Heat and mass transport in non-isothermal partially saturated oil-wax solutions[*]

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Abstract

Deposition of wax at the wall of pipelines during the flow of mineral oils is a phenomenon with relevant technical implications. In this paper we present some general ideas about one of the main mechanisms at the origin of wax deposition, i.e. diffusion in non-isothermal solutions. We formulate a mathematical model taking into account heat and mass transfer in the saturated and in the unsaturated regions, as well as the process of segregation (and dissolution) of solid wax and its deposition on the boundary.

1   Introduction

The aim of this paper is to better understand a phenomenon which is of crucial importance for instance in the pipelining of waxy crude oils (WCO's), i.e. of mineral oils containing heavy hydrocarbons (with the generic name of wax or in more specific cases of wax). The presence of wax makes the rheology of WCO's extremely complicated. The literature devoted to the technology of WCO's is quite large and we refer to the recent survey paper [?]. The peculiar phenomenon inspiring this paper is the wax deposition on the pipeline wall. Although the question is somehow controversial, various authors propose that wax migration to the wall is mainly driven by two mechanisms: (1) displacement of crystals suspended in oils saturated with wax, due to presence of a shear rate, (2) molecular diffusion to the wall generated by a radial concentration gradient in the saturated oil, induced by a thermal gradient (a typical situation encountered in submarine pipelines, where heat loss to the surroundings takes place in a significant way).

Although there are flow models including (1) and (2) (separately or simultaneously) a theoretical investigation of such processes is missing.

While (1) has a purely mechanical origin and is connected to the flow, the latter mechanism can be studied also in static conditions and in a small scale laboratory device. The paper [?] is a first attempt to derive wax diffusivity from experimental observation of deposition on a cold wall.

Here we want to investigate the specific problem of diffusion-driven migration in saturated solutions in a non-uniform thermal field, including the phenomenon of deposition of the segregated material on part of the boundary.

In [?] this problem has been considered precisely in the framework of WCO's pipelining. In our paper the physical situation we want to discuss is different because we deal with static conditions in general geometry, allowing some diffusivity of the segregated phase and the onset of desaturation.

Our approach will be mainly focussed on the mass transport process, in the sense that the (rather weak) coupling between this process and the evolution of the thermal field will be neglected in a first instance. However we will also give some hints on how to deal with the case in which such a coupling is taken into account. The aim of this paper is to present some general ideas, but further developments will be necessary to deal with the WCO's flow problem, where the transport of the various components is likely to be substantially influenced by the strain rate of the mixture.

In the next section we illustrate some general features and we present the classical statement of the problem. A weak solution is defined in Sect. 3. Generalizations with (i) a coupled thermal field, and (ii) segregated phase in a gel state are subsequently discussed.

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2 The basic model

Consider a bounded domain $\Omega \subset \Re^3$ with smooth boundary, filled by a WCO at rest in which the dissolved substance S is monocomponent or behaving as such.

Denote by $T(x,t)$ and by $c_{TOT}(x,t)$, $x \in \Omega$, $t \geq 0$ the temperature of the mixture and the total concentration of S.

For T in the range in which the system is liquid a saturation concentration $c_S(T)$ is defined, so that at all points where $c_{TOT} > c_S$ a solid segregated phase is present with concentration

$$G(x,t) = [c_{TOT}(x,t) - c_S(T(x,t))]_+, \tag{2.1}$$

where $[f]_+ = max(f,0)$. According to experience $c_S(T)$ is a given function, positive, increasing and smooth.

Remark 1 *Although $c_s(T)$ represents the solute concentration in the liquid phase, when we write (2.1) we use it as the concentration in the whole system (liquid plus the segregated phase). This is acceptable if the solvent is relatively abundant, a situation which will be assumed throughout the paper.*

Then, we define the concentration of the dissolved substance

$$C(x,t) = min[c_{TOT}(x,t), c_S(T(x,t))], \tag{2.2}$$

so that in any case

$$c_{TOT}(x,t) = C(x,t) + G(x,t).$$

For the specific case of WCO's the densities of S (both in its dissolved and segregated phases) are essentially equal to that of the solvent and their variations with temperature are negligible in the range of interest. Therefore we assume that the density ρ of the mixture is constant and that sedimentation due to gravity can be neglected, at least on the time scale we are interested in.

Remark 2 *Consistently with Remark 1, we suppose that solvent is at rest so that convection is systematically neglected. In the same spirit, even in the presence of a growing layer of solid wax on the boundary, neither the thickness of the layer nor the displacement of its front affect the transport process. We will resume this question in a more general framework in a forthcoming paper adopting the point of view of mixture theory.*

The approximation adopted here can be of help in most practical cases.

Consider the region $\Omega_S \subset \Omega$ where $G > 0$ (saturated region). There, the dissolved phase has concentration $c_S(T(x,t))$ and its mass balance equation

$$\frac{\partial c_S}{\partial t} - D\nabla^2 c_S = Q(x,t), x \in \Omega_S, t > 0 \tag{2.3}$$

provides the expression of the volumetric rate at which the segregated component S dissolves ($Q > 0$) or is produced ($Q < 0$) in terms of the thermal field:

$$Q(x,t) = c_S'(T)(T_t - D\nabla^2 T) - Dc_S''(T)(\nabla T)^2, x \in \Omega_S, t > 0. \tag{2.4}$$

The corresponding mass balance for the segregated material is

$$\frac{\partial G}{\partial t} - D_G\nabla^2 G = -Q(x,t), x \in \Omega_S, t > 0. \tag{2.5}$$

If the region $\Omega \backslash \Omega_S$ is non-empty, there $C = c_{TOT}$ and we have pure diffusion

$$\frac{\partial C}{\partial t} - D\nabla^2 C = 0, x \in \Omega \backslash \Omega_S, t > 0. \tag{2.6}$$

Let us assume that the part of the boundary of $\partial\Omega_S$ not lying on $\partial\Omega$ is a set $\Gamma(t)$ which is the union of a finite number of connected components that are smooth surfaces. There, we impose the continuity of c_{TOT} implying

$$G|_\Gamma = 0, C|_\Gamma = c_S(T|_\Gamma) \tag{2.7}$$

and the continuity of mass flux, i.e.

$$D\frac{\partial C}{\partial n}\Big|_\Gamma = D\frac{\partial c_S}{\partial n}\Big|_\Gamma + D_G\frac{\partial G}{\partial n}\Big|_\Gamma. \tag{2.8}$$

Discussing boundary conditions on $\partial\Omega$ is more delicate, because we have to distinguish between its "warm" part Γ_W (i.e. where $\dfrac{\partial T}{\partial n} \geq 0$, n being the outward normal) and its "cold" part Γ_C (where $\dfrac{\partial T}{\partial n} < 0$). Indeed, only on the latter deposition may take place.

On Γ_W we impose that the total mass flux vanishes:

$$D_G\frac{\partial G}{\partial n} + D\frac{\partial c_S}{\partial n} = 0, \text{ on } \Gamma_{WS} = \partial\Omega_S \cap \Gamma_W, \tag{2.9}$$

$$\frac{\partial C}{\partial n} = 0, \quad \text{on } \Gamma_{WU} = \Gamma_W \backslash \Gamma_{WS}, \tag{2.10}$$

According to Remark 2, we neglect the thickness of the deposit so that deposition front is assumed to lie on $\partial\Omega$.

Thus, we formulate the conditions on Γ_C starting with $\Gamma_C \cap \partial\Omega_S = \Gamma_{CS}$. We assume that a given fraction $\chi \in (0,1]$ of the incoming flux on T_{CS} is (irreversibly) converted into a layer of solid deposit. Hence

$$-D_G\frac{\partial G}{\partial n} = (1-\chi)D\frac{\partial C_S}{\partial_n}, x \in \Gamma_{CS}. \tag{2.11}$$

Of course $\chi = 0$ (no deposit and total recirculation) corresponds to the trivial case in which mass flux vanishes on the whole of $\partial\Omega$, whereas in case $\chi = 1$ (all incoming dissolved substance is withdrawn from the diffusion process) the no-flux condition applies to the phase G.

Passing to $\Gamma_{CU} = \Gamma_C \backslash \Gamma_{CS}$, two different situations can arise: either $C = c_S$ or $C < c_S$. In the former case $\dfrac{\partial C}{\partial n} \in [\dfrac{\partial c_S}{\partial n}, 0]$, while in the latter $\dfrac{\partial C}{\partial n} = 0$. We can reformulate the condition on Γ_{CU} as

$$C - c_S \leq 0, \frac{\partial C}{\partial n} \leq 0, (C - c_S)\frac{\partial C}{\partial n} = 0, x \in \Gamma_{CU} \tag{2.12}$$

i.e. a Signorini-type unilateral condition.

To complete the formulation of the mass transport problem an initial condition has to be specified

$$c_{TOT}(x, 0) = c_{TOT}^0(x), x \in \Omega. \tag{2.13}$$

Let us come to the equations for the thermal field. We have

$$\frac{\partial T}{\partial t} - \alpha_S\nabla^2 T = -\frac{\lambda}{\rho\gamma_0}Q, x \in \Omega_S, t > 0, \tag{2.14}$$

$$\frac{\partial T}{\partial t} - \alpha_U\nabla^2 T = 0, x \in \Omega\backslash\Omega_S, t > 0.$$

In (2.14) γ_0 represents specific heat and λ is the latent heat required to dissolve the unit mass of segregated phase. Moreover α_S and α_U are the thermal diffusivities in the two regions.

Usual conditions of continuity of temperature and thermal flux are meant to hold on Γ.

We also prescribe boundary and initial temperatures

$$T(x, t) = T_B(x), x \in \partial\Omega, t > 0, \quad T(x, 0) = T_0(x), x \in \Omega. \tag{2.15}$$

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Remark 3 *Of course, neglecting the thickness of Ω_d as well as convection, along with the assumption $C_{TOT}/\rho << 1$, is a very relevant simplification of the problem, but the model is still realistic in the practical case of WCO pipelining over a not too long time interval. Although in principle the formation of a thick deposit may occur, such a situation must be avoided in practice. The model stated in the fixed domain Ω allows anyway the computation of the growth rate of the deposit. Denoting by V_n the normal component of the growth velocity, we have*

$$V_n = \frac{\chi}{\rho} D \frac{\partial c_S(T)}{\partial n}, x \in \Gamma_{CS}, \tag{2.16}$$

$$V_n = \frac{D}{\rho} \frac{\partial C}{\partial n}, x \in \Gamma_{CU}. \tag{2.17}$$

Now we introduce non-dimensional variables

$$\hat{G} = G/\tilde{C}, \ \ \hat{C} = C/\tilde{C}, \ \ \hat{T} = T/\tilde{T},$$

$$\hat{c}_S(\hat{T}) = c_S(\hat{T}\tilde{T})/\tilde{C}, \ \ \hat{x}_i = x_i/L, i = 1, 2, 3, \ \ \hat{t} = t/\hat{t},$$

with $\tilde{C}, \tilde{T}, L$ suitably selected (for instance $\tilde{T} = maxT|_{\partial\Omega}, \tilde{C} = c_S(\tilde{T}), L = diam\Omega$, and $\tilde{t} = \frac{L^2}{D}$). We can immediately realize that the rescaled velocity $|V_n|\frac{\tilde{t}}{L}$ is small if $\frac{c_S}{\rho} << 1$, consistently with our approach.

We denote by $\hat{\nabla}^2, \hat{\nabla}$ the operators acting on the new space variables and we set

$$\hat{Q} = \hat{c}'_S(\hat{T})(\frac{\partial \hat{T}}{\partial \hat{t}} - \hat{\nabla}^2 \hat{T}) - \hat{c}''_S(\hat{T})(\hat{\nabla}\hat{T})^2. \tag{2.18}$$

Equations (2.5), (2.6), (2.13), (2.14) become

$$\frac{\partial \hat{G}}{\partial \hat{t}} - \theta \hat{\nabla}^2 \hat{G} = -\hat{Q}, \ \ \text{in} \ \ \{\hat{G} > 0\}, \ \ t > 0, \tag{2.19}$$

$$\frac{\partial \hat{T}}{\partial \hat{t}} - \frac{1}{\epsilon_S} \hat{\nabla}^2 \hat{T} = -\hat{\Theta}\hat{Q}, \ \ \text{in} \ \{\hat{G} > 0\}, \ \ t > 0, \tag{2.20}$$

$$\frac{\partial \hat{C}}{\partial \hat{t}} - \hat{\nabla}^2 \hat{C} = 0, \ \ \text{in} \ \{\hat{G} = 0\}, \ \ t > 0, \tag{2.21}$$

$$\frac{\partial \hat{T}}{\partial \hat{t}} - \frac{1}{\epsilon_U} \hat{\nabla}^2 \hat{T} = 0, \ \ \text{in} \ \{\hat{G} = 0\}, \ \ t > 0, \tag{2.22}$$

where

$$\theta = D_G/D, \epsilon_S^{-1} = \alpha_S/D, \epsilon_U^{-1} = \alpha_U/D, \tag{2.23}$$

and

$$\Theta = \frac{\lambda \tilde{C}}{\rho_0 \gamma_0 \tilde{T}}. \tag{2.24}$$

The initial and boundary conditions can be written accordingly. In particular, condition (2.11) becomes

$$-\theta \frac{\partial \hat{G}}{\partial n} = (1 - \chi) \frac{\partial \hat{c}_S(\hat{T})}{\partial n}, \hat{x} \in \Gamma_{CS}, \tag{2.25}$$

and (2.9) becomes

$$\theta \frac{\partial \hat{G}}{\partial n} + \frac{\partial \hat{c}_S(\hat{T})}{\partial n} = 0, \hat{x} \in \hat{\Gamma}_{WS}. \tag{2.26}$$

We re-write (2.8) as a jump condition

$$\left[\frac{\partial \hat{C}}{\partial n}\right]_{\hat{\Gamma}_-}^{\hat{\Gamma}_+} = -\theta \frac{\partial \hat{G}}{\partial n}\Big|_{\hat{\Gamma}_+}, \tag{2.27}$$

where $\hat{\Gamma}^+$ (resp. $\hat{\Gamma}^-$) is the side of $\hat{\Gamma}$ facing the set $\{\hat{G} > 0\}$ (resp. $\{\hat{G} \leq 0\}$) and $\left[\frac{\partial C}{\partial n}\right]_{\hat{\Gamma}_-}^{\hat{\Gamma}_+}$ is the jump.

Note that in the above expressions $\frac{\partial}{\partial n}$ is also non-dimensional.

From now on we eliminate hats ($\hat{C} \to C, \hat{G} \to G$ and so on) to simplify notation.

3 Weak formulation

Using generalized derivatives in a standard way, we derive a unified formulation of the mass transfer process, still assuming that equations (2.18)-(2.22) hold classically in their respective domains and that the set $\{C_{TOT} = c_S\} \cap \Omega$ is a smooth connected surface $\Gamma(t)$ for any t. In the following we assume $\chi = 1$ for simplicity and we adopt the notation of [**?**] for functional spaces.

We introduce the function

$$u(x,t) = c_{TOT}(x,t) - c_S(T(x,t)), \text{in} \quad \Omega, \tag{3.1}$$

so that

$$u(x,t) = G(x,t), \text{where} \quad G > 0, \tag{3.2}$$

and

$$u(x,t) = C(x,t) - c_S(T(x,t)), \text{where} \quad G = 0. \tag{3.3}$$

Thus $u > 0$ corresponds to the saturated region (i.e. to the region where segregated phase exists).

Moreover, u is continuous across Γ, where it vanishes

$$u|_{\Gamma_+} = u|_{\Gamma_-} = 0. \tag{3.4}$$

If we assume that equation

$$\frac{\partial u}{\partial t} - \nabla \cdot \left\{[1 + H(u)(\theta - 1)]\nabla u\right\} = -Q, x \in \Omega, t > 0 \tag{3.5}$$

holds in a suitable generalized sense, we not only encompass (2.19) and (2.21) in their respective domain of validity, but we include the Rankine-Hugoniot condition

$$\theta \frac{\partial u}{\partial n}\Big|_{\Gamma_+} = \frac{\partial u}{\partial n}\Big|_{\Gamma_-}, \tag{3.6}$$

which is precisely (2.27).

Writing

$$A(u) \equiv 1 + H(u)(\theta - 1), \tag{3.7}$$

and defining on $\partial\Omega$

$$\eta(\frac{\partial c_S}{\partial n}, u) = H(\frac{\partial c_S}{\partial n}) - A(u)H(-u)H(-\frac{\partial c_S}{\partial n}), \tag{3.8}$$

we can synthetize (2.9), (2.10), (2.11), (2.12), i.e. the boundary conditions on $\Gamma_{WS} \cup \Gamma_{WU} \cup \Gamma_{CS} \cup \Gamma_{CU}$, as follows

$$A(u)\frac{\partial u}{\partial n} = -\eta(\frac{\partial c_S}{\partial n}, u)\frac{\partial c_S}{\partial n}, x \in \partial\Omega, t > 0. \tag{3.9}$$

Coming back to (3.5), it is clear that the function space in which u will be sought has to have enough regularity so that (3.9) is meaningful.

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Let τ be a fixed positive constant and $\phi(x, t)$ be a test function belonging the space $W_2^{1,1}(\Omega \times (0, \tau))$ with

$$\phi(x, \tau) = 0, \qquad x \in \Omega. \tag{3.10}$$

Assume that $T(x, t)$ is given and that our problem has a classical solution with regular interface Γ. Then, passing to the variable u, we write

$$\int_0^\tau \int_\Omega u_t \phi \, dx \, dt = -\int_0^\tau \int_\Omega u \phi_t \, dx \, dt - \int_\Omega u_0(x) \phi(x, 0) \, dx. \tag{3.11}$$

Then, since for any $t \in (0, \tau)$ and $\Omega_1 \subseteq \Omega$

$$\int_{\Omega_1} \nabla \cdot [\phi A(u) \nabla u] \, dx = \int_{\partial \Omega_1} \phi A(u) \frac{\partial u}{\partial n} \, d\sigma,$$

using (3.4) and (3,6) we have

$$\int_0^\tau \int_\Omega \phi \nabla \cdot [A(u) \nabla u] \, dx \, dt = -\int_0^\tau \int_\Omega \nabla \phi \cdot A(u) \nabla u \, dx \, dt + \int_0^\tau \int_{\partial \Omega} \phi A(u) \frac{\partial u}{\partial n} \, d\sigma. \tag{3.12}$$

Taking into account (3.9) we finally have that, if the problem admits a classical solution as specified above, then the following equation holds for any τ and for any choice of the test functions in the selected space

$$\int_0^\tau \int_\Omega [u \phi_t - \nabla \phi \cdot A(u) \nabla u] \, dx \, dt = \int_0^\tau \int_\Omega \phi Q \, dx \, dt - \int_\Omega u_0(x) \phi(x, 0) \, dx - \int_0^\tau \int_{\partial \Omega} \phi \eta(\frac{\partial c_S}{\partial n}, u) \frac{\partial c_S}{\partial n} \, d\sigma \, dt. \tag{3.13}$$

In (3.13) $u_0(x)$ is obviously given by

$$u_0(x) = c_{TOT}^0(x) - c_S(T_0(x)), \qquad x \in \Omega. \tag{3.14}$$

Then we give the following definition

Definition 1 *A weak solution to the mass diffusion problem in $Q_\tau = \Omega \times (0, \tau)$ is a function $u \in H^{\beta, \beta/2}(Q_\tau) \cap W_2^{1,0}(Q_\tau)$, for some $\beta \in (0, 1)$, satisfying (3.13) for any $\phi \in W_2^{1,1}(Q_\tau)$ vanishing for $t = \tau$.*

Now, assuming u is known, we go back to the thermal problem. Writing

$$\alpha(u) = \frac{1}{\epsilon_U} + H(u)(\frac{1}{\epsilon_S} - \frac{1}{\epsilon_U}) \tag{3.15}$$

we combine (2.20) and (2.22) as follows

$$T_t - \alpha(u) \nabla^2 T = -\Theta H(u) Q, x \in \Omega, t > 0. \tag{3.16}$$

Recalling (2.18) we can also write

$$(1 + \Theta H(u) c_S'(T)) T_t - [\alpha(u) + \Theta H(u) c_S'(T)] \nabla^2 T = \Theta H(u) c''(T)(\nabla T)^2. \tag{3.17}$$

Both (3.16) and (3.17) include continuity of temperature and heat flux across Γ, so that the problem is in the class of the so-called "diffraction problems" (see [**?**]).

Remark 4 *We note that in the approximation $\Theta \simeq 0$ and $\epsilon_U = \epsilon_S = \epsilon$, implying $\alpha(u) = \frac{1}{\epsilon}$, the thermal problem is completely uncoupled, so that T can be regarded as a known function of x and t with the required regularity at the boundary*

4 An alternative model

So far diffusion has been considered as the transport mechanism of the segregated phase. It makes sense, however, to deal with the extreme case in which $D_G \simeq 0$. A remarkable example is the one of those WCO's in which the segregated wax in static conditions aggregates producing a gel structure. In this case we can no longer rely on the diffusivity of G to ensure instantaneous equilibrium between the phases and we have to revise our approach drastically, admitting the possibility that for instance we have $G > 0$ even in presence of desaturation. In that case the dissolution of the segregated phase will not be instantaneous, but will develop with some relaxation, i.e. according to some kinetics. This point of view is not necessarily peculiar to the case we are discussing. We may think of an intermediate situation in which $D_G > 0$, but diffusion is not effective enough to supply all the material that would be necessary e.g. to prevent immediate desaturation at the "warm" wall. In that case, instead of the balance condition $D_G \dfrac{\partial G}{\partial n} + D \dfrac{\partial c_S(T)}{\partial n} = 0$, we would have a condition of the type

$$-D_G \frac{\partial G}{\partial n} = \min(\beta_G G, D\frac{\partial c_S(T)}{\partial n}), \ \text{ on } \Gamma_{WS},$$

where β_G is a positive constant, if we have chosen e.g. a simple linear dissolution kinetics. Thus, if $\beta_G G < D\dfrac{\partial c_S(T)}{\partial n}$ the solution will become desaturated and, instead of the former condition $\dfrac{\partial C}{\partial n} = 0$, we have now $D_G \dfrac{\partial G}{\partial n} + \dfrac{\partial C}{\partial n} = 0$.

Many more changes are necessary. Here we want to deal briefly with the case $D_G = 0$.

Once this choice has been made, various scenarios are still possible. Indeed we may or may not allow a substantial degree of oversaturation. If we admit oversaturation, now denoting by $C(x,t)$ the concentration of the dissolved substance, we can describe both segregation and dissolution by means of a kinetic equation of the form

$$\frac{\partial G}{\partial t} = -f(C,T,G), \tag{4.1}$$

where

(a) $f > 0$ if $C < c_S(T)$ and $G > 0$ (dissolution), with $f(C,T,0) = 0$, f being continuously differentiable w.r.t. C,T and also w.r.t. G, for $G > 0$, while it is only required to be Hölder continuous for $G = 0$

(b) $f < 0$ if $C > c_S(T)$, with $\dfrac{\partial f}{\partial G} = 0$ (segregation)

(c) for $C = c_S(T)$ we can take $f = 0$, if we suppose that phase segregation is generated only through supersaturation.

However, we can choose to exclude supersaturation and keep (4.1) only for dissolution, replacing it by

$$\frac{\partial G}{\partial t} = -Q \tag{4.2}$$

when Q, defined by (2.4), is negative, meaning that segregation takes place with no relaxation.

Clearly, C satisfies in any case

$$\frac{\partial C}{\partial t} - D\nabla^2 C = -\frac{\partial G}{\partial t} \tag{4.3}$$

If we impose the obstacle $C \leq c_S(T)$, a saturated region may still exist but of course the conditions (2.7), (2.8) on the interface Γ must be modified as follows

$$C|_\Gamma = c_S(T|_\Gamma), \tag{4.4}$$

$$\frac{\partial c_S(T)}{\partial n}\Big|_\Gamma = \frac{\partial C}{\partial n}\Big|_\Gamma. \tag{4.5}$$

All other boundary conditions must be changed.

First of all, only total deposition makes sense. If there is no supersaturation, the growth rate of the deposit is still related to $\dfrac{\partial c_S(T)}{\partial n}$ as in (2.16) with $\chi = 1$.

If however the solution is supersaturated the deposition mechanism can be described by a law of the type

$$V_n = -\frac{1}{\rho}F(C - c_S(T))H(-\frac{\partial T}{\partial n}), \text{for} \quad C > c_S(T), \tag{4.6}$$

with $F' > 0$ and $F(0) = 0$, expressing that the deposit growth rate is proportional to the supersaturation degree and is not zero only at those points of the boundary when heat flows out of the system.

We can extend (4.6) to the whole of $\partial\Omega$ by taking $F(\xi) = 0$ for $\xi \le 0$.

Accordingly, the boundary condition for C will be

$$D\frac{\partial C}{\partial n} = F(C - c_S(T)). \tag{4.7}$$

Of course we must specify the initial value $C_0(x)$ of C.

Equations (4.1) or (4.2) require the initial condition $G(x,0) = G_0(x)$. Extinction of G at a place where $G_0(x) > 0$ can take place in a finite time only if the function f in (4.1) is not Lipschitz for $G = 0$.

Passing to the thermal problem, if we do not neglect the latent heat, we must express the source term as $\Lambda\dfrac{\partial G}{\partial t}$, irrespectively of the way we model phase transition. Further discussion of this model is out of the scope of the present paper.

5   Analogy with fast chemical reaction problems

In order to analyze problem (3.13), (3.16), we first consider the simplified case in which heat diffusion is much faster than mass diffusion. As a matter of fact, taking $\epsilon_S = \epsilon_U >> 1, \Theta << 1$, temperature satisfies

$$\nabla^2 T = 0, \qquad x \in \Omega, t > 0 \tag{5.1}$$

with conditions

$$T(x,t) = T_B(x), \qquad x \in \partial\Omega, \tag{5.2}$$

and problem (5.1), (5.2) can be solved independently of the knowledge of u.

Thus we are led to considering (3.13) where Q, given by (2.18), is an assigned smooth function of x and t, while η, given by (3.8), is a prescribed graph of u, depending in a known way on x and t.

In this case, we can identify (3.13) with the weak formulation of a problem modelling the transport of two chemical substances diffusing in a solvent and undergoing an immediate reaction at the reaction front (playing the role of Γ in our model). The concentration of the two species are G and $c_S(T) - C$.

The fast reaction problem of two diffusing species has been studied in [**?**] and in [**?**]. There are some differences with respect to the scheme treated here (the most important is the presence of u in the boundary term in (3.13)), but the same technique can be used in our case to prove well-posedness.

We will not deal with such details.

The model including the thermal problem is obviously more difficult. We envisage the following strategy. Let $h = \tau/n$ and define $u(x,t), T(x,t)$ for $t \in (0,h)$ to coincide with the initial data. Then, for $t \in (h, 2h)$,

(i) solve (3.16) where $u(x,t)$ is replaced by $u(x,t-h)$;

(ii) solve (3.13) where, in η and Q, $T(x,t)$ is replaced by $T(x,t-h)$.

Of course, (i) is a standard "diffraction" problem, while (ii) is a problem of the fast chemical reaction type just considered.

Iterating the procedure we find a pair (T_h, u_h). Convergence can be proved on the basis of a compactness argument. Again, we postpone the analysis of the details to a forthcoming paper.

6   Conclusions

We have modelled mass transport in non-isothermal solutions in the presence of a segregated phase in the case in which all the components (including the solvent) have the same density. A relevant application is the one of waxy crude oils, where such a phenomenon (molecular diffusion) is one of the main mechanisms of wax deposition on the pipe wall during transport.

We consider the case in which the solvent is relatively abundant and the thickness of the deposit is negligible, leaving to a forthcoming paper the study of a more general situation.

As long as the segregated phase is present - in equilibrium with the solution - the model describes the following processes:

a) diffusive mass flow within the solution towards the cold wall, induced by the thermal gradient

b) the convexflow of the segregated phase towards the warm wall

c) the mass exchange between the solute and the segregated phase.

Although we disregard the geometric and kinematic effects of deposition, the corresponding boundary condition for mass transport is discussed in detail.

The situation is much more complicated when a region appears in which the concentration of the solute is below saturation. In this case we give a generalized formulation of the corresponding free boundary problem (the free boundary, in simple geometric cases, is the surface separating the unsaturated solution from the saturated region) including the nontrivial analysis of the boundary conditions that are formulated in terms of unilateral (or Signorini type) constraints.

We also note that, in simple geometric situations, the problem can be essentially reduced to the parabolic free boundary problem modelling a fast chemical reaction.

References

[1] A. Fasano, L. Fusi, S. Correra, *Mathematical models for waxy crude oils.* To appear

[2] S. Correra, M. Andrei, C. Carniani, *Wax diffusivity: is it a physical property or a pivotable parameter?* Accepted or publication on Petroleum Science and Technology.

[3] L. Fusi, *On the stationary flow of a waxy crude oil in a loop.* Nonlinear Analysis, 53 (2003) 507-526.

[4] J.R. Cannon, C.D. Hill, *On the movement of a chemical reaction interface.* Indiana Math. J. 20 (1970) 429-454.

[5] J.R. Cannon, A. Fasano, *Boundary value multidimensional problems in fast chemical reactions.* Arch. Rat. Mech. Anal. 53 (1973) 1-13.

[6] O.A. Ladyzenskaya, V.A. Solonnikov, N.N. Uralceva, *Linear and quasilinear equations of parabolic type.* AMS Translations of Mathematical Monographs 27, Providence R.I. (1968).