1 & \frac{\phi_W-\phi_0}{1-\phi_W} \frac{1}{\sqrt{t_2}}(t_1-t_2) + \\
& + 4(1-\phi_0)\mu_1 \frac{1}{(1-\phi_M)^2} F_M (t_1-t_2)\sqrt{\tau},
\end{aligned}
\tag{84}
$$

(deducible from (69)) we get the inequality

$$
\left| \frac{1}{\sqrt{t_1}} B(t_1,0;\Xi) - \frac{1}{\sqrt{t_2}} B(t_2,0;\Xi) \right| \leq C\mu_1 \frac{t_1-t_2}{t_2}, \quad t_1 > t_2 > \varepsilon, \tag{85}
$$

valid for T sufficiently small and a suitable constant C, independent on T, μ_1. The other terms in (82) are less important, due to the presence of the integral, so we can say that

$$
|\Sigma(t_1)-\Sigma(t_2)| \leq C\|\Sigma\|\mu_1 \frac{t_1-t_2}{t_2}, \quad t_1 > t_2 > \varepsilon, \tag{86}
$$

for some other constant C.

Now we can use the estimate (80) for $\|\Sigma\|$ to derive the expression of $L(\varepsilon)$ in terms of μ_1. The above estimate is too crude near the origin because it cumulates singularities that instead should cancel. Therefore the analysis near $t=0$ should be performed more carefully.

We are just interested in the lowest order of the increment. Let us add one more restriction to the set of functions Ξ, requiring that

$$
|\Xi(t)-\Xi(0)| \leq \lambda\sqrt{t}, \tag{87}
$$

where λ must be established so that the same inequality is true for the function $\Sigma(t) = \mathcal{M}\Xi$.

The difference $\Sigma(t)-\Sigma(0)$ can be evaluated directly from (76). We realise immediately that

$$\Sigma(t)\frac{1}{\sqrt{t}}B(t,0;\Xi) - \Sigma(0)C = O(t), \tag{88}$$

where

$$C = \lim_{t\to 0}\frac{B}{\sqrt{t}} = \frac{2\Sigma(0)}{R^2 k(\phi_W)(1-\phi_W)}.$$

Since we are interested in the $\sqrt{t}$ term only, we may say that

$$|\Sigma(t) - \Sigma(0)| \approx \frac{1}{C}\left|\frac{1}{\sqrt{t}}B(t,0;\Xi) - C\right|\Sigma(t). \tag{89}$$

On the right hand side we may replace $\Sigma(t)$ by $\Sigma(0)$, once we have checked that $\Sigma(t) - \Sigma(0) = O(\sqrt{t})$.

Let us now compute:

$$\begin{aligned}
\left|\frac{1}{\sqrt{t}}B(t,0;\Xi) - C\right| &= \frac{1}{\sqrt{t}}\left|\int_0^t \frac{1}{\sqrt{\tau}}\left\{\frac{\Xi(\tau)}{r^2 k(Z)(1-Z)} - \frac{\Xi(0)}{R^2 k(\phi_W)(1-\phi_W)}\right\}d\tau\right| \leq \\
&\leq \frac{\Sigma(0)}{\sqrt{t}}\int_0^t \frac{1}{\sqrt{\tau}}\left|\frac{1}{r^2 k(Z)(1-Z)} - \frac{1}{R^2 k(\phi_W)(1-\phi_W)}\right|d\tau + \\
&+ \frac{\lambda}{\sqrt{t}}\int_0^t \frac{d\tau}{r^2 k(Z)(1-Z)}.
\end{aligned}$$

Neglecting some $O(t)$ terms, the last member of the above inequality is

$$\frac{1}{R^2 k(\phi_W)(1-\phi_W)}\left\{\frac{\Sigma(0)}{\sqrt{t}}\int_0^t \frac{1}{\sqrt{t}}\frac{|R^2 - r^2|}{R^2}d\tau + \lambda\sqrt{t}\right\}$$

From (69) and (71) we see that

$$r^2(s(t),t) - R^2 = 2R\int_0^t U(R,\tau)d\tau - 2\int_0^t \frac{1-\phi_0}{1-Z}\frac{\Xi(\tau'}{\tau'}d\tau'$$

with

$$\int_0^t U(R,\tau)d\tau = 2\frac{\Sigma(0)}{R}\frac{\phi_W - \phi_0}{1-\phi_W}\sqrt{t} + O(t).$$

Therefore after some algebra we obtain that

$$r^2(s(t),t) - R^2 = -4\Sigma(0)\sqrt{t} + O(t).$$

Summing up the above results and remembering that

$$\frac{\Sigma(0)}{C} = \frac{R^2 k(\phi_W)(1-\phi_W)}{2},$$

we reach the conclusion

$$\begin{aligned} |\Sigma(t) - \Sigma(0)| &\approx \left\{ \frac{4\Sigma(0)}{R^2} + \lambda \right\} \sqrt{t} \\ &= \left(\alpha + \frac{1}{2}\lambda \right) \sqrt{t}. \end{aligned} \tag{90}$$

Therefore $\Sigma(t)$ satisfies the same inequality (87) as $\Xi(t)$ provided that $\alpha + \lambda/2 \leq \lambda$, meaning that we have simply to choose $\lambda \geq 2\alpha$.

It is worth nothing that λ can now be selected independently of the other parameters entering the definition of the set $\hat{S}$, thus providing uniform bounds for Ξ for some other interval T_λ. Since the $O(t)$ terms depend on μ_1, the length of this time interval may depend on μ_1.

From what we have seen, we want in practice that $\lambda\sqrt{T_\lambda} > C\mu_1 T_\lambda$, for some C independent of μ_1, implying that $T_\lambda < (\lambda/C\mu_1)^2$. We may choose $\mu_1 = 2\Sigma(0) = \alpha R^2$. Next, using the Lipschitz estimate we can look for a time $T_1 > T_\lambda$ such that over (T_λ, T_1), $\Sigma(t)$ has a further decrement less than $\Sigma(0)$: $3\Sigma(0)C_1(T_1 - T_\lambda)T_\lambda^{-1} < \Sigma(0)$, for a suitable C_1 independent of $\|\Sigma\|$. Thus we find $(T_1 - T_\lambda)t_\lambda^{-1} < (3C_1)^{-1}$. Allowing a further decrement not exceeding $\Sigma(0)$, we can look for T_2 such that $4\Sigma(0)C_1(T_2 - T_1)T_1^{-1} < \Sigma(0)$, i.e. $(t_2 - T_1)T_1^{-1} < (4C_1)^{-1}$. Continuing this procedure, we may say that $\Sigma(t) < (n+2)\Sigma(0)$ for $t < T_n = \Pi_{j=3}^{n}(1 + (jC_1)^{-1})T_\lambda$.

In this way, we may select μ_1 and T (and consequently μ_0 and $L(\varepsilon)$), i.e. all the parameters in the set $\hat{S}$, so to guarantee that $\mathcal{M}\hat{S} \subset \hat{S}$.

Let's turn our attention to the continuity of $\mathcal{M}$. This is easy, since from (69), (71), (73) (76) we obtain the estimate

$$\|\Sigma_1 - \Sigma_2\| \leq X\sqrt{T}\|\Xi_1 - \Xi_2\|, \tag{91}$$

where X is a constant depending on the parameters defining $\hat{S}$. Thus $\mathcal{M}$ is not only Lipschitz continous, but even contractive for T small enough. $\square$

Remark 3. *Existence and uniqueness can be easily extended up to the time t_g at which ϕ reaches Φ_M and that we suppose to be such that $s(t_g) > 0$. Indeed in practical cases gelatinization has to start much before water reaches the axis.*

6 Study of the gelification stage.

For the sake of brevity we confine to the case $\eta_0 = 0$, characterized by the continuity of all quantities through the interface $r = h(t)$.

Recalling (30), we see that the equation

$$k(\phi)\frac{\partial p}{\partial r} = u$$

extends in the region G. Consequently, equation (49) is still valid.

Concerning the link between $\sigma(t)$ and $s(t)$, we see from (42), (51) and (53) that it can be written as

$$\sigma^2(t) - s^2(t) = 2\int_{s(t)}^{R} \frac{1-\phi_0}{1-\tilde{\Phi}(\xi,t)}\xi d\xi, \tag{92}$$

where

$$\tilde{\Phi}(\xi,t) = \begin{cases} \Phi(\xi,t), & s(t) \le \xi \le \hat{h}(t) \\ \phi_M, & \hat{h}(t) \le \xi \le R. \end{cases} \tag{93}$$

We recall that $\hat{h}(t) = s(t - t_g)$, so that (92) really provides the mapping $s \to \sigma$.

The expression of the velocity field $u(r,t)$ is

$$ru(r,t) = -\frac{\phi_W - \phi_0}{1-\phi_W}s\dot{s} + \int_s^r \frac{r'}{1-\phi(r',t)}F(\phi(r',t))dr', \quad s \le r \le h, \tag{94}$$

as before, and

$$ru(r,t) = -\frac{\phi_W - \phi_0}{1-\phi_W}s\dot{s} + \int_s^h \frac{r}{1-\Phi(r,t)}F(\phi(r))dr, \quad h \le r \le \sigma, \tag{95}$$

owing to (27). Remembering (44), we have that (95) is also the expression of $\sigma\dot{\sigma}$.

It is advantageous to use the Lagrangian variable ξ because the function $\phi(r,t)$ has a simpler expression. We just have to modify the definition (65) of $\Phi(\xi,t)$ as follows,

$$\Phi(\xi,t) = \begin{cases} Z(t-\tau(\xi)), & \xi \le \hat{h}(t) \\ \phi_M, & \xi \ge \hat{h}(t). \end{cases} \tag{96}$$

In this way we can write the explicit form of the functional equation for the free boundary $s(t)$ and we realise that it is formally identical to the one of the soaking stage with the only change that Φ is defined as in (96) and $F(\Phi)$ is consequently frozen to zero in the gelatinization region.

Therefore the existence proof is very similar to the one illustrated in detail in sect. 5.

7 A numerical scheme

We recall that (56), (57) give a good representation of $s(t)$, $\sigma(t)$ for $t << \alpha^{-2}$. Thus, we select a partition

$$(0, t_g) = \cup_{i=1}^{N-1}(t_i, t_{i+1})$$

with $t_0 = 0$, $t_1 << \alpha^{-2}$, $T_N = t_g$, and we identify $s(t)$, $\sigma(t)$ with their approximations (56) in the first interval $(0, t_1)$, which we call $s_0(t)$, $\sigma_0(t)$:

$$s_0(t) = R(1 - \alpha\sqrt{t}), \quad \sigma_0(t) = R\left(1 + \frac{\phi_W - \phi_0}{1 - \phi_W}\alpha\sqrt{t}\right). \tag{97}$$

According to (69), the corresponding $O(\sqrt{t})$ approximation of ε^2 for $0 < \tau < t < t_1$ is

$$\begin{aligned} r^2 &\approx \sigma_0^2(t) - \frac{1 - \phi_0}{1 - \phi_W}(R^2 - s_0^2(\tau)) \\ &\approx R^2\left\{1 + \frac{r\alpha}{1 - \phi_W}[(\phi_W - \phi_0)\sqrt{t} - (1 - \phi_0)\sqrt{\tau}]\right\}, \end{aligned} \tag{98}$$

where we have used the approximation $Z \approx \phi_W$.

Before we proceed further, it is convenient to take nondimensional variables, rescaling lengths by R ($r = \tilde{r}R$, $s = \tilde{s}R$, $\sigma = \tilde{\sigma}R$) and time by $t_0 = \alpha^{-2}$, so that $\alpha\sqrt{t} = \sqrt{\tilde{t}}$, $\alpha\sqrt{\tau} = \sqrt{\tilde{\tau}}$. We rescale k by $k_W = k(\phi_W)$ and we introduce the nondimensional quantity

$$\Theta = A\alpha^{-2} \tag{99}$$

(note that Θ is the ratio between the time scale α^{-2} associated with the front penetration and the time scale A^{-1} associated to the soaking kinetics). Moreover, we write

$$\tilde{s}(\tilde{t})\frac{d\tilde{s}}{d\tilde{t}} = -\frac{\tilde{S}(\tilde{t})}{2\sqrt{\tilde{t}}}.$$

Remembering (57) we can now write the non-dimensional form of (68) in the following form, where all tildes have been omitted to simplify notations:

$$\begin{aligned} 1 = &\frac{S(t)}{\sqrt{t}}\int_0^t \frac{1}{r^2}\frac{S(\tau)}{2\sqrt{\tau}}\frac{1}{k[Z(t-\tau)]}\frac{1 - \phi_W}{1 - Z(t-\tau)}d\tau + \\ &+ 2\Theta\frac{1 - \phi_0}{\phi_W - \phi_0}\int_0^t \left\{\frac{S(\tau)}{r\sqrt{\tau}}\frac{1}{r^2}\frac{1}{k[Z(t-\tau)]}\frac{1 - \phi_W}{1 - Z(t-\tau)}\cdot\right. \\ &\left.\cdot\int_\tau^t \frac{S(\tau')}{2\sqrt{\tau'}}[\phi^* - Z(t-\tau')]^2\frac{1 - \phi_W}{[1 - Z(t-\tau)]^2}d\tau'\right\}d\tau \end{aligned} \tag{100}$$

Note that we have specified $n = 2$ in (100).

In the new variable, starting from $s_0 = 1 - \sqrt{t}$ we define $S_0 = 1 - \sqrt{t}$ and we may decide to approximate $S(t)$ in (t_1, t_2) by the constant S_1 obtained from (100) taking $t = t_1$, $S(t) = S_1$ and keeping just the approximation $O(\sqrt{t_1})$:

$$S_1 \approx 1 + \left(\frac{1}{2} + 2\frac{\phi_W - \phi_0}{1 - \phi_0} - \frac{1 - \phi_0}{2} \right) \sqrt{t_1}, \tag{101}$$

where we have used the nondimensional approximations

$$\sigma_0(t) \approx 1 + \frac{\phi_W - \phi_0}{1 - \phi_W}\sqrt{t}, \tag{102}$$

$$r^2 \approx 1 + 2\frac{\phi_W - \phi_0}{1 - \phi_W} t - 2\frac{1 - \phi_0}{1 - \phi_W}\sqrt{\tau}. \tag{103}$$

We can proceed in a recursive way to derive a constant approximation for $S(t)$, that we call s_n, in the interval (t_n, t_{n+1}).

To this end we need the non-dimensional version of (69), (71), namely (with a slight abuse of notation)

$$r^2(\tau, t) = \sigma^2(t) - (1 - \phi_0) \int_0^\tau \frac{S(\tau')}{\sqrt{\tau'}} \frac{1}{1 - Z(t - \tau')} d\tau', \tag{104}$$

$$\begin{aligned} \sigma = 1 + \int_0^t \frac{1}{\sigma(\tau)} \Bigg\{ & \frac{\phi_W - \phi_0}{1 - \phi_W} \frac{S(\tau)}{2\sqrt{\tau}} + \\ & + \Theta \int_0^\tau \frac{1 - \phi_0}{1 - Z} \frac{S(\tau')}{2\sqrt{\tau'}} \frac{[\phi^* - Z(t - \tau')]}{1 - Z(t - \tau')} d\tau' \Bigg\} d\tau \end{aligned} \tag{105}$$

The recursive system for the determination of the triples (S_n, r_n, σ_n) is the following

$$\begin{aligned} 1 = {} & S_n \sum_{i=0}^{n-1} \frac{S_i}{r_{i,n}^2} \frac{1}{k_i} \frac{1 - \phi_W}{1 - Z_{i,n}} \frac{\sqrt{t_{i+1}} - \sqrt{t_i}}{\sqrt{t_n}} + \\ & + 2\Theta \frac{1 - \phi_0}{\phi_W - \phi_0} \sum_{i=0}^{n-1} \frac{S_i}{r_{i,n}^2} \frac{1}{k_i} \frac{1 - \phi_W}{1 - Z_{i,n}} (\sqrt{t_{i+1}} - \sqrt{t_i}) \cdot \\ & \cdot \left\{ \sum_{j=i}^{n-1} S_j \frac{1 - \phi_W}{1 - Z_{j,n}} (\phi^* - Z_j, n)^2 (\sqrt{t_{j+1}} - \sqrt{t_j}) \right\} \end{aligned} \tag{106}$$

where $Z_{i,n} = Z(t_n - t_i)$,

$$r_{i,n}^2 = \sigma_n - (1 - \phi_0) \sum_{j=0}^{i-1} S_j \frac{1}{1 - Z_{j,n}} (\sqrt{t_{j+1}} - \sqrt{t_j}), \tag{107}$$

$$\sigma_n = 1 + (\sqrt{t_{i+1}} - \sqrt{t_i}) \left\{ \sum_{i_0}^{n-1} \frac{S_i}{\sigma_i} \frac{\phi_W - \phi_0}{1 - \phi_W} (\sqrt{t_{i+1}} - \sqrt{t_i}) + \right.$$
$$\left. + (1 - \phi_0)\Theta \sum_{i=0}^{n-1} \frac{1}{\sigma_i} \left[\sum_{j=0}^{i-1} \frac{S_j}{1 - Z_{j,n}} \frac{[\phi^* - Z_{j,n}]^2}{1 - Z_{j,n}} (\sqrt{t_{j+1}} - \sqrt{t_j}) \right] \right\}. \tag{108}$$

Once (106-108) has been solved, the approximations s_n are obtained via

$$s_n = \left\{ R^2 - 2 \sum_{i=0}^{n-1} S_i (\sqrt{t_{i+1}} - \sqrt{t_i}) \right\}^{\frac{1}{2}}. \tag{109}$$

8 Comparison with experiments

In [1] measures of total water intake are reported with reference to several different geometries.

Using the asymptotic analysis of Section 4, we deduce the total water intake during the first stage of the process, during which the progression of the water penetration front has the behaviour $s(t) \approx R - \alpha\sqrt{t}$, we can easily calculate the total water intake as a function of time. Indeed, from (56) we deduce a simple expression for $\sigma(t)$, $s(t)$. To be consistent with this approximation, we take $\phi \approx \phi_W$ and we just neglect the pristine porosity ϕ_0 which is very small.

The volume of water present in the sample at time t is $\pi[\sigma^2(t) - s^2(t)]$. Thus, taking into account (56), (57) (with $\phi_0 = 0$), the mass of water uptaken per unit length, computed at the $O(\sqrt{t})$ order, is

$$M(t) = 2\pi R \rho_W \frac{\alpha}{1 - \phi_W} \sqrt{t}, \tag{110}$$

where ρ_W is the water density and α is given by (57).

The same quantity, divided by the mass of pasta per unit length, i.e. $\pi \rho_{starch} R^2$, is plotted in Fig. 4, in which the experimental data from [1] are shown. The fitting of the coefficient

$$a = 2 \frac{\rho_W}{\rho_{starch}} \frac{\phi_W}{R} \frac{\alpha}{1 - \phi_W}$$

by the least sqares method gives $a = 0.048$ sec$^{-1/2}$.

Taking $\phi_W = 0.35$, $\rho_W = 1$g cm^{-3}, $\rho_{starch} = 1.4$g cm^{-3} (as in [6]), and $R = 0.07$cm (as in [1]), this value of a corresponds to $p_0 k_W \approx 7.6 \cdot 10^{-6}$cm^{2}sec^{-1}, which in our scheme is the driving quantity.

We took advantage of the fact that in [1] there also the water intake results for plane geometry and we perform tha same data fitting procedure,

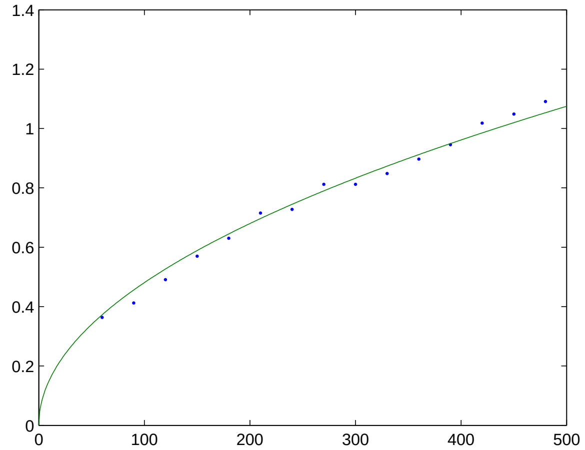

Figure 4: Early stage of water penetration in cylindrical symmetry (spaghetti) vs. experimental data

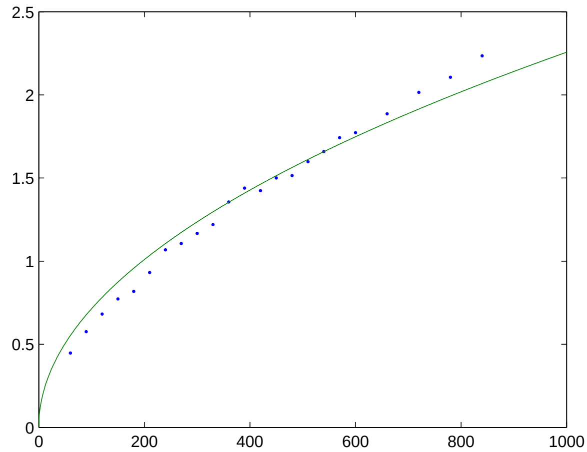

Figure 5: Early stage of water penetration in plane symmetry (lasagna) vs. experimental data

this time based on the formula (see the Appendix, formula (113), and consider that $-\sigma \approx \frac{\phi_W}{1-\phi_W} s$)

$$M(t) = \rho_W \frac{\phi}{1-\phi_W} \alpha \sqrt{t}, \quad \alpha = (1-\phi_W)\sqrt{\frac{2 p_0 k_W}{\phi_W}}.$$

The quantity to be compared with the data is $\frac{M(t)}{\rho_{starch} L}$, L being the half thickness of the sample ($L = 0.025$cm). The value identified for the coefficient of $\sqrt{t}$ is $a = 0.07 \text{sec}^{-1/2}$, corresponding to $p_0 k_W = 1.5 \cdot 10^{-6} \text{cm sec}^{-1}$, which is not much different from the previous one (see Fig. 4). Part of the discrepancy could be attributed to the longitudinal expansion of spaghetti, which has been neglected here, but also to very small thickness of the flat pasta sample that has been used.

Appendix. Plane geometry and qualitative remarks

We deal briefly with the case of plane geometry with the main scope of emphasizing the influence of some parameters on the soaking process, taking advantage of the much simpler structure of the equations. The problem with a plane geometry has a practical interest, as we pointed out in the introduction.

Confining to the water invasion stage, we choose the space coordinate x so that the moisturised region is $\sigma(t) < 0 < x < s(t)$, for $t > 0$, and $\sigma(0) = s(0) = 0$. We keep all other symbols used so far, and in particular the form (35) of the function determining the soaking kinetics:

$$\dot{\phi} = A(\phi^* - \phi)^n, \quad \phi^* \geq \phi_M, \quad n > 0, \quad A > 0. \tag{111}$$

We want to examine the influence of the exponent n, here allowed to be any positive number.

The equation replacing (68) turns out to be

$$p_0 = \frac{(1-\phi_0)(\phi_W - \phi_0)}{1-\phi_W} \dot{s}(t) \int_0^t \frac{\dot{s}(\tau)}{k[Z(t-\tau)][1-Z(t-\tau)]} d\tau + \\ + (1-\phi_0)^2 A \int_0^t \frac{\dot{s}(\tau)}{k[Z(t-\tau)][1-Z(t-\tau)]} \int_\tau^t \frac{[\phi^* - Z(t-\tau')]^n}{[1-Z(t-\tau')]^2} \dot{s}(\tau') d\tau' d\tau, \tag{112}$$

which again gives a singular asymptotic behaviour for small time:

$$s(t) \approx \alpha t^{\frac{1}{2}}, \quad \alpha = \sqrt{2 \frac{(1-\phi_W)^2 k(\phi_W)}{(\phi_W - \phi_0)(1-\phi_0)} p_0} \tag{113}$$

(see Fig. 5).

Equation (112) is much simpler than equation (68) because the latter involved also the function $r(\xi, t)$ and consequently also $\sigma(t)$. Therefore the argument used to prove existence for equation (68) applies to (112) too with great simplifications.

Numerical computations performed on (112) show that a non-monotone behaviour for $s(t)$ is possible for $n \leq 1$. A possible inversion of the front motion, although not expected in practice, fits the physics of the model. Indeed we have assumed that, while water is driven in the medium by capillarity, it is also required to feed the imbibition process at each point. The need of water required by the latter may not be matched by the transport mechanism (which is Darcyan in our scheme). When this happens water can be forced to invert its motion. Of course this is not the kind of behaviour we expect for pasta cooking and we must select the parameter so to guarantee monotonicity. A crucial parameter is the exponent n in the kinetics of imbibition. Taking $n < 1$ accelerates imbibition to the point that a front regression can be induced.

In order to have an idea of how the selection of n influences the solution we can argues as follows. Put $\omega(t) = \dot{s}(t)$ in (112) and suppose that $\omega(t)$ vanishes for the first time at some instant $\bar{t} > 0$. If we differentiate (112) w.r.t. t and we take $t = \bar{t}$, thanks to the fact $\omega(\bar{t}) = 0$ and $\dot{\omega}(t) \leq 0$, we obtain

$$0 = \Theta_1 + \Theta_2,$$

where Θ_1, Θ_2 come from the differentiation of the first and of the second term on the r.h.s., respectively. It is easily seen that $\Theta_1 \leq 0$, thanks to $\dot{\omega}(t) \leq 0$ and to $\omega(t) = 0$ in $\bar{t}$.

Therefore, if we want to contradict the assumption $\omega(\bar{t}) = 0$, we need $\Theta_2 < 0$.

Consider for simplicity the case $k =$ constant . The computation of Θ_2 leads to

$$\frac{k\Theta_2}{(1-\phi_0)^2} = \int_0^{\bar{t}} \frac{\omega(\tau)}{[1-\Psi(\bar{t}-\tau]^2} \dot{\Psi}(\bar{t}-\tau) \int_\tau^{\bar{t}} \frac{[\phi^* - \Psi(\bar{t}-\tau')]^n}{[1-\Psi(\bar{t}-\tau')]^2} \omega(\tau') d\tau' d\tau +$$
$$+ \int_0^{\bar{t}} \frac{\omega(\tau)}{[1-\Psi(\bar{t}-\tau)]} \cdot$$
$$\left\{ \int_\tau^{\bar{t}} \frac{\dot{\Psi}(\bar{t}-\tau')[\phi^* - \Psi(\bar{t}-\tau')]^{n-1}}{[1-\Psi(\bar{t}-\tau')]^3} \left[-n(1-\Psi(\bar{t}-\tau') + 2(\phi^* - \Psi(\bar{t}-\tau'))) \right] d\tau' \right\} d\tau \tag{114}$$

This formula emphasizes that a necessary condition for $\Theta_2 < 0$ is that

$$\frac{n}{2} > \frac{\phi^* - Z}{1 - Z}.$$

For $Z \in (\phi_W, \phi_M)$ we have

$$\frac{\phi^* - \phi_M}{1 - \phi_M} < \frac{\phi^* - Z}{1 - Z} < \frac{\phi^* - \phi_W}{1 - \phi_W} < 1.$$

Although this is not a conclusive argument, it suggests that acceptable values for n are in the range $n \geq 2$.

From (112) we can also obtain an indication of how the coefficient A influences the solution. Setting $\omega_A = \frac{\partial \omega}{\partial A}$, by differentiation w.r.t. A we obtain

$$\begin{aligned} 0 = & \frac{\phi_W - \phi_0}{1 - \phi_W} \left\{ \omega_A(t) \int_0^t \frac{\omega(\tau)}{k(Z)(1-Z)} d\tau + \omega(t) \int_0^t \frac{\omega_A(t)}{k(Z)(1-Z)} d\tau \right\} + \\ & + (1 - \phi_0) \int_0^t \frac{\omega(\tau)}{k(Z)(1-Z)} \left\{ \int_\tau^t \frac{(\phi^* - Z)^n}{(1-Z)^2} \omega(\tau') d\tau' + \right. \\ & \left. + A \int_\tau^t \frac{(\phi^* - Z)^n}{(1-Z)^2} \omega_A(\tau') d\tau' \right\} d\tau + \\ & + (1 - \phi_0) A \int_0^t \frac{\omega_A(\tau)}{k(Z)(1-Z)} \int_\tau^t \frac{(\phi^* - Z)^n}{(1-Z)^2} \omega(\tau') d\tau' d\tau. \end{aligned} \tag{115}$$

This is a linear integral equation in ω_A, which allows to conclude that $\omega_A < 0$ as long as $\omega > 0$.

The physical implication is that increasing the coefficient A (i.e. that local imbibition rate) reduces the front speed. Indeed, as we said, the two processes are in mutual competition.

In the same way it is possible to show the following. If we write $k(Z) = k_0 \tilde{k}(Z)$ and we investigate the dependence of ω on k_0, we conclude that ω increases if k_0 increases. The results agrees with physical intuition, since enhancing the water transport accelerates the front penetration.

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