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Gelification and mass transport in a static non-isothermal waxy solution

A. FASANO[1], L. FUSI[1], J. R. OCKENDON[2] and M. PRIMICERIO[1]

[1]*Dipartimento di Matematica 'U. Dini', Università degli Studi di Firenze, Viale Morgagni 67/A, 50134 Firenze, Italy*
[2]*OCIAM, Mathematical Institute, 24-29 St. Giles, Oxford, OX1 3LB, UK*

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We consider a solution of a mono-component oil and wax. The latter is dissolved in the oil if the temperature is above the so-called cloud point (which depends on the concentration) and it segregates in the form of solid crystals if temperature is below the cloud point. As the solid fraction of wax increases, the diffusivity of liquid wax in the oil decreases (gelification), eventually vanishing. We study a one-dimensional model where temperature is initially above the cloud point and then it is lowered to induce diffusion and gelification. We formulate the relevant mathematical problem (a free boundary problem), studying its well-posedness and showing some qualitative results.

1 Introduction

A waxy oil is a mixture of heavy hydrocarbons (referred to as *wax*) that, for sufficiently high temperatures, are dissolved in a lighter mixture (referred to as *oil*), which in this respect has the role of a solvent. When the temperature is lowered below the *wax appearing temperature* (WAT or *cloud point*) $T_{\rm cp}$ depending on the concentration of dissolved wax, the solution becomes saturated and wax segregates in the form of solid crystals possessing a very low mobility in the mixture. Since the concentration at saturation depends on temperature, a temperature gradient will induce mass transport by Fickian diffusion.

When waxy oils are transported through pipelines this phenomenon may cause the formation of solid deposits on the pipe walls owing to radial migration of dissolved wax. It is clearly very important to predict the deposit growth rate.

In addition to diffusional transport, another phenomenon contributing to the formation and consolidation of the deposit is the aggregation of solid crystals in a gel-like structure with a large oil inclusion (*gelification*), which occurs at a temperature $T_{\rm gel}$ ($<T_{\rm cp}$) depending on the concentration of solid wax. Other mechanisms such as shear dispersion and sedimentation are usually neglected in the deposition process (see [1]).

In this paper we investigate and model deposition taking into account diffusion and gelification. We will confine ourselves to the static condition of that of the so-called 'cold finger' device (an apparatus used to infer wax diffusivity from measurements of the rate of wax deposition), studied in [4] and [5].

An important difference between the present study and the models investigated in previous papers (see [10–12]) is that mass transport is not assumed to take place in a

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stationary thermal field and we consider mass and heat diffusion to have comparable time scales. Moreover, we assume that the diffusivity coefficient of liquid wax depends on the solid wax fraction that has been formed and diffusion is no longer allowed when a critical solid wax fraction has been reached. When the gel has attained the non-diffusive stage we call it a *deposit*. We also assume that solid wax does not diffuse in the solution, even when it has not yet entered the gel state. Finally, we suppose that the segregated solid phase can be present only when the solution is saturated and that super-saturation is never achieved (a different approach for modelling crystallization can be found in [17]).

For simplicity we consider a plane geometry (a system confined between two parallel planes $x=0$ and $x=L$), but it would not be difficult to study a cylindrical geometry like the one of the cold finger device. Modelling and analysing other geometries will be significantly more difficult. The oil is initially at a temperature $T_w > T^*_{cp}$, where T^*_{cp} is the WAT corresponding to the initial uniform wax concentration c^*. Thus we start with an unsaturated solution. The wall $x=L$ is kept at the temperature T_w, while the wall $x=0$ is progressively cooled to an asymptotic temperature T_a sufficiently low to produce gelification. The extension to cylindrical geometry and the case in which both walls are cooled below T^*_{cp} is not difficult.

In this situation the system is described by the evolution of the thermal field and of the solid/liquid wax fraction. It may go through five stages characterized by

(i) *pre-cooling*: the temperature is everywhere greater than T^*_{cp}, the wax concentration stays constant and no mass flux takes place;

(ii) *onset of deposition at the cold wall*: the layer is partitioned into a deposition region (a non-diffusive gel) and an unsaturated region. The interface concentration is less than c^*, causing a mass flux that creates the deposit. For a reason that will be clear later, this stage can be considered a 'waiting time';

(iii) *onset of saturation*: at the end of the waiting time, the mass flux in the unsaturated region has become large enough to allow the formation of a saturated region with segregated solid wax, interposed between the unsaturated region and the deposition region. The new region will eventually evolve into a gel, which in turn, undergoes further changes becoming a deposit;

(iv) *onset of crystal depletion*: in a finite time, the unsaturated phase stops shrinking and expands, consuming the suspended solid phase;

(v) *asymptotic stage*: after the crystal depletion front meets the deposition front, we are back in the situation of stage (ii) and the system goes to its asymptotic state, with a uniform concentration in the unsaturated solution and a totally inert deposit.

We shall see that stages (iii) and (iv) may not appear, depending on the cooling rate, but if they do, they lead to non-trivial free-boundary problems. In addition, the transition from (iv) to (v) can be rather complicated. However, the unique limit thickness of the deposition region can be evaluated. Besides formulating the model, analytical results concerning existence, uniqueness and regularity of the solution are provided. Also a careful analysis of the behaviour of the free boundaries is presented.

We believe that the present study may contribute to a better interpretation of the process leading to pipe blockage, and it can also help in designing experimental strategies

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for static devices like the cold finger. For instance, the well-known anomalous behaviour of the diffusivity, which increases when the cold-finger temperature is decreased, can be easily interpreted in terms of the formation of a gel; if mass is eventually measured as a deposit, the diffusivity is over-estimated.

2 Physical overview

In a waxy solution, the saturation concentration (*solubility*) is an increasing function $c_s(T)$ of temperature in a certain range. Correspondingly, if we consider a solution with wax concentration c^*, the temperature T_{cp} at which wax crystals begin to appear is an increasing function of c^*. If we assume that the solid phase can exist only in the presence of saturation, the oil entrapped in the gel is necessarily saturated. An important consequence of the temperature dependence of c_s is that temperature gradients induce molecular diffusion within the saturated oil.

If we lower the temperature sufficiently below T_{cp} the solid crystals tend to form a network which is usually referred to as gel. This process, known as gelification, will take place if the concentration of crystallized wax G in the solution is greater than a certain value $G_{gel} = G_{gel}(T)$, where G_{gel} is an increasing function of temperature. The inverse of G_{gel} is the gelification temperature $T_{gel}(G)$ which is, in turn, an increasing function of G.

It is assumed that diffusivity of the dissolved wax in the gel is a function of G that decreases to 0 when G ranges from $G_{gel}(T)$ to some $G_{dep} > G_{gel}(T)$. The function $G_{gel}(T)$ is bounded by G_{dep} and, when $G > G_{dep}$, diffusion of liquid wax in the oil is not allowed. This approach is in contrast with the assumption we find, for instance, in [3] where the gelification front is simply identified with a level set $T = T_{cp}$, so that the front propagates with the Stefan condition for traditional phase change, which suggests that we are dealing with a solidification front.

We assume that the densities of segregated wax, dissolved wax and oil are constant and all equal to ρ, so that in the segregation/dissolution process no volume change nor sedimentation occurs[1].

In the layer $x \in [0, L]$, we denote by $G(x,t)$ the concentration of solid crystals (also referred to as segregated wax) and with $c(x,t)$ the concentration of dissolved wax. When the solution is saturated by wax, $c(x,t) = c_s(T(x,t))$, where c_s is wax solubility, i.e. the maximum amount of wax that can be dissolved in a unit volume of solution at the given temperature T. We assume that c_s is linear in T (see [4]) so that

$$\frac{dc_s}{dT} = \beta > 0, \tag{1}$$

where β is a positive constant. Even though solubility $c_s(T)$ represents the concentration of wax in the liquid phase, we consider it as the concentration in the whole system. Indeed we assume that the solution is dilute, i.e. the oil fraction is by far greater than the wax fraction. As a consequence of this assumption, which will be kept throughout the model, the oil will be considered immobile and convection will be neglected. We define the total wax concentration

$$c_{tot}(x,t) = G(x,t) + c(x,t), \tag{2}$$

[1]Since the wax density ρ is constant, all concentrations can be expressed as mass/volume.

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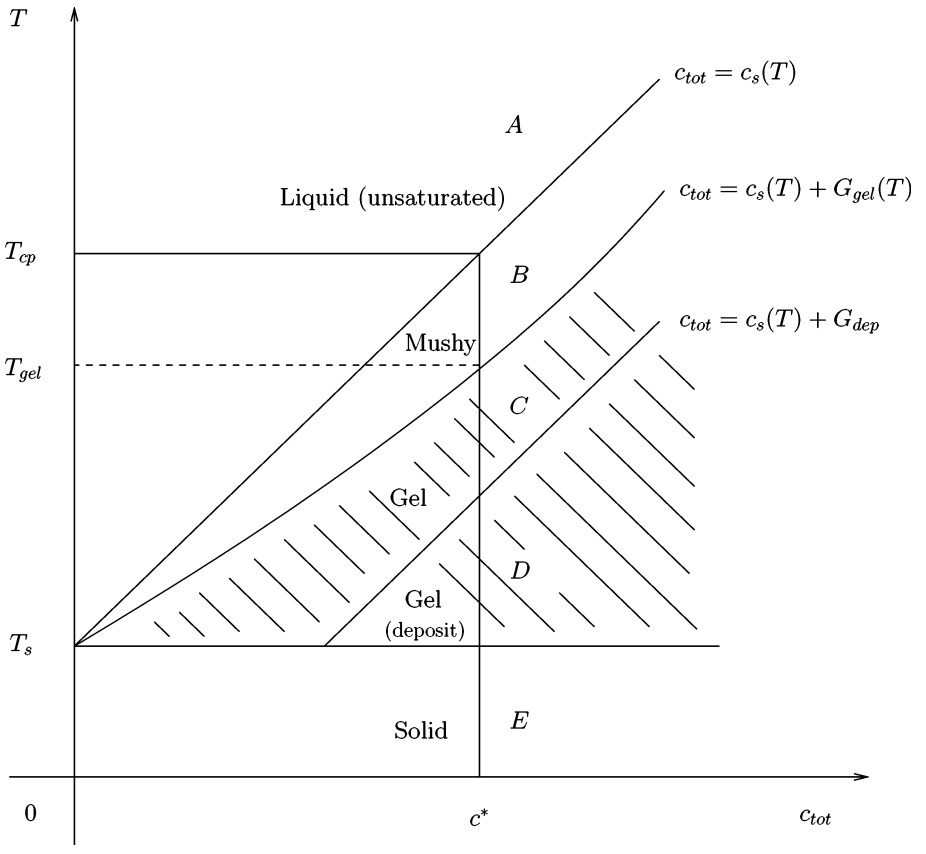


FIGURE 1. Phase diagram of wax.

where

$$G(x,t) = [c_{\mathrm{tot}}(x,t) - c_{\mathrm{s}}(T(x,t))]_+, \tag{3}$$

$[..]_+$ representing the positive part. In Figure 1, a phase diagram for the total wax concentration c_{tot} is shown. T_{s} represents the solidification temperature of the oil. The diagram is consistent with our mono-component approach for wax and oil. The five separated domains A, B, C, D, E shown in Figure 1 represent

A *Liquid phase*. This is the region with $0 < c_{\mathrm{tot}} < c_{\mathrm{s}}(T)$. Here all wax is dissolved in the oil and no solid phase is present ($G \equiv 0$). As we said, solubility is taken as a linear function of temperature.

B *'Mushy' region with constant diffusivity*. This is the region where $0 < G < G_{\mathrm{gel}}(T)$ and liquid wax diffuses with constant diffusivity. In this region the solid fraction is not enough to form the gel structure.

C *Gel in which wax diffuses*. This is the region where $G_{\mathrm{gel}}(T) < G < G_{\mathrm{dep}}$ and liquid wax diffuses with a diffusivity depending on G and T. Since $G > G_{\mathrm{gel}}(T)$, here the solution is gelled.

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D *Deposit, i.e. gel with no diffusion of liquid wax*. This is the region where the solution is in the gel state and $G_{\mathrm{dep}} < G$. Here liquid wax does not diffuse.

E *Solid phase*. This is the region where the temperature is below the oil solidification point T_{s}. Here both oil and wax are present in the solid phase only.

3 A model problem

We model the process of gelification and mass diffusion of wax for a stationary non-isothermal waxy oil. For simplicity we study the one-dimensional case of a solution confined between two parallel plates $x = 0$ (the cold wall) and $x = L$ (the warm wall). All the quantities entering the model depend on (x, t) only. The system consists of a waxy solution with concentration c^* that is pre-heated to a temperature $T_{\mathrm{w}} > T^*_{\mathrm{cp}}$. Subsequently the temperature at the wall $x = 0$ is gradually lowered to a temperature below T^*_{cp}.

Denoting the thermal field by $T(x, t)$, we thus impose $T(0, t) = T_{\mathrm{c}}(t) \in C^1([0, \infty))$, where $T_{\mathrm{c}}(0) = T_{\mathrm{w}}$, $\dot{T}_{\mathrm{c}}(t) < 0$ and $\lim_{t\to\infty} T_{\mathrm{c}}(t) = T_{\mathrm{a}} < T^*_{\mathrm{cp}}$, meaning that the temperature at the cold wall falls below T^*_{cp} in a finite time. Moreover, we require that $T_{\mathrm{a}} > T_{\mathrm{s}}$, the oil solidification temperature.

3.1 The thermal problem

We start by studying the thermal problem in the region $0 < x < L$, taking into account the latent heat of fusion of wax λ and assuming that the heat conductivity k, density ρ and specific heat c_{T} are everywhere constant. The thermal problem is given by

$$\begin{cases} \dfrac{\partial T}{\partial t} = \left(\dfrac{k}{\rho c_{\mathrm{T}}}\right)\dfrac{\partial^2 T}{\partial x^2} + \left(\dfrac{\lambda}{\rho c_{\mathrm{T}}}\right)\dfrac{\partial G}{\partial t}, & 0 < x < L, \quad t > 0, \\ T(0, t) = T_{\mathrm{c}}(t), & t > 0, \\ T(L, t) = T_{\mathrm{w}}, & t > 0, \\ T(x, 0) = T_{\mathrm{w}}, & 0 < x < L, \end{cases} \tag{4}$$

where the source term in the heat equation is due to the formation of solid crystals (see [16]). Such a term can be actually neglected. As we shall see in Section 3.5, G evolves basically according to

$$\frac{\partial G}{\partial t} = -\beta\left(1 - \frac{D}{D_{\mathrm{T}}}\right)\frac{\partial T}{\partial t}, \tag{5}$$

where D is dissolved wax diffusivity and $D_{\mathrm{T}} = k/\rho c_{\mathrm{T}}$ is thermal diffusivity (taking (5) is enough to determine the order of magnitude). Therefore equation $(4)_1$ becomes

$$\frac{\partial T}{\partial t} = \left(\frac{k}{\rho c_{\mathrm{T}}}\right)\frac{\partial^2 T}{\partial x^2} - \left(\frac{\lambda\beta}{\rho c_{\mathrm{T}}}\right)\left(1 - \frac{D}{D_{\mathrm{T}}}\right)\frac{\partial T}{\partial t}. \tag{6}$$

From (1) a natural scaling for temperature T and concentration G is

$$T^* = \frac{T\beta}{c'}, \qquad G^* = \frac{G}{c'}, \tag{7}$$

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where c' represents a typical concentration. The non-dimensional version of (6) is

$$\frac{\partial T^*}{\partial t^*} = \left(\frac{t'k}{\rho c_T L^2}\right)\frac{\partial^2 T^*}{\partial x^{*2}} - \left(\frac{\lambda\beta}{\rho c_T}\right)\left(1 - \frac{D}{D_T}\right)\frac{\partial T^*}{\partial t^*}, \tag{8}$$

where time and space have been re-scaled by t' and L respectively. The natural choice for t' is

$$t' = \frac{\rho c_T L^2}{k}, \tag{9}$$

and (8) becomes

$$\frac{\partial T^*}{\partial t^*} = \frac{\partial^2 T^*}{\partial x^{*2}} - \left(\frac{\lambda\beta}{\rho c_T}\right)\left(1 - \frac{D}{D_T}\right)\frac{\partial T^*}{\partial t^*}. \tag{10}$$

In $(10)_1$ we are interested in the non-dimensional quantity

$$\frac{\lambda\beta}{\rho c_T}\left(1 - \frac{D}{D_T}\right), \tag{11}$$

where $D < D_T$. With typical values $\lambda = 2 \times 10^5$ (J/kg), $\rho = 8 \times 10^2$ (kg/m^3), $c_T = 2 \times 10^3$ (J/kg K), $\beta = 2 \times 10^{-2}$ (kg/m^{3}K) we get

$$\frac{\lambda\beta}{\rho c_T} = 2.5 \times 10^{-3}, \tag{12}$$

so that the term involving the latent heat in the heat balance equation can be neglected and problem (4) becomes

$$\begin{cases} \dfrac{\partial T}{\partial t} = \left(\dfrac{k}{\rho c_T}\right)\dfrac{\partial^2 T}{\partial x^2}, & 0 < x < L, \quad t > 0, \\ T(0,t) = T_c(t), & t > 0, \\ T(L,t) = T_w, & t > 0, \\ T(x,0) = T_w, & 0 < x < L. \end{cases} \tag{13}$$

The thermal problem is thus de-coupled from the one for the evolution G. The asymptotic steady state of (13) is given by

$$T_\infty(x) = T_a + \frac{x}{L}(T_w - T_a), \quad \frac{dT_\infty}{dx} = \frac{(T_w - T_a)}{L}. \tag{14}$$

We will assume that the initial and boundary data of (13) are such that $\frac{\partial T}{\partial t}(x,t) < 0$, $\frac{\partial T}{\partial x}(x,t) > 0$, $\frac{\partial^2 T}{\partial t \partial x}(x,t) > 0$ for any (x,t). This could be obtained for example, by imposing a gradient $\frac{\partial T}{\partial x}(0,t) > 0$ such that $\frac{\partial T}{\partial t}(0,t) < 0$ and $\frac{\partial^2 T}{\partial t \partial x}(0,t) > 0$. The feasibility of this procedure is easy to prove.

3.2 Evolution of the system

In stage 1 the solution is everywhere unsaturated, since initially temperature is above T^*_{cp} and all wax is dissolved in the solution at the uniform concentration c^*. Stage 1 ends when temperature at the cold wall reaches T^*_{cp}. In stage 2 a deposition front starts propagating

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from the cold wall with a growth rate proportional to the flux of liquid wax. Indeed, as we have seen in the previous sections, the wax flux through a saturated region not occupied by the deposit is proportional to the temperature gradient, whereas there can be no wax flux through the boundary $x=0$. This fact prevents the formation of a saturated region soon after the exit of stage 1, since the wax flux cannot reach immediately the required value (by continuity the flux is initially close to zero, while the temperature gradient is already away from zero). Therefore the incoming liquid wax segregates, forming a deposition region of increasing thickness η in which there is no mass transfer. On the deposit front, the flux of dissolved wax steadily increases (due to the progressively depletion of the unsaturated region) and, depending on the cooling rate of the system, it may become equal to the flux necessary for saturation to occur, i.e. $D\frac{\partial c(\eta,t)}{\partial x}=D\frac{\partial c_s(T(\eta,t))}{\partial x}$. If this happens the system enters stage 3 and we observe the growth of a mushy region of co-existence of liquid wax, at saturation concentration, and of segregated wax. At the beginning of stage 3, a saturation front $x=\xi(t)$ appears and the domain that does not contain the deposition region is divided into a mushy zone and an unsaturated zone.

The saturation front moves away from the deposit front as long as $\frac{\partial c(\xi,t)}{\partial x}-\frac{\partial c_s(T(\xi,t))}{\partial x}=0$. However, when the liquid wax diffusing from the unsaturated phase becomes insufficient to feed the liquid wax diffusing towards the mushy region, the front reverses direction and solid wax is dissolved to keep the flux balance at the interface between the saturated and unsaturated regions. This marks the passage to stage 4, which is therefore characterized by the depletion of solid wax. Stage 4 ends when only the unsaturated region and the deposition region are left in the system. Thus, in stage 5 the system is divided into the still growing deposit and the unsaturated zone. In the limit $t\to\infty$, the concentration profile in the unsaturated part becomes uniform and equilibrium is reached. If stages 3 and 4 are not present the whole process consists of only the first two stages.

During stage 1, $G(x,t)=0$, $c(x,t)=c^*$, no deposition occurs and we have just a standard thermal problem. In stage 2 we have a free boundary problem in the unsaturated zone. The free boundary represents the deposition front. During stages 3 and 4, in the unsaturated region, $G=0$ and c is obtained solving a free boundary problem for the interface between the saturated and unsaturated phases. In stage 4, the free boundary is generally non-monotone. In stages 2 and 5 we have a free boundary problem for the deposition front. In figure 3 the domain of the problem and the free boundaries are shown.

A parameter playing a major role in the model is the diffusivity of dissolved wax D_c, which in the previous literature was assumed to be constant out of the 'solid' deposit (see [4, 5, 10–12]). Here we assume that the gel allows the diffusion of dissolved wax, but only to a certain extent. In particular we assume that $D_c\in C^2$ and

$$\begin{cases} D_c(G,T)=D>0, & \text{when } G<G_{gel}(T),\\ \dfrac{\partial D_c(G,T)}{\partial T}>0,\ \dfrac{\partial^2 D_c(G,T)}{\partial T^2}<0 & \text{when } G_{gel}(T)<G<G_{dep},\\ \dfrac{\partial D_c(G,T)}{\partial G}<0,\ \dfrac{\partial^2 D_c(G,T)}{\partial G^2}<0 & \text{when } G_{gel}(T)<G<G_{dep},\\ D_c(G,T)=0 & \text{when } G>G_{gel}(T). \end{cases} \tag{15}$$

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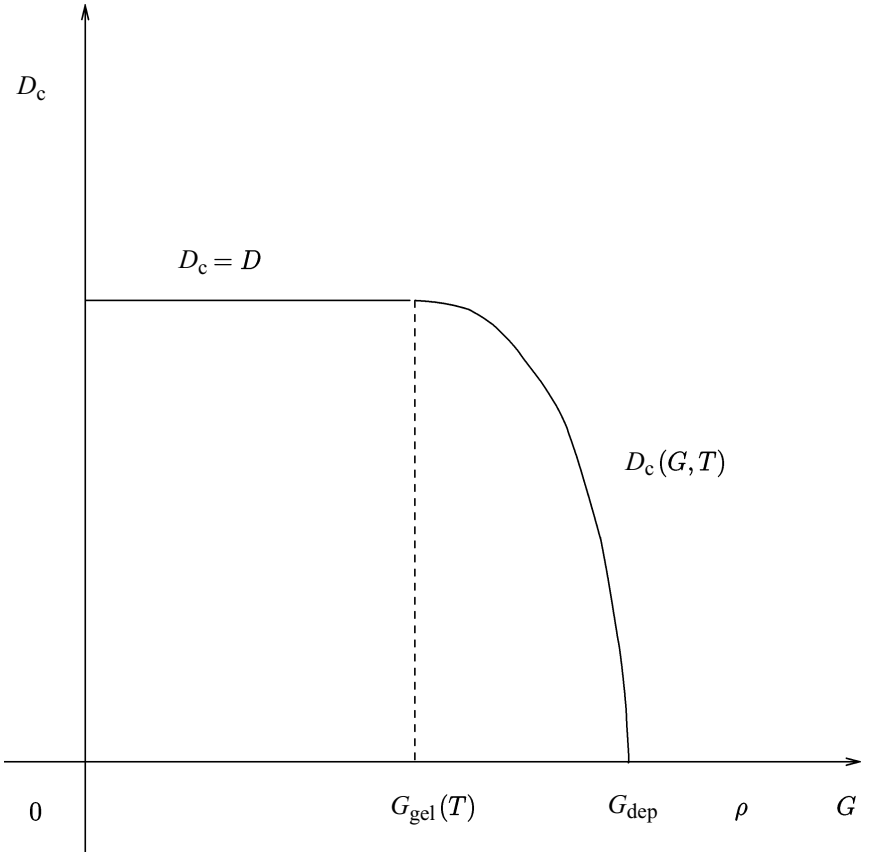


FIGURE 2. Plot of $D_c(G, T)$ for a fixed $T < T^*_{cp}$.

With reference to Figure 1, (15) is equivalent to

$$\begin{cases} D_c(G,T) = D > 0, & \text{in } A \text{ and } B, \\ \dfrac{\partial D_c(G,T)}{\partial T} > 0, \ \dfrac{\partial^2 D_c(G,T)}{\partial T^2} < 0, & \text{in } C, \\ \dfrac{\partial D_c(G,T)}{\partial G} < 0, \ \dfrac{\partial^2 D_c(G,T)}{\partial G^2} < 0, & \text{in } C, \\ D_c(G,T) = 0 & \text{in } D. \end{cases} \tag{16}$$

The reason for assumptions (15) will be clarified in Section 4, while an example of D_c with the above properties is given in the appendix. The behaviour of D_c for a fixed $T < T^*_{cp}$ is depicted in Figure 2.

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3.3 Stage 1

The concentration of wax c^*defines $T^*_{\rm cp}$ via

$$c^* = c_{\rm s}(T^*_{\rm cp}) \quad [< c_{\rm s}(T_{\rm w})]. \tag{17}$$

The solution is initially everywhere unsaturated with $c(x,t) = c^*$ and, as long as the temperature stays above $T^*_{\rm cp}$, no diffusion of wax occurs. Indeed, neglecting the Soret's effect, when the solution is unsaturated a temperature gradient does not induce a concentration gradient and consequently there is no diffusion of liquid wax. Of course during this stage $G(x,t) = 0$ everywhere.

3.4 Stage 2

At some time $t_\eta > 0$ the temperature at the cold wall $x = 0$ falls below the cloud point $T^*_{\rm cp}$ and a deposition region of increasing thickness $\eta(t)$ is formed. On the front $x = \eta(t)$, G takes the value $G_{\rm dep}$ at which $D_{\rm c}$ vanishes. Such a front is obtained by solving the free boundary problem

$$(FBP2)\begin{cases} \dfrac{\partial c}{\partial t} = \dfrac{\partial}{\partial x}\left(D\dfrac{\partial c}{\partial x}\right), & \text{in } \eta(t) < x < L, \quad t > t_\eta, \\ c(x,t_\eta) = c^*, & 0 = \eta(t_\eta) \leqslant x \leqslant L, \\ \dfrac{\partial c}{\partial x}(L,t) = 0, & t > t_\eta, \\ c(\eta,t) = c_{\rm s}(T(\eta,t)), & t > t_\eta, \\ D\dfrac{\partial c}{\partial x}(\eta,t) = \dot\eta G_{\rm dep}, & t > t_\eta, \\ \eta(t_\eta) = 0. \end{cases} \tag{18}$$

Note that the deposit front grows with initial zero velocity, i.e. $\dot\eta(t_\eta) = 0$, since the initial mass flux $D\frac{\partial c}{\partial x}(\eta(t_\eta), t_\eta) = 0$. Indeed the front on which $c = c_{\rm s}$ cannot enter the region in which $T > T^*_{\rm cp}$ and therefore it must have a finite slope implying the continuity of $\frac{\partial c}{\partial x}$. It is precisely for this reason that the mass flowing to the cold wall cannot diffuse further and has to segregate forming a deposition region. Depending on the way the system is cooled, it may happen that at some time $t_\xi > t_\eta$ we have

$$D\frac{\partial c}{\partial x}_{|(\eta(t_\xi),t_\xi)} = D\frac{\partial c_{\rm s}}{\partial x}_{|(\eta(t_\xi),t_\xi)} = D\beta\frac{\partial T}{\partial x}_{|(\eta(t_\xi),t_\xi)}, \tag{19}$$

where $0 < \beta = dc_{\rm s}/dT$, thus allowing the appearance of a mushy region. In this case a saturation front $x = \xi(t)$ starting from $x = \eta(t_\xi)$ will propagate and the system passes to stage 3. The duration of stage 2 will be called *waiting time*, since it is the time interval needed to build up the mass flux (19). It can be finite, in which case the process evolves through stage 3, or infinite, in which case the saturated region never appears.

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3.5 Stage 3

Suppose that the system enters stage 3. In the unsaturated zone the pair (c, ξ) satisfies the free boundary problem

$$(FBP3)\begin{cases} \dfrac{\partial c}{\partial t} = \dfrac{\partial}{\partial x}\left(D\dfrac{\partial c}{\partial x}\right), & \text{in } \xi(t) < x < L, \quad t > t_\xi, \\ c(x, t_\xi) = \bar{c}(x), & 0 = \xi(t_\xi) \leqslant x \leqslant L, \\ \dfrac{\partial c}{\partial x}(L, t) = 0, & t > t_\xi, \\ c(\xi, t) = c_s(T(\xi, t)), & t > t_\xi, \\ \dfrac{\partial c}{\partial x}(\xi, t) = \beta\dfrac{\partial T}{\partial x}(\xi, t), & t > t_\xi, \\ \xi(t_\xi) = \eta(t_\xi), \end{cases} \tag{20}$$

where $\bar{c}(x)$ is obtained from stage 2. The last equation expresses flux continuity across the saturation interface, consistent with the assumption that the segregated phase has no mobility and so it does not contribute to the mass balance at the boundary $x = \xi(t)$. In the domain $\{(x, t) : \ \eta(t) < x < \xi(t), \ \ t > t_\xi\}$ the solution is saturated so that $c = c_s(T)$ and $G > 0$.

The evolution of G is determined by the different diffusivities of heat and mass. Indeed, from $dc_s/dT = \beta$, it follows that

$$\left(\frac{\partial}{\partial t} - D\frac{\partial^2}{\partial x^2}\right) c_s(T) = -Q \neq 0, \tag{21}$$

expressing the fact that, in order to keep local equilibrium, the transformation $c_s \to G$ has to occur at the rate Q per unit volume, namely

$$\frac{\partial G}{\partial t} = Q. \tag{22}$$

From (21), (22) we get

$$\frac{\partial G}{\partial t} = -\mu\frac{\partial T}{\partial t}, \tag{23}$$

where

$$\mu = \beta\left(1 - \frac{D}{D_T}\right) > 0, \tag{24}$$

$D_T = (k/\rho c_T)$ being thermal diffusivity. The constant μ is positive since D is smaller than D_T. Integrating (23) between $\xi^{-1}(x)$ (where $G = 0$) and t we get

$$G(x, t) = -\mu[T(x, t) - T(x, \xi^{-1}(x))], \tag{25}$$

which gives the concentration of solid wax in the saturated region (region B of Figure 1). As G evolves, dissolved wax keeps diffusing towards the deposition front, and, once it

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meets $x = \eta(t)$, it segregates, forming a deposit of saturated oil and solid crystals, which now grows according to[2]

$$[G_{\text{dep}} - G(\eta^+, t)]\dot{\eta} = D\beta \frac{\partial T}{\partial x}(\eta, t), \tag{26}$$

where $G(\eta^+, t)$ is given by (25) evaluated at $x = \eta(t)$, that is

$$G(\eta^+, t) = -\mu \left[T(\eta^+, t) - T(\eta^+, \xi^{-1}(\eta^+)) \right]. \tag{27}$$

The deposit growth is due to the combined action of diffusion of dissolved wax and absorption of solid crystals by the advancing front.

3.6 Stage 4

At some time $t_\delta > t_\xi$, the dissolved wax diffusing to the interface $x = \xi(t)$ from the unsaturated region will no longer be enough to balance the wax leaving the same interface in the saturated zone, so that $\dot{\xi}(t_\delta) = 0$. For $t > t_\delta$ solid crystals must be dissolved in order to balance the mass flux on the saturation front $x = \xi(t)$, which for $t > t_\delta$, will be towards the boundary. This new front, which may be called the *crystal depletion front*, will thus be given by a temporarily non-increasing function $x = \delta(t)$, obtained by solving the free boundary problem

$$(FBP4) \begin{cases} \dfrac{\partial c}{\partial t} = \dfrac{\partial}{\partial x}\left(D \dfrac{\partial c}{\partial x} \right), \quad \text{in } \delta(t) < x < L, \quad t > t_\delta, \\ c(x, t_\delta) = \bar{\bar{c}}(x), \quad \delta(t_\delta) \leqslant x \leqslant L, \\ \dfrac{\partial c}{\partial x}(L, t) = 0, \quad t > t_\delta, \\ c(\delta, t) = c_{\text{s}}(T(\delta, t)), \quad t > t_\delta, \\ -G(\delta, t)\dot{\delta} + D \dfrac{\partial c}{\partial x}(\delta, t) = D_{\text{c}}(G, T)_{|(\delta,t)} \beta \dfrac{\partial T}{\partial x}(\delta, t), \quad t > t_\delta, \\ \delta(t_\delta) = \xi(t_\delta), \end{cases} \tag{28}$$

where $\bar{\bar{c}}(x)$ is obtained from stage 3 and $G(\delta, t)$ is given by (25) evaluated at $x = \delta(t)$, that is

$$G(\delta, t) = -\mu[T(\delta, t) - T(\delta, \xi^{-1}(\delta))]. \tag{29}$$

On the deposit front, at some time $t = t_\gamma$, the function $G(\eta^+, t)$ may reach G_{gel}, i.e.

$$G(\eta^+(t_\gamma), t_\gamma) = G_{\text{gel}}(T(\eta^+(t_\gamma), t_\gamma)). \tag{30}$$

In this case the front $x = \gamma(t)$, defined by the implicit equation

$$G_{\text{gel}}(T(\gamma(t), t)) = -\mu[T(\gamma(t), t) - T(\gamma(t), \xi^{-1}(\gamma(t)))], \tag{31}$$

[2] $G(z^+, t)$ stands for $\lim_{x \to z^+ 0} G(x, t)$.

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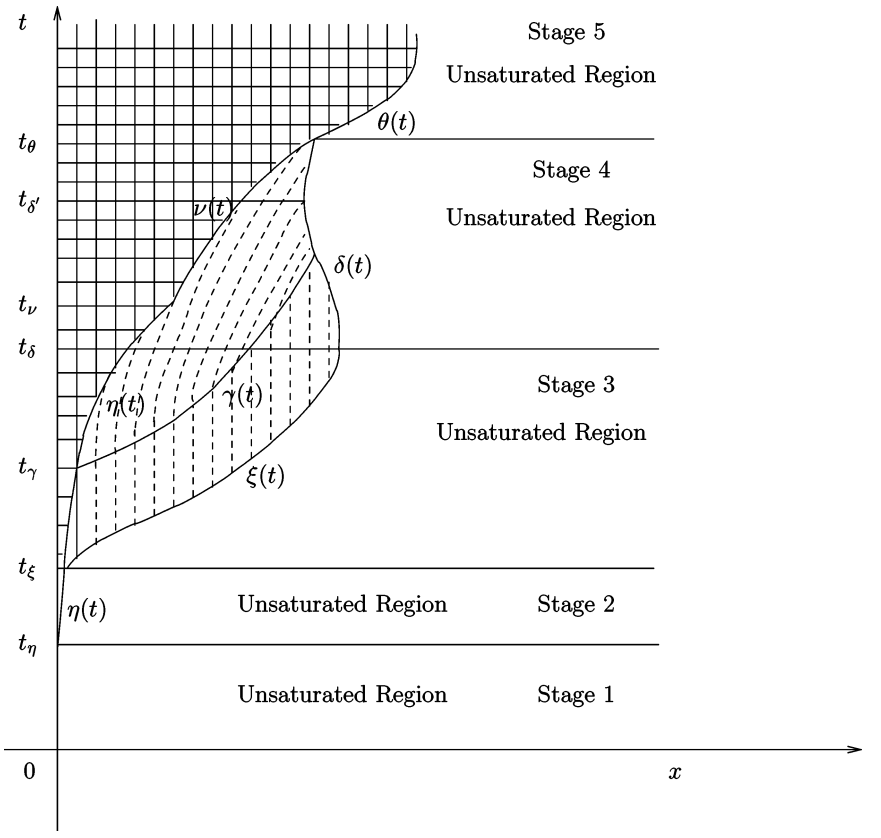


FIGURE 3. Sketch of the interfaces. The grid represents the deposition region. The dotted lines are the characteristics in the saturated region.

appears[3]. For $x > \gamma(t)$, $G(x,t)$ is still evaluated from (25). For $\eta(t) < x < \gamma(t)$, we have to reformulate the problem for G and c_s, since in this region the diffusivity D_c depends on G and T, according to (15). We have

$$\frac{\partial G}{\partial t} = \frac{\partial}{\partial x}\left(\beta D_c \frac{\partial T}{\partial x}\right) - \beta \frac{\partial T}{\partial t}, \tag{32}$$

and we obtain

$$\begin{cases} \dfrac{\partial G}{\partial t} - \dfrac{\partial G}{\partial x}\left(\beta \dfrac{\partial D_c}{\partial G}\dfrac{\partial T}{\partial x}\right) = \beta\left(\dfrac{D_c}{D_T} - 1\right)\dfrac{\partial T}{\partial t} + \beta \dfrac{\partial D_c}{\partial T}\left(\dfrac{\partial T}{\partial x}\right)^2, \\ G(\gamma,t) = G_{gel}(T(\gamma,t)) = -\mu[T(\gamma,t) - T(\gamma,\xi^{-1}(\gamma))], \end{cases} \tag{33}$$

where the r.h.s. of $(33)_1$ is obtained making use of $(13)_1$.

[3]This front is more correctly defined as $t = \Gamma(x)$, but we will see later that this function is invertible.

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The solution of (33) can be obtained by the method of characteristics, which requires us to solve the non-linear system

$$\begin{cases} \dfrac{dt}{d\tau} = 1, \\ \dfrac{dx}{d\tau} = -\left(\beta \dfrac{\partial D_c}{\partial G}\dfrac{\partial T}{\partial x}\right), \\ \dfrac{dG}{d\tau} = \beta\left(\dfrac{D_c}{D_T} - 1\right)\dfrac{\partial T}{\partial t} + \beta \dfrac{\partial D_c}{\partial T}\left(\dfrac{\partial T}{\partial x}\right)^2. \end{cases} \tag{34}$$

Note that the r.h.s of $(34)_3$ is positive (recall that $\frac{\partial T}{\partial t} < 0$ and $D_c < D_T$), meaning that G is increasing along the characteristics. Of course due to the non-linearity of problem (33) we might have self-intersecting characteristics. The mathematical structure of this problem will be studied in Section 4.3.

In the region $\eta(t) < x < \gamma(t)$ the function $G(x,t)$ is given by the solution of (33). For $t > t_\gamma$ the deposit layer continues to grow according to (26), where $G(\eta^+, t)$ is now evaluated by means of the solution $G(x,t)$ of (33). Since G is increasing along the characteristics, at some time $t = t_v$ it may reach G_{dep}, so that

$$D_c(G(\eta^+(t_v), t_v), T(\eta(t_v), t_v) = 0. \tag{35}$$

For $t > t_v$ the deposit interface grows along the level set $x = v(t)$ defined by the implicit relation[4] $G(x,t) = G_{dep}$, where $G(x,t)$ is the solution of (33). On $x = v(t)$ the diffusivity $D_c = 0$ and the deposit grows only because the gel thickens due to cooling.

If the front v does not appear, the front $x = \delta(t)$ may hit the deposit front while still decreasing and we pass directly to stage 5. If, on the other hand, the front v does appear, the interface $\delta(t)$ has to reverse its motion before meeting the deposition front. Indeed if we assume that $\delta = v$ and $\dot{\delta} \leqslant 0$ for some finite time, then by $(28)_5$,

$$G_{dep}\dot{\delta} = D\left.\frac{\partial c}{\partial x}\right|_{|x=\delta}, \tag{36}$$

where the l.h.s is non-positive and the r.h.s is positive. Therefore, in this case, there must be a finite time $t_{\delta'}$ such that $\dot{\delta}(t_{\delta'}) = 0$ leaving a gap $\delta(t_{\delta'}) - v(t_{\delta'}) > 0$. The characteristics of problem (33) entering the gap belong to two families: one defines the continuation of v and the other provides the value of G to be used in the free boundary condition $(28)_5$, where $\dot{\delta}$ is now positive. Stage 4 ends at time t_θ when $v(t)$ meets $\delta(t)$.

[4]We shall see that under our assumptions the representation $x = v(t)$ is appropriate.

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3.7 Stage 5

For $t > t_\theta$ we have to solve the following problem in the unsaturated domain:

$$(FBP5)\begin{cases} \dfrac{\partial c}{\partial t} = \dfrac{\partial}{\partial x}\left(D\dfrac{\partial c}{\partial x}\right), \quad \text{in } \theta(t) < x < L, \quad t > t_\theta \\ c(x,t_\theta) = \bar{\bar{c}}(x), \qquad \theta(t_\theta) < x < L \\ \dfrac{\partial c}{\partial x}(L,t) = 0, \quad t > t_\theta \\ c(\theta,t) = c_s(T(\theta,t)), \qquad t > t_\theta \\ G_{dep}\dot{\theta} = D\dfrac{\partial c}{\partial x}(\theta,t), \qquad t > t_\theta \\ \theta(t_\theta) = \delta(t_\theta) = v(t_\theta), \end{cases} \tag{37}$$

where $\bar{\bar{c}}(x)$ is taken from stage 4. The free boundary condition $(37)_5$ is the evolution equation for the deposition region, whose growth is now due to diffusion of liquid wax only, as in stage 2. In the limit $t \to +\infty$, the concentration profile in the unsaturated region becomes uniform and $\theta \to \theta_\infty < L$. The concentration of wax in the unsaturated region will be given by $c(\theta_\infty) = c_s(T(\theta_\infty))$. The final deposit thickness θ_∞ can be evaluated by means of the following mass balance

$$c^* L = \int_0^{\theta_\infty} G_\infty(x)\,dx + \int_0^{\theta_\infty} c_s(T_\infty(x))\,dx + c_s(T_\infty(\theta_\infty))(L - \theta_\infty). \tag{38}$$

In (38) $G_\infty(x)$ is the asymptotic concentration of solid wax in the deposit and it will be found in the next section. In Lemma 7 of Section 4.1 we will give a sufficient condition for the existence and uniqueness of θ_∞.

3.8 Evolution of the deposition region: The ageing process

The deposition region is characterized by the fact that no diffusion of liquid and solid wax is allowed. The evolution of the solid wax concentration (ageing) is thus given by

$$\frac{\partial G}{\partial t} = -\beta\frac{\partial T}{\partial t}, \tag{39}$$

i.e. (23) with $D = 0$. Integration yields

$$G(x,t) = G_{dep} - \beta[T(x,t) - T(x,\eta^{-1}(x))]. \tag{40}$$

Taking the limit $t \to \infty$ we get

$$G_\infty(x) = G_{dep} - \beta[T_\infty(x) - T(x,\eta^{-1}(x))]. \tag{41}$$

Notice that, due to the dependence on η, G_∞ depends on whole history of the deposition region.

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4 Analytical results

The inequalities

$$\frac{\partial T}{\partial t} < 0, \quad \frac{\partial T}{\partial x} > 0, \quad \frac{\partial^2 T}{\partial t \partial x} > 0, \tag{42}$$

already discussed in the previous section, play a fundamental role in what follows. We stress this fact by stating the assumption

(HT) The boundary data for $T(x,t)$ guarantee $T(x,t) \in C^{4+\alpha,2+\alpha}([0,L]\times[0,\infty))$ and (42).

Concerning the function $D_c(G,T)$ we suppose

(HD) $D_c(G,T) \in C^2([0,G_{\text{dep}}]\times[T_a,T_w])$ and satisfies (15).

We also recall that

(HG) $G_{\text{gel}}(T) \in C^1$ with $G'_{\text{gel}} > 0$ and $G_{\text{gel}} < G_{\text{dep}}$ in its domain of definition.

4.1 Some *a priori* properties of the interfaces

Remark 1 Having $\frac{\partial T}{\partial t}(x,0) = \frac{\partial^2 T}{\partial x^2}(x,0) = \frac{\partial T}{\partial t}(L,t) = 0$ and requiring $\frac{\partial T}{\partial x}(0,t) > 0$ forces $\frac{\partial^2 T}{\partial t^2}(0,t)$ to take negative values. The implication is that $\frac{\partial^2 T}{\partial t^2}(x,t)$ cannot have constant sign, since $\frac{\partial^2 T}{\partial t^2}$ has to become positive to satisfy $T(0,t) \to T_a$.

Remark 2 By the maximum principle, $c(x,t) < c^*$ for all $t > t_\eta$, since $\frac{\partial c}{\partial x} = 0$ on $x = L$ and $\frac{\partial c}{\partial x} > 0$ on all the interfaces bounding the unsaturated region. As a consequence all the interfaces at which the value $c = c_s$ will stay to the left of the isotherm $T = T^*_{\text{cp}}$.

Lemma 1 *The boundary $x = \gamma(t)$ is strictly increasing, i.e. $\dot\gamma(t) > 0$.*

Proof Differentiating (31) w.r.t. time we get

$$\left[G'_{\text{gel}}(T(\gamma,t))\frac{\partial T}{\partial x}(\gamma,t) + \mu\frac{\partial T}{\partial x}(\gamma,t) - \mu\frac{\partial T}{\partial x}(\gamma,\xi^{-1}(\gamma)) - \mu\frac{\partial T}{\partial t}(\gamma,\xi^{-1}(\gamma))\frac{d\xi^{-1}}{dx}(\gamma)\right]\dot\gamma$$
$$= -\mu\frac{\partial T}{\partial t}(\gamma,t). \tag{43}$$

Relation (43) can be rewritten as

$$\left[G'_{\text{gel}}(T(\gamma,t))\frac{\partial T}{\partial x}(\gamma,t) + \mu\frac{\partial^2 T}{\partial x \partial t}(\gamma,\tau)(t-\xi^{-1}(\gamma)) - \mu\frac{\partial T}{\partial t}(\gamma,\xi^{-1}(\gamma))\frac{d\xi^{-1}}{dx}(\gamma)\right]\dot\gamma = -\mu\frac{\partial T}{\partial t}(\gamma,t), \tag{44}$$

where the terms in square brackets are positive from *(HT)* and *(HG)*, and where τ is a suitable instant in $(\xi^{-1}(\gamma),t)$. This yields $\dot\gamma > 0$. □

Lemma 2 *The boundary $x = \gamma(t)$ never meets either $x = \xi(t)$ or $x = v(t)$.*

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Proof If $\gamma(t)=\xi(t)$ for some finite t, then $G(\xi(t),t)=G_{\rm gel}(T(\xi(t),t))=0$, which is admissible only if $T(\xi(t),t)=T_{\rm s}$ (see Figure 1), which contradicts $\inf|T|=T_{\rm a}>T_{\rm s}$. As to $v(t)$, supposing $\gamma(t)=v(t)$, we have $G_{\rm gel}(T(v,t))=G_{\rm dep}$, contradicting $G_{\rm dep}>G_{\rm gel}$. □

The front v is generated when and if G reaches the value $G_{\rm dep}$. Such a front is defined implicitly but it can be represented as $x=v(t)$ by the following:

Lemma 3 *Under assumptions (HT), (HD)we have*

$$\frac{\partial G}{\partial x}<0 \tag{45}$$

throughout the gel.

Proof Let us first study the sign of $\frac{\partial G}{\partial x}$ on $\gamma(t)$. From (25)

$$G(\gamma,t)+\mu[T(\gamma,t)-T(\gamma,\xi^{-1}(\gamma))]=0. \tag{46}$$

Differentiating w.r.t. time

$$\frac{\partial G}{\partial x}\dot\gamma+\frac{\partial G}{\partial t}+\mu\left[\frac{\partial T}{\partial x}\dot\gamma+\frac{\partial T}{\partial t}\right]-\mu\left[\frac{\partial T}{\partial x}\dot\gamma+\frac{\partial T}{\partial t}\frac{\dot\gamma}{\dot\xi}\right]\Bigg|_{t=\xi^{-1}(\gamma)}=0. \tag{47}$$

From (23) we have that $\frac{\partial G}{\partial t}=-\mu\frac{\partial T}{\partial t}$ and therefore

$$\frac{\partial G}{\partial x}\Big|_{x=\gamma}=-\mu\left(\frac{\partial T}{\partial x}-\frac{\partial T}{\partial x}\Big|_{t=\xi^{-1}(\gamma)}\right)+\frac{\mu}{\dot\xi}\frac{\partial T}{\partial t}\Big|_{t=\xi^{-1}(\gamma)}<0 \tag{48}$$

by (HT). We set $\Lambda=\frac{\partial G}{\partial x}$ and differentiate equation $(33)_1$ w.r.t. x, obtaining

$$\begin{aligned}\frac{\partial\Lambda}{\partial t}-\frac{\partial\Lambda}{\partial x}\left(\beta\frac{\partial D_{\rm c}}{\partial G}\frac{\partial T}{\partial x}\right)&=\Lambda\beta\left[2\frac{\partial^2 D_{\rm c}}{\partial G\partial T}\left(\frac{\partial T}{\partial x}\right)^2+\frac{1}{D_{\rm T}}\frac{\partial D_{\rm c}}{\partial G}\frac{\partial T}{\partial t}+\frac{\partial D_{\rm c}}{\partial G}\frac{\partial^2 T}{\partial x^2}\right]\\&+\Lambda^2\beta\left[\frac{\partial^2 D_{\rm c}}{\partial G^2}\frac{\partial T}{\partial x}\right]+\beta\left[\frac{1}{D_{\rm T}}\frac{\partial D_{\rm c}}{\partial T}\frac{\partial T}{\partial x}\frac{\partial T}{\partial t}+\left(\frac{D_{\rm c}}{D_{\rm T}}-1\right)\frac{\partial^2 T}{\partial x\partial t}+\frac{\partial^2 D_{\rm c}}{\partial T^2}\left(\frac{\partial T}{\partial x}\right)^3\right.\\&\left.+2\frac{\partial D_{\rm c}}{\partial T}\frac{\partial T}{\partial x}\frac{\partial^2 T}{\partial x^2}\right]=:A\Lambda^2+B\Lambda+C.\end{aligned} \tag{49}$$

Notice that, owing to (HT), (HD), the coefficients A and C are negative. Equation (49) can be rewritten as

$$\frac{d\Lambda}{d\tau}-B\Lambda=A\Lambda^2+C, \tag{50}$$

where $d\Lambda/d\tau$ represents the rate of change of Λ along the characteristic. Integrating (50) with the initial datum $\Lambda|_\gamma$ we get

$$\Lambda=\exp\left\{\int_0^\tau B\,d\tau'\right\}\left[\Lambda|_\gamma+\int_0^\tau[A\Lambda^2+C]\exp\left\{-\int_0^{\tau'}B\,d\tau''\right\}d\tau'\right], \tag{51}$$

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where the quantity in square brackets in (51) is negative since $\Lambda|_\gamma = \frac{\partial G}{\partial x}|_\gamma < 0$ and $A\Lambda^2 + C < 0$. We conclude that $\Lambda < 0$ everywhere in the gel. Therefore, when it appears, the level set $G = G_{\text{dep}}$ defines a front $x = v(t)$. □

We can say more:

Lemma 4 *The same assumptions as Lemma 3 guarantee that, when it exists, the boundary $x = v(t)$ propagates faster than the characteristics of equation (33).*

Proof We differentiate G w.r.t. time along the level set $G = G_{\text{dep}}$, and along a characteristic we get

$$\frac{\partial G}{\partial x}\dot{v} + \frac{\partial G}{\partial t} = 0, \tag{52}$$

$$\frac{\partial G}{\partial x}\dot{x} + \frac{\partial G}{\partial t} = H > 0, \tag{53}$$

where $H > 0$ is the r.h.s. of $(33)_1$ and $\dot{x}$ is the slope of the characteristic. Subtracting

$$\frac{\partial G}{\partial x}(\dot{v} - \dot{x}) = -H < 0. \tag{54}$$

Since $\frac{\partial G}{\partial x} < 0$ we conclude that $\dot{v} > \dot{x}$. □

An example of D_c satisfying (15) is given in the appendix. We also have the following:

Lemma 5 *The boundaries $x = \gamma(t)$ and $x = \delta(t)$ meet in a finite time.*

Proof No matter how thin the region between these boundaries is, it carries a mass flux which is bounded away from zero. If we allow the region to exist for all times we arrive at a contradiction, since asymptotically the concentration c in the unsaturated region will be uniform. □

Lemma 6 *The boundary $x = v(t)$ can only exist for a finite time.*

Proof This is a simple consequence of $(34)_3$ and (HD), which imply that the time taken by G to reach the value G_{dep} along any characteristic is finite. □

Remark 3 Lemmas 5 and 6 imply that both the mushy region and the diffusive gel disappear in a finite time.

Lemma 7 *If*

$$G_{\text{dep}} > \beta\left(T^*_{\text{cp}} - \frac{T_a + T_w}{2}\right) = c^* - c_s\left(\frac{T_a + T_w}{2}\right), \quad T \in [T_a, T_w], \tag{55}$$

then (38) defines the asymptotic thickness of the deposition region θ_∞ uniquely.

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Proof Recalling (1) we have

$$c_s(T_1) = c_s(T_2) + \beta(T_1 - T_2) \tag{56}$$

for given temperatures T_1, T_2. Therefore, from (41),

$$G_\infty(x) + c_s(T_\infty(x)) = G_{dep} + c_s(T(x, \eta^{-1}(x))). \tag{57}$$

We define the function

$$F(\theta_\infty) =: \int_0^{\theta_\infty} [G_{dep} + c_s(T(x, \eta^{-1}(x)))]\, dx + c_s(T_\infty(\theta_\infty))(L - \theta_\infty) - c^* L, \tag{58}$$

which is continuously differentiable in θ_∞. We have

$$F(0) = c_s(T_\infty(0))L - c^* L = \beta L \left[T_a - T^*_{cp}\right] < 0. \tag{59}$$

Moreover, since $T(x, \eta^{-1}(x)) > T_\infty(x)$, we have that $c_s(T(x, \eta^{-1}(x))) > c_s(T_\infty(x))$ and

$$F(\theta_\infty) > \int_0^{\theta_\infty} [G_{dep} + c_s(T_\infty(x))]\, dx + c_s(T_\infty(\theta_\infty))(L - \theta_\infty) - c^* L. \tag{60}$$

Thus

$$F(L) > \int_0^L [G_{dep} + c_s(T_\infty(x))]\, dx - c^* L = \int_0^L [G_{dep} + c^* + \beta[T_\infty(x) - T^*_{cp}]\, dx - c^* L,$$

and

$$F(L) > G_{dep} L + \beta L \left(\frac{T_a + T_w}{2} - T^*_{cp} \right) > 0, \tag{61}$$

because of (55). Differentiating (58) w.r.t. θ_∞ we get

$$\frac{dF}{d\theta_\infty} = G_\infty(\theta_\infty) + \beta \frac{T_w - T_a}{L}(L - \theta_\infty) > 0 \tag{62}$$

when $\theta_\infty \in (0, L)$. Inequalities (59), (61) and (62) prove the lemma. □

4.2 Existence of a classical solution of problems (FBP2), (FBP3), (FBP4)

Throughout this section, we assume that hypotheses *(HT)*, *(HD)*, *(HG)* hold true.

Theorem 1 *Problem (FBP2) has a unique solution* (c, η) *in the classical sense during the whole waiting time. The boundary* $x = \eta(t)$ *is such that* $0 < G_{dep}\dot{\eta} < \beta \frac{\partial T}{\partial x}(\eta, t)$ *and* $\dot{\eta}(t_\eta) = 0$. *Moreover,* $c < c_s$ *for* $\eta(t) < x < L$.

Proof Problem (FBP2) has Stefan data on the free boundary and well-posedness can be proved by means of standard arguments (see [8]). Reformulating (FBP2) for the difference

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$u(x,t) = c(x,t) - c_s(T(x,t))$, we get

$$\begin{cases} \dfrac{\partial u}{\partial t} - D\dfrac{\partial^2 u}{\partial x^2} = -\mu\dfrac{\partial T}{\partial t} > 0, \quad \text{in } \eta(t) < x < L, \quad t > t_\eta, \\ u(x,t_\eta) = c^* - c_s(T(x,t_\eta)) < 0, \quad 0 < x < L, \\ \dfrac{\partial u}{\partial x}(L,t) = -\beta\dfrac{\partial T}{\partial x}(L,t) < 0, \quad t > t_\eta, \\ u(\eta,t) = 0, \quad t > t_\eta, \\ G_{\text{dep}}\dot{\eta} = D\left(\dfrac{\partial u}{\partial x}(\eta,t) + \beta\dfrac{\partial T}{\partial x}(\eta,t)\right), \quad t > t_\eta, \\ \eta(t_\eta) = 0. \end{cases} \tag{63}$$

We have $\dot{\eta}(t_\eta) = 0$ and by definition $\frac{\partial u}{\partial x} < 0$ on the free boundary, and on the whole domain because $\frac{\partial^2 T}{\partial x \partial t} > 0$. Therefore we have the *a priori* bound $0 < G_{\text{dep}}\dot{\eta} < \beta\frac{\partial T}{\partial x}(\eta,t)$, guaranteeing existence up to $t = t_\xi$. Finally, we can establish that $\frac{\partial u}{\partial x} < 0$ by the maximum principle; $\frac{\partial u}{\partial x}(L,t) < 0$, $\frac{\partial u}{\partial x}(\eta,t) < 0$ by definition and $\frac{\partial^2 u}{\partial t \partial x} - D\frac{\partial^3 u}{\partial x^3} = -\mu\frac{\partial^2 T}{\partial x \partial t} < 0$, which implies $u < 0$. □

The retreating free boundary in (63) is due to the forcing term $\beta\frac{\partial T}{\partial x}$ in the Stefan condition and not to 'supercooling', thus excluding instabilities related to phase shrinking. Since the end of stage 2 (and thus of problem (FBP2)) is marked by $\frac{\partial u}{\partial x} = 0$, we find that the slope of the deposition front at the end of the waiting time is given by setting $\frac{\partial u}{\partial x} = 0$ in $(63)_5$:

$$\dot{\eta}(t_\xi) = \frac{D\beta}{G_{\text{dep}}}\frac{\partial T}{\partial x}(\eta(t_\xi), t_\xi). \tag{64}$$

The analysis of (FBP3) can also be based on [8] concerning local existence, but global existence is more complicated for a reason that will be clear soon (see [6] for a Stefan problem with non-monotone boundary). We conjecture that the assumptions used so far should guarantee not only existence and uniqueness, but also $\ddot{\xi} < 0$. However, we can give sufficient conditions to preclude the occurrence of blow-up which, in our case, is the only event which could terminate the solution in a finite time.

For t in a finite time interval (t_ξ, t^*) we put

$$A(t^*) = \sup_{t \in (t_\xi, t^*)} \left(-\mu\frac{\partial T}{\partial t}\right). \tag{65}$$

We observe that $A(t^*) > 0$ for all finite t^* by assumption. Next we get an upper estimate of time t_δ by calculating the finite time t^* at which the function $\tilde{c}(x,t)$ vanishes, where

$$\begin{cases} D\dfrac{\partial^2 \tilde{c}}{\partial x^2} - \dfrac{\partial \tilde{c}}{\partial t} = 0, \quad \text{in } \eta(t_\xi) < x < L, \quad t > t_\xi, \\ \tilde{c}(x,t_\xi) = c(x,t_\xi), \qquad \eta(t_\xi) = \xi(t_\xi) \leqslant x \leqslant L, \\ \dfrac{\partial \tilde{c}}{\partial x}(L,t) = 0, \quad t > t_\xi, \\ \dfrac{\partial \tilde{c}}{\partial x}(\eta(t_\xi),t) = b, \qquad t > t_\xi, \end{cases} \tag{66}$$

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and $b = \inf \frac{\partial c_s}{\partial x}$ for $t > t_\xi$, i.e. $b = \inf \beta \frac{\partial T}{\partial x}$ for $t > t_\xi$, which we know to be positive and given by $\beta \frac{\partial T}{\partial x}(L, t_\xi)$. Clearly $\tilde{c} > c$ for $t > t_\xi$. Therefore the lifespan of stage 3 is necessarily less than $t^* - t_\xi$, and hence $t_\delta < t^*$. We use precisely this t^* in (65).

In order to study the possible occurrence of blow-up, we first reformulate the problem in terms of the function $u = c - c_s$ as

$$\begin{cases} \dfrac{\partial u}{\partial t} - D\dfrac{\partial^2 u}{\partial x^2} = -\mu \dfrac{\partial T}{\partial t}, \quad \text{in } \xi(t) < x < L, \quad t > t_\xi, \\ u(x, t_\xi) = c(x, t_\xi) - c_s(T(x, t_\xi)), \qquad \eta(t_\xi) = \xi(t_\xi) \leqslant x \leqslant L, \\ \dfrac{\partial u}{\partial x}(L, t) = -\beta \dfrac{\partial T}{\partial x}(L, t), \quad t > t_\xi, \\ u(\xi, t) = 0, \qquad t > t_\xi, \\ \dfrac{\partial u}{\partial x}(\xi, t) = 0, \qquad t > t_\xi, \end{cases} \tag{67}$$

where $c(x, t_\xi)$ is taken from stage 2. We reduce this to a Stefan problem by taking the new unknown $Z = \frac{\partial u}{\partial t} = \frac{\partial}{\partial t}(c - c_s)$

$$\begin{cases} \dfrac{\partial Z}{\partial t} - D\dfrac{\partial^2 Z}{\partial x^2} = -\mu \dfrac{\partial^2 T}{\partial t^2}, \quad \text{in } \xi(t) < x < L, \quad t > t_\xi, \\ Z(x, t_\xi) = \dfrac{\partial c}{\partial t}(x, t_\xi) - \beta \dfrac{\partial T}{\partial t}(x, t_\xi), \qquad \eta(t_\xi) = \xi(t_\xi) \leqslant x \leqslant L, \\ \dfrac{\partial Z}{\partial x}(L, t) = -\beta \dfrac{\partial^2 T}{\partial x \partial t}(L, t), \quad t > t_\xi, \\ Z(\xi, t) = 0, \qquad t > t_\xi, \\ \dfrac{\partial Z}{\partial x}(\xi, t) = -\dfrac{\mu}{D} \dfrac{\partial T}{\partial t}(\xi, t)\dot{\xi}, \qquad t > t_\xi. \end{cases} \tag{68}$$

It is easy to see that Z does not have a constant sign (see also Remark 1 of Section 4.1). In particular we expect Z to be positive near the free boundary, but it can become negative, e.g. on $x = L$. In particular, the fact that $Z > 0$ close to the free boundary, so that phase is shrinking, makes it similar to a supercooled Stefan problem, for which blow-up can be a typical feature (for a review on non-standard Stefan problems see [7]).

A rather comprehensive analysis of the phenomenon of blow-up for parabolic free boundary problems with data of Cauchy type (like (67)) or of supercooled (superheated) Stefan type (like (68)) has been performed in a series of papers [9, 13, 14], but only in case of constant coefficients. We note for instance that in (68) the source is not constant and even has variable sign, and the 'latent heat', though of constant sign, is non-constant (although, by assumption, it is bounded away from zero in the time interval considered). Therefore the aforementioned results are not directly applicable to our case. However, we can give sufficient conditions for a supersolution not to blow-up. This result, jointly with the result of [8], enables us to continue the solution of (FBP3) up to the desired time.

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Lemma 8 *Suppose that at the end of stage 2 we have*

$$\frac{\partial u}{\partial t}(x, t_\xi) < A(t^*), \tag{69}$$

then there will be no blow-up during stage 3.

Proof We introduce the supersolution $(\hat{u}(x,t), \hat{\xi}(t))$ satisfying

$$\begin{cases} \dfrac{\partial \hat{u}}{\partial t} - D\dfrac{\partial^2 \hat{u}}{\partial x^2} = A(t^*), \quad \text{in } \hat{\xi}(t) < x < L, \ t > t_\xi, \\ \hat{u}(x, t_\xi) = u(x, t_\xi^-), \quad \eta(t_\xi) \leqslant x \leqslant L, \\ \dfrac{\partial \hat{u}}{\partial x}(L, t) = -b, \quad t > t_\xi, \\ \hat{u}(\hat{\xi}, t) = 0, \quad t > t_\xi, \\ \dfrac{\partial \hat{u}}{\partial x}(\xi, t) = 0, \quad t > t_\xi, \\ \hat{\xi}(t_\xi) = \eta(t_\xi), \end{cases} \tag{70}$$

where b has been defined above. By taking this supersolution, we have increased the chance of blow-up. Therefore our strategy to exclude blow-up for (FBP3) is to exclude it for (70).

In order to make use of the theory developed in [9, 13, 14], we introduce the variables

$$y = \frac{x - \eta(t_\xi)}{L - \eta(t_\xi)} \in (0,1), \quad \zeta = \frac{\hat{\xi} - \eta(t_\xi)}{L - \eta(t_\xi)}, \tag{71}$$

$$\tau = \frac{t - t_\xi}{t_{\mathrm{D}}}, \quad t_{\mathrm{D}} = \frac{(L - \eta(t_\xi))^2}{D}, \quad t_{\mathrm{D}} A(t^*) U(y, \tau) = \hat{u}(x, t), \tag{72}$$

obtaining

$$\begin{cases} \dfrac{\partial U}{\partial \tau} - \dfrac{\partial^2 U}{\partial y^2} = 1, \quad \text{in } \zeta(\tau) < y < 1, \ \tau > 0, \\ U(y, 0) = U_o(y) = \dfrac{1}{t_D A(t^*)} \hat{u}(x, t_\xi), \quad 0 \leqslant y \leqslant 1, \\ \dfrac{\partial U}{\partial y}(1, \tau) = -\dfrac{(L - \eta(t_\xi))}{t_D A(t^*)} b, \quad \tau > 0, \\ U(\zeta, \tau) = 0, \quad \tau > 0, \\ \dfrac{\partial U}{\partial y}(\zeta, \tau) = 0, \quad \tau > 0, \\ \zeta(0) = 0. \end{cases} \tag{73}$$

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Note that $U_o'(1) = U_y(1,0)$. Setting $\frac{\partial U}{\partial \tau} = W$, we formulate the superheated Stefan problem

$$\begin{cases} \dfrac{\partial^2 W}{\partial y^2} - \dfrac{\partial W}{\partial \tau} = 0, \quad \text{in } \zeta(\tau) < y < 1, \ \tau > 0, \\ W(y,0) = \dfrac{1}{A(t^*)} \dfrac{\partial u}{\partial t}(x, t_\xi), \quad 0 \leqslant y \leqslant 1 \\ \dfrac{\partial W}{\partial y}(1,\tau) = 0, \quad \tau > 0, \\ W(\zeta,\tau) = 0, \quad \tau > 0, \\ \dfrac{\partial W}{\partial y}(\zeta,\tau) = \dfrac{d\zeta}{d\tau}, \quad \tau > 0, \\ \zeta(0) = 0. \end{cases} \tag{74}$$

According to [9] blow-up can be excluded if the level curve $W = 1$ never appears. Thus, the condition (69) is enough to prevent blow-up for (70). □

As a consequence we may state

Theorem 2 *Under the assumptions of the Lemma (8) (FBP3) is well posed. Moreover,* $\dot\eta(t_\xi) \leqslant \dot\xi(t_\xi)$.

Proof We only need to show the last inequality. The function $\frac{\partial u}{\partial x}(\eta(t), t)$ is increasing in $[t_\eta, t_\xi]$ with $\frac{\partial u}{\partial x}(0, t_\eta) < 0$ and $\frac{\partial u}{\partial x}(\eta(t_\xi), t_\eta) = 0$. Therefore $\frac{\partial u}{\partial x}$ has a maximum in $t = t_\xi$ and

$$\frac{d}{dt}\left\{\frac{\partial u}{\partial x}(\eta(t),t)\right\}\Big|_{t=t_\xi} = \left\{\frac{\partial^2 u}{\partial x^2}\dot\eta + \frac{\partial^2 u}{\partial t \partial x}\right\}\Big|_{t=t_\xi} \geqslant 0. \tag{75}$$

Recalling that $\frac{\partial u}{\partial t} = 0$ on ξ, we have $\frac{\partial^2 u}{\partial x^2} = \mu D^{-1} \frac{\partial T}{\partial t}$ on ξ. Thus

$$\frac{\partial Z}{\partial x} + \frac{\mu}{D}\frac{\partial T}{\partial t}\dot\eta \geqslant 0, \tag{76}$$

$$\frac{\partial Z}{\partial x} + \frac{\mu}{D}\frac{\partial T}{\partial t}\dot\xi = 0, \tag{77}$$

yielding $\dot\eta(t_\xi) \leqslant \dot\xi(t_\xi)$. □

For (FBP4) we want to see how the boundary $x = \delta(t)$ evolves. Of course, since the flux of dissolved wax coming from the unsaturated region cannot balance the one leaving into the saturated region, we have the inequality

$$D_c(G,T)|_{(\delta,t)} \frac{\partial T}{\partial x}(\delta,t) > D\frac{\partial c}{\partial x}(\delta,t), \quad t > t_\delta. \tag{78}$$

From $(28)_5$ we thus have the *a priori* estimate $\dot\delta(t) < 0$ at least near t_δ. Problem (28) is very close to a Stefan problem in an expanding phase, which is known to be well posed. The only difficulty is that the coefficient playing the role of 'latent heat', namely $G(\delta, t)$,

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vanishes for $t = t_\delta$. Thus it is by no means evident that the new free boundary has a smooth matching with the previous one $x = \xi(t)$.

We want to perform an *a priori* analysis with the aim of showing that necessarily $\dot{\delta} = 0$ at the regression point. Without loss of generality, we set $D = 1$ and we translate the origin to the regression point. We reformulate problem (28) for the difference $u = c - c_s$

$$\begin{cases} \dfrac{\partial^2 u}{\partial x^2} = \dfrac{\partial u}{\partial t} + \beta \left(1 - \dfrac{1}{D_T}\right) \dfrac{\partial T}{\partial t}, \\ u(x,0) = u_o(x), \\ u(\delta, t) = 0, \\ -G(\delta,t)\dot{\delta} + \dfrac{\partial u}{\partial x}(\delta,t) = \beta \dfrac{\partial T}{\partial x}(\delta,t))[D_c(G,T) - 1]. \end{cases} \tag{79}$$

We notice that

$$u_o(0) = u_o'(0) = 0, \tag{80}$$

and that, since, on $x = \xi$, we have $u = \partial u/\partial x = 0$ which implies that $\partial u/\partial t = 0$, we also have

$$u_o''(0) = \beta \left(1 - \frac{1}{D_T}\right) \frac{\partial T}{\partial t}(0,0). \tag{81}$$

Also $D_c(G,T) = 1$ in a neighbourhood of $G = 0$, so that we may write $-G\dot{\delta} + \frac{\partial u}{\partial x} = 0$ in (79). The following *a priori* result is our starting point:

Lemma 9 *If δ/t does not tend to zero, then for small t, we have*

$$G(\delta(t), t) = O(\xi^{-1}(\delta)). \tag{82}$$

Proof From (29) we have

$$G(\delta,t) = \mu \left| \frac{\partial \bar{T}}{\partial t} \right| \left[t - \xi^{-1}(\delta) \right], \quad (\xi^{-1}(\delta) < 0), \tag{83}$$

where $|\frac{\partial \bar{T}}{\partial t}|$ is non-zero in every finite time interval. We note that $|\xi^{-1}(\delta)|/|\delta| \to \infty$, owing to the fact that $\dot{\xi}(0) = 0$. Suppose now that t is the leading term in (83). This would require that $\delta = o(t)$, contradicting the assumption. □

If we want to prove that $\dot{\delta}(0) = 0$, a useful lemma is the following:

Lemma 10 *Let (δ, u) be a solution of (79) and suppose that near the origin*

$$\left| \frac{\partial u}{\partial x}(\delta(t), t) \right| \leqslant O(\delta), \tag{84}$$

or

$$\left| \frac{\partial u}{\partial x}(\delta(t), t) \right| \leqslant O(\delta)\dot{\delta}, \tag{85}$$

then $\dot{\delta}(0) = 0$.

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Proof It follows immediately from (82) and the fact that $G(\delta,t)\dot{\delta} = \frac{\partial u}{\partial x}(\delta,t)$. If (84) applies then the ratio $\frac{\partial u/\partial x}{G}$ behaves at most like $\delta/\xi^{-1}(\delta)$, which goes to 0 as $t \to 0$. The same free boundary condition is compatible with (85) only if $\dot{\delta} = 0$. □

Now we consider the class $\mathscr{C}$ of function δ such that $\lim_{t\to 0^+} \delta/t$ exists; if it is not bounded then $\dot{\delta}(t)$ tends monotonically to $-\infty$ as $t \to 0^+$. We can prove the following:

Lemma 11 *Let (δ,u) be a solution of (79), with $\delta \in \mathscr{C}$. Then $\dot{\delta}(0) = 0$.*

Proof We apply the following strategy. Postulating some behaviour of δ near the origin we compute the local behaviour of $\frac{\partial u}{\partial x}(\delta,t)$. Next we compare $\frac{\partial u}{\partial x}(\delta,t)$ and $G(\delta,t)$ as in the previous lemma to reach our conclusion. Since the analysis is purely local, we may replace the data with the following approximation:

$$\beta\left(1 - \frac{1}{D_{\mathrm{T}}}\right)\frac{\partial T}{\partial t} \simeq f_o + f_1 x + f_2 t, \tag{86}$$

where f_i, $i = 0,1,2$, are known constants and according to (80), (81)

$$u_o(x) \simeq \frac{1}{2} f_o x^2. \tag{87}$$

Introducing the function

$$v = u + f_1 x t + \frac{1}{2} f_2 t^2 - \frac{1}{2} f_o x^2, \tag{88}$$

we are led to consider the problem

$$\begin{cases} \dfrac{\partial^2 v}{\partial x^2} - \dfrac{\partial v}{\partial t} = 0, \quad x > \delta(t), \ \ t > 0, \\ v(x,0) = 0, \quad x > 0, \\ v(\delta,t) = f_1 \delta t + \dfrac{1}{2} f_2 t^2 - \dfrac{1}{2} f_o \delta^2 =: \varrho(t). \end{cases} \tag{89}$$

Clearly

$$v(\delta,t) = O(\delta^2) \ \text{ if } \ \lim_{t\to 0^+} \frac{|\delta|}{t} = +\infty, \ \text{ or if } \ |\delta| = O(t), \tag{90}$$

$$v(\delta,t) = O(t^2) \ \text{ if } \ \lim_{t\to 0^+} \frac{|\delta|}{t} = 0. \tag{91}$$

We use the representation formula

$$v(x,t) = \int_0^t \mu(\tau)\left\{\frac{1}{4\sqrt{\pi}} \frac{x - \delta(\tau)}{(t-\tau)^{3/2}} \exp\left[-\frac{(x-\delta(\tau))^2}{4(t-\tau)}\right]\right\} d\tau \tag{92}$$

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and the jump relation (see [2, 15, 18]) to derive the following integral equation for the unknown $\mu(\tau)$

$$\varrho(t) = \frac{1}{2}\mu(t) + \int_0^t \mu(\tau)\left\{\frac{1}{4\sqrt{\pi}}\frac{\delta(t)-\delta(\tau)}{(t-\tau)^{3/2}}\exp\left[-\frac{(\delta(t)-\delta(\tau))^2}{4(t-\tau)}\right]\right\}d\tau, \tag{93}$$

where, by assumption, $\delta(t)$ is differentiable, but with $\dot{\delta}$ non-necessarily bounded near the origin.

If, in $[0, T]$, $\delta(t)$ is uniformly Hölder continuous with exponent larger than $1/2$, then the integral in (93) goes to zero as $t \to 0^+$ faster than $\mu(t)$, implying that $\mu = O(\varrho)$.

Let us continue with the case $\delta(t) = o(t^{1/2})$ and shift our attention to

$$\frac{\partial u}{\partial x}(\delta, t) = \frac{\partial v}{\partial x}(\delta, t) - f_1 t + f_o \delta, \tag{94}$$

where

$$\frac{\partial v}{\partial x}(x, t) = -\int_0^t \mu(\tau)\frac{\partial^2 \Gamma}{\partial x^2}(x, t; \delta(\tau), \tau)\, d\tau. \tag{95}$$

We use

$$\frac{\partial^2 \Gamma}{\partial x^2} = \frac{\partial \Gamma}{\partial t} = -\frac{\partial \Gamma}{\partial \tau}, \qquad \frac{d\Gamma}{d\tau}(x, t; \delta(\tau), \tau) = \frac{\partial \Gamma}{\partial \zeta}\dot{\delta} + \frac{\partial \Gamma}{\partial \tau} = \frac{\partial \Gamma}{\partial \tau} - \frac{\partial \Gamma}{\partial x}\dot{\delta} \tag{96}$$

to obtain

$$\begin{aligned}\frac{\partial v}{\partial x}(x, t) &= \int_0^t \mu(\tau)\left[\frac{d\Gamma}{d\tau} + \frac{\partial \Gamma}{\partial x}\dot{\delta}(\tau)\right]d\tau \\ &= \mu(\tau)\Gamma(x, t; \delta(\tau), \tau)\big|_{\tau \to 0}^{\tau \to t} - \int_0^t \dot{\mu}(\tau)\Gamma(x, t; \delta(\tau), \tau)\, d\tau \\ &\quad + \int_0^t \mu(\tau)\dot{\delta}(\tau)\frac{\partial \Gamma}{\partial x}(x, t; \delta(\tau), \tau)\, d\tau,\end{aligned} \tag{97}$$

where the first term of the r.h.s. vanishes identically. Taking the limit $x \to \delta(t)^+$

$$\frac{\partial v}{\partial x}(\delta(t), t) = -\frac{1}{2}\mu(t)\dot{\delta}(t) + \int_0^t \mu(\tau)\dot{\delta}(\tau)\frac{\partial \Gamma}{\partial x}(\delta(t), t; \delta(\tau), \tau)\, d\tau - \int_0^t \dot{\mu}(\tau)\Gamma(\delta(t), t; \delta(\tau), \tau)\, d\tau. \tag{98}$$

At this point we only have to consider the case $\mu = O(\delta^2)$, since the alternative $\mu = O(t^2)$ occurs only when $\dot{\delta}(0) = 0$, which is what we want to prove. Taking $\delta(t) \simeq t^{1/2}\epsilon(t)$, with $\epsilon(t)$ infinitesimal, we see that $\mu\dot{\delta} \simeq t^{1/2}\epsilon^3$ dominates the second term in (98), while the last term behaves like $t^{1/2}\epsilon^2$. Therefore $\frac{\partial v}{\partial x}(\delta(t), t) = o(\delta)$. Going back to (94) we see that $\frac{\partial u}{\partial x}(\delta, t) = O(\delta)$, and the previous lemma yields the desired result.

Now we have to examine the case in which $\delta \sim \sqrt{t}$ or slower. When $\delta \sim \sqrt{t}$ we neglect the contribution of the exponential in (93) and, setting $\theta = \tau/t$, we see that $(\delta(t)-\delta(\tau))/(t-\tau)^{3/2}$ is integrable, showing that once more $\mu = O(\varrho)$. Proceeding as before we finally conclude that all terms in (98) are $O(\sqrt{t})$, i.e. $\frac{\partial v}{\partial x}(\delta(t), t) = O(\delta)$, so that $\frac{\partial u}{\partial x}(\delta(t), t)$ has the same property and we can apply Lemma 10.

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Suppose now $\delta/t \to +\infty$ as $t \to 0$. We restart from (93) and we suppose that $\dot{\delta}(t)$ tends monotonically to $-\infty$ as $t \to 0^+$. In such a case we may write, for any $\tau \in (0,t)$ and t sufficiently small,

$$\dot{\delta}(t)(t-\tau) \leqslant |\delta(t)-\delta(\tau)| \leqslant |\dot{\delta}(\tau)|(t-\tau). \tag{99}$$

The integral in (93) is dominated in absolute value by

$$I(t) = \frac{1}{4\sqrt{\pi}} \int_0^t |\mu(\tau)| \frac{|\dot{\delta}(\tau)|}{\sqrt{t-\tau}} \exp\left[-\frac{1}{4}\dot{\delta}^2(t)(t-\tau)\right] d\tau. \tag{100}$$

To be specific, let us take $\dot{\delta}(t) \sim -kt^{-(\alpha+1/2)}$, with $\alpha \in (0,1/2)$, $k>0$, and perform the transformation $\theta = \tau/t$, obtaining

$$J(t) = kt^{-\alpha} \int_0^1 |\mu(t\theta)| \frac{\theta^{-\alpha-1/2}}{\sqrt{1-\theta}} \exp\left[-\frac{k^2}{4} t^{-2\alpha}(1-\theta)\right] d\theta. \tag{101}$$

The case $\alpha = 0$ yields $I = O(\mu)$ immediately. Suppose $\alpha > 0$. Let us set

$$\frac{k^2}{4} t^{-2\alpha}(1-\theta) = z \tag{102}$$

and define z_o as the only real solution of

$$\exp(-z_o) = \sqrt{z_o}. \tag{103}$$

We split the integral (101) over the interval $(0, \theta_o(t))$, $(\theta_o(t), 1)$, with $\theta_o(t)$ defined through (102), (103):

$$\theta_o(t) = 1 - z_o \frac{4}{k^2} t^{2\alpha} \tag{104}$$

which is close to 1. In the integral over $(\theta_o(t), 1)$ we use $\theta \sim 1$ (remember $\theta_o \sim 1$ and so is θ) to obtain

$$\left| \int_{\theta_o(t)}^1 \ldots\ldots d\theta \right| \leqslant 2 \int_0^{z_o} |\mu| \frac{e^{-z}}{\sqrt{z}}\, dz, \tag{105}$$

which is $O(\mu)$. On the remaining interval we have

$$\left| \int_0^{\theta_o(t)} \ldots\ldots d\theta \right| = 2 \int_{z_o}^{4k^{-2}t^{-2\alpha}} |\mu| \frac{e^{-z}}{\sqrt{z}} \left[1 - \frac{4}{k^2} t^{2\alpha} z\right]^{-\alpha-1/2} dz. \tag{106}$$

When $t \to 0^+$ the upper limit goes to $+\infty$ and the term of e^{-z} keeps the integral bounded. Thus also the second contribution is $O(\mu)$. This holds true any time $\dot{\delta}/\sqrt{t}$ tends to ∞ not necessarily as a power of t. Hence, from (93), we conclude once more that $\mu = O(\varrho) = O(\delta^2)$.

Proceeding to the estimate of $\frac{\partial v}{\partial x}$, and therefore of $\frac{\partial u}{\partial x}$, we see that now $\frac{\partial u}{\partial x} = O(\mu\dot{\delta})$ and again we apply Lemma 10 to conclude that $\dot{\delta}(0) = 0$. □

We can now investigate more closely the short-time behaviour of $\delta(t)$, which is dictated by the one of $\xi(t)$.

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Lemma 12 *Let us define the function*

$$\Xi(\delta) = \int_0^{\delta} |\xi^{-1}(\delta')|\, d\delta'. \tag{107}$$

Then

$$|\delta(t)| = O(\Xi^{-1}(t^2)). \tag{108}$$

Proof Knowing that $\dot{\delta}(0) = 0$, i.e. $|\delta(t)| = o(t)$, we can now conclude that $|\frac{\partial u}{\partial x}(\delta, t)| = O(t)$. Thus, from Lemma 9, the product $\xi^{-1}(\delta)\dot{\delta}$ must be $O(t)$, i.e. $\Xi(\delta) = O(t^2)$. □

Corollary 1 *If* $|\xi(t)| \sim |t|^m$, *with* $m > 1$, *then* $|\delta(t)| \sim t^{2m/(m+1)}$ (*so, if* $\ddot{\xi}(0)$ *exists and is not zero, then* $|\delta| \sim t^{4/3}$).

The coefficient of $t^{2m/(m+1)}$ can be found once $\xi(t)$ is known. This gives us a rather precise information of the initial stage of the crystal depletion phase and suggests a procedure for constructing the solution of (28). For a small time interval θ, we prescribe the boundary as indicated by the corollary. Then, solving (28) for $t > \theta$ is straightforward. This introduces a small error because the free boundary condition will not be met exactly at $t = \theta$. However, such an error can be compensated by introducing a higher order correction on the approximation in the first step.

This provides a satisfactory answer to the question of existence of the solution to stage 4 during the time interval in which $\dot{\delta} < 0$. To complete the analysis of the transition to stage 5 we have to examine problem (33) more carefully.

4.3 Some remarks on problem (33)

For problem (33), the initial datum is given on the curve γ where G is given by $(33)_2$. The curve γ is not a characteristic since $\dot{\gamma} > 0$ while the characteristics have initial zero slope. The non-linearity of the problem may lead to mutually intersecting characteristics and hence to admissible shocks. Under the assumption $(\partial^2 D_c/\partial G^2) \leqslant 0$, it is easy to prove that the entropy condition is satisfied (indeed the coefficient $-D_c$ is uniformly convex in G) and along the shock $G^- > G^+$. The velocity of a possible shock is given by the Rankine–Hugoniot relation

$$\dot{\sigma} = -\beta \frac{[[D_c]]}{[[G]]} \frac{\partial T}{\partial x}. \tag{109}$$

Thus the occurrence of shocks cannot be excluded by simple inspection of problem (33). Nevertheless, we shall prove that no shocks will be formed. Since the data on γ has the same regularity as γ, the only way the solution can break down is by forming an envelope before G reaches G_{dep}. Comparing the slope of the deposit front

$$\dot{\eta} = D_c \frac{\beta \frac{\partial T}{\partial x}}{G_{dep} - G}, \tag{110}$$

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with the slope of the characteristics

$$\dot{x} = -\beta \frac{\partial T}{\partial x} \frac{\partial D_c}{\partial G}, \tag{111}$$

we see that the deposit front travels faster than the characteristics. Therefore if the characteristics form an envelope before G_{dep} is reached, we will not see it because they have already been intersected by the front $x = \eta(t)$ (which also carries the value $G = G_{dep}$). This observation holds only if we ignore the possibility that the front switches from $x = \eta(t)$ to $x = v(t)$.

Moreover, we observe that when $\dot{\delta}(t) > 0$ (transition from stage 4 to stage 5) we have

$$\dot{\delta} = \left\{ \frac{D}{G} \frac{\partial c}{\partial x} - \frac{D_c}{G} \frac{\partial c_s}{\partial x} \right\} \Bigg|_{x=\delta}, \tag{112}$$

and the characteristic slope is

$$\dot{x} = \left\{ -\frac{\partial D_c}{\partial G} \frac{\partial c_s}{\partial x} \right\} \Bigg|_{x=\delta}. \tag{113}$$

Subtracting

$$\dot{\delta} - \dot{x} = \frac{\partial c_s}{\partial x} \left[\frac{\partial D_c}{\partial G} - \frac{D_c}{G} \right] + \frac{D}{G} \frac{\partial c}{\partial x}. \tag{114}$$

Recalling that $0 < \frac{\partial c}{\partial x} < \frac{\partial c_s}{\partial x}$ we have

$$\dot{\delta} - \dot{x} < \frac{\partial c_s}{\partial x} \left[\frac{D - D_c}{G} + \frac{\partial D_c}{\partial G} \right] < 0 \tag{115}$$

since

$$0 < \frac{D - D_c}{G} < \left| \frac{\partial D_c}{\partial G} \right|. \tag{116}$$

The latter inequality is due to (15). Hence the characteristics travel faster than the free boundary $x = \delta(t)$. This guarantees that in equation $(28)_5$ the coefficient $G(\delta, t)$ playing the role of 'latent heat' in the corresponding Stefan-like problem is well defined and strictly positive. Therefore the well-posedness of the final portion of stage 4 at this point is standard.

5 Conclusions

We have studied diffusive mass transport and gelification in a waxy stationary solution under the effect of an evolving thermal field.

Gelification and molecular diffusion are believed to be the main mechanisms responsible for the formation of waxy deposits in pipelines, but most of the models we find in the literature usually tend to select one phenomenon disregarding the other. This is likely to be true for specific thermal conditions and cooling rates but we believe that, in general, both processes play a crucial role in the formation of a deposition region.

We have presented a model in which both these phenomena are taken into account. The problem has been studied for the one-dimensional case and in static conditions, a

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situation that occurs in laboratory experimental devices used to study wax deposition (cold finger). In contrast to other models here we have assumed mass and heat to have comparable diffusivities, so that the thermal field is evolving throughout the process.

The system is described by the evolution of the liquid and solid wax fraction and it goes through several stages exhibiting free boundaries. The model allows us to evaluate the asymptotic thickness of the deposition region which grows as a result of the combined action of diffusion and gelification.

The model is based on the assumption that solid segregated wax and dissolved wax co-exist only at saturation and no super-saturation can occur.

Appendix

A possible D_c satisfying (15) is given by

$$D_c = D\{1 - F^n\}, \tag{117}$$

where $n \geqslant 2$, $G \in [G_{gel}, G_{dep}]$ and

$$F(G,T) = \frac{G - G_{gel}}{G_{dep} - G_{gel}} > 0 \quad \text{for} \quad G > G_{gel}. \tag{118}$$

Of course $D_c|_{G_{gel}} = D$ and $D_c|_{G_{dep}} = 0$. Differentiating F we get

$$\frac{\partial F}{\partial G} = \frac{1}{G_{dep} - G_{gel}} > 0, \qquad \frac{\partial^2 F}{\partial G^2} = 0, \tag{119}$$

$$\frac{\partial F}{\partial T} = \frac{G'_{gel}(G - G_{dep})}{(G_{dep} - G_{gel})^2} \leqslant 0, \quad \frac{\partial^2 F}{\partial T^2} = \frac{(G - G_{dep})[G''_{gel}(G_{dep} - G_{gel}) + 2[G'_{gel}]^2]}{(G_{dep} - G_{gel})^3}. \tag{120}$$

Exploiting (119) and (120) we obtain

$$\frac{\partial D_c}{\partial G} = -nDF^{n-1}\frac{\partial F}{\partial G} < 0, \quad \frac{\partial^2 D_c}{\partial G^2} = -n(n-1)DF^{n-2}\left(\frac{\partial F}{\partial G}\right)^2 < 0, \tag{121}$$

$$\frac{\partial D_c}{\partial T} = -nDF^{n-1}\frac{\partial F}{\partial T} \geqslant 0, \quad \frac{\partial^2 D_c}{\partial T^2} = -n(n-1)DF^{n-2}\left(\frac{\partial F}{\partial T}\right)^2 - nDF^{n-1}\left(\frac{\partial^2 F}{\partial T^2}\right). \tag{122}$$

A possible way for requiring that $(\partial^2 D_c/\partial T^2) \leqslant 0$ is to impose

$$[G''_{gel}(G_{dep} - G_{gel}) + 2[G'_{gel}]^2] \leqslant 0, \tag{123}$$

so to have $(\partial^2 F/\partial T^2) \geqslant 0$. If we take (123) with the equality sign and set $y = G_{dep} - G_{gel}(T)$ we end up with the differential equation

$$-y''y + 2(y')^2 = 0, \tag{124}$$

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whose integration leads to

$$y = \frac{y_o}{1 - Cy_o(T - T_o)}, \tag{125}$$

that is

$$G_{\text{gel}}(T) = G_{\text{dep}} - \frac{G_{\text{dep}} - G_{\text{gel}}(T_o)}{1 + C(T - T_o)(G_{\text{dep}} - G_{\text{gel}}(T_o))}, \tag{126}$$

where $C > 0$, T_o and $G_{\text{gel}}(T_o)$ are given constants.

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