Stefan Problem with a Kinetic Condition at the Free Boundary (*).

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Summary. – *In the one-dimensional two-phase Stefan problem, the standard equilibrium condition* $\theta = 0$ *at the free boundary* $x = s(t)$ *is replaced by the kinetic law*

$$(1) \qquad s'(t) = \beta(\theta(s(t), t)) ;$$

here β *is a continuous and increasing function* $\boldsymbol{R} \to \boldsymbol{R}$ *and* $\beta(0) = 0$. *This introduces supercooled and superheated states. Existence of at least one solution is proved. Then* (1) *is replaced by*

$$(2) \qquad s'_\varepsilon(t) := \beta(\theta_\varepsilon(s_\varepsilon(t), t)) \qquad (\varepsilon \text{ constant } < 0) ,$$

and it is shown that as $\varepsilon \to 0^+$ *a subsequence of the corresponding solutions* $(\theta_\varepsilon, s_\varepsilon)$ *converges to a solution* (θ, s) *of the reduced problem, which is characterized by the free boundary condition*

$$(3) \qquad \beta(\theta(s(t), t)) = 0 .$$

Then the case of a radially symmetric multidimensional system is dealt with, taking also account of the surface tension effect. Denoting by $s(t)$ *the radial co-ordinate of the free boundary, the following linearized kinetics is considered for a water ball surrounded by ice*

$$(4) \qquad ls'(t) + \frac{\lambda}{s(t)} = \theta(s(t), t) , \qquad \textit{where } s(t) < 0 .$$

An existence result is proved for the problem obtained by coupling (4) *with the heat equation.*

1. – Introduction and presentation of the model.

1). At first we consider a two-phase Stefan problem in one dimension of space. Let a, T, c, k, L be positive constants, $s^0 \in [0, a]$. Let g_1, g_2: $[0, T] \to \boldsymbol{R}$ and θ^0: $[0, a] \to \boldsymbol{R}$ be given « smooth » functions. We set $Q :=]0, a[\times]0, T[$. We look for a couple of « smooth » functions $\theta: \bar{Q} \to \boldsymbol{R}$ and s: $[0, T] \to [0, a]$ such that, setting $\mathcal{S} := \{(s(t), t))\ t \in]0, T[\}$,

$$(1.1) \qquad c\frac{\partial\theta}{\partial t} - k\frac{\partial^2\theta}{\partial x^2} = 0 \qquad \text{in } Q \setminus \mathcal{S}$$

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(1.2) $\theta(s(t), t) = 0$ in $]0, T[$

(1.3) $k\left[\frac{\partial\theta}{\partial x}(s(t)+0, t) - \frac{\partial\theta}{\partial x}(s(t)-0, t)\right] = Ls'(t)$ on $S \cap Q$

(1.4) $k\frac{\partial\theta}{\partial x}(0, t) = g_1(t)$ in $]0, T[$

(1.5) $k\frac{\partial\theta}{\partial x}(a, t) = g_2(t)$ in $]0, T[$

(1.6) $\theta(x, 0) = \theta^0(x)$ in $]0, a[$

(1.7) $s(0) = s^0$.

Here θ denotes the difference between the actual temperature and the equilibrium phase transition temperature; $0 < x < s(t)$ corresponds to the liquid and $s(t) < x < a$ to the solid (water and ice, say); c is the product between the specific heat and the density, k the termic conductivity and L the product of the latent heat of phase transition by the density. In a more precise formulation, c and k change across the interphase S. In the usual form of the Stefan problem, supercooled and superheated states are excluded:

$$(1.8)\qquad \begin{cases} \theta(x, t) \geqslant 0 & \text{for } 0 \leqslant x < s(t),\ 0 < t < T\ , \\ \theta(x, t) \leqslant 0 & \text{for } s(t) < x \leqslant a,\ 0 < t < T\ ; \end{cases}$$

accordingly, in the standard model the following compatibility conditions are required for the data

$$(1.9)\qquad \begin{cases} \theta^0(x) \geqslant 0 \quad \text{if } x < s^0,\ \theta^0(x) \leqslant 0 \quad \text{if } x > s^0\ , \\ g_1(t)\ ,\ g_2(t) \leqslant 0 \quad \text{in }]0, T[\ . \end{cases}$$

As general references for Stefan-type problems, we quote the proceedings [11, 14, 15, 24].

2) The condition (1.2) corresponds to the case in which the interphase is at equilibrium, without supercooling and superheating effects. Now it happens that the phase transition is triggered by a *non-vanishing interphase temperature*: « If the interface is not at the equilibrium temperature, then either melting or solidification occurs at a rate that increases with the difference between the actual temperature and the equilibrium temperature. For small departures from equilibrium, the rate is approximately proportional to the departure » ([6, p. 91]). Here melting and solidification correspond to $s(t)$ increasing and decreasing, respectively.

Thus the supercooling and superheating effects *drive* the phase transition. For high transition rates, these effects appear also on a macroscopic scale [4, pp. 222-223; 8].

Taking account of this physical picture, we replace (1.2) by the conditions

(1.10) θ is continuous on S

(1.11) $s'(t) = \beta\big(\theta(s(t), t)\big)$, where $0 < s(t) < a$, in $]0, T[$ (1);

here $\beta \in C^0(\boldsymbol{R})$, $\beta(0) = 0$ and β is increasing. (1.11) represents relaxation towards the equilibrium condition (1.2); this introduces supercooled and superheated states, corresponding to water regions at negative temperature and ice zones at positive temperature, respectively.

In section 2 we introduce a variational problem equivalent to the system (1.1), (1.3), ..., (1.7), (1.10), (1.11); then we prove that this problem has at least one solution. There the only assumption on β is that it be Lipschitz-continuous; since the function β is not required to be monotone, this existence result can also be applied to a model for glass formation, described later on. The uniqueness of the solution is an open question.

Besides the variational approach, also other techniques could be used for proving the existence of a solution of the previous boundary and initial value problem. As for the standard one-dimensional Stefan problem, one could use for instance layer potentials to reduce the problem to an integral equation, or apply a procedure of approximation step by step in time.

In section 3 we extend the existence result to the case in which the specific heat and the conductivity depend on both the temperature and the phase.

3) In many practical cases the relaxation towards equilibrium at the interface is very fast, that is the function β has a high slope near 0. This can be represented by (1.11) with a function β of the form

$$\beta(\theta) := \begin{cases} \gamma \dfrac{|\theta|^\alpha}{\theta} & \text{if } \theta \neq 0 \ \ (\gamma, \alpha\text{: constants, } \gamma > 0, 1 < \alpha < 2) \\ 0 & \text{if } \theta = 0\,; \end{cases}$$

this is compatible with the assumptions of the existence theorem. Another possibility is to replace (1.11) by

(1.12) $\varepsilon s_\varepsilon'(t) = \beta\big(\theta_\varepsilon(s_\varepsilon(t), t)\big)$, where $0 < s_\varepsilon(t) < a$, in $]0, T[$

and to take $\varepsilon \to 0^+$. In section 4 we show that, possibly extracting a subsequence, the solutions $(\theta_\varepsilon, s_\varepsilon)$ converge to a solution of the reduced problem, which is charac-

(1) More precisely, taking account of the constraint acting on $s(t)$, (1.11) should be replaced by the following variational inequality:

(1.11′)
$$\begin{cases} 0 \leqslant s(t) \leqslant a\,; \quad \forall \xi \in [0, a] \\ \big[s'(t) - \beta\big(\theta(s(t), t)\big)\big] \cdot [\xi - s(t)] \geqslant 0\,. \end{cases}$$

terized by the usual equilibrium condition (1.2). This problem coincides with the standard two-phase Stefan problem if and only if no supercooled nor superheated states appear in the interior of each phase. Thus the « relaxed Stefan problem » corresponding to (1.12) can also be regarded as a physically justified approximation of the standard two-phase Stefan problem.

The Stefan problem with supercooling has been recently studied by DI BENEDETTO and FRIEDMAN [9] in the case of several space dimensions.

4) In the multidimensional case, a more precise interphase condition takes account of the *surface tension* effect. Accordingly, (1.2) is replaced by the classical *Gibbs-Thomson law* (cf. [6], chapter 3)

$$\theta = -\lambda\varkappa \quad \text{on } S\,; \tag{1.13}$$

here k is a positive physical constant and $\varkappa$ denotes the local mean curvature of S, assumed « smooth ». The sign of $\varkappa$ is determined by assuming that it be positive for an ice ball surrounded by water; thus for a planar interface $\varkappa = 0$ and (1.13) degenerates into the usual condition $\theta = 0$ on S. We stress that (1.13) is an equilibrium condition, like (1.2).

For general geometries, it does not seem easy to work with (1.13). The case of a radially symmetric system is much easier, since one can use a single space variable, namely the radial coordinate; we denote this by x and the interphase by $x = s(t)$. For a water ball, $0 \leqslant x < s(t)$ corresponds to water and $s(t) < x \leqslant a$ to ice; the local mean curvature is then $-1/s(t)$ and (1.13) becomes

$$\theta(s(t), t) = \frac{\lambda}{s(t)}, \quad \text{where } s(t) > 0, \text{ in }]0, T[\,. \tag{1.14}$$

Thus here the interface is superheated even at equilibrium. Here (1.4) and (1.1) are replaced by

$$\frac{\partial\theta}{\partial x}(0, t) = 0 \quad \text{in } [0, T] \tag{1.15}$$

$$c\frac{\partial\theta}{\partial t} - \frac{k}{x^{N-1}}\frac{\partial}{\partial x}\left(x^{N-1}\frac{\partial\theta}{\partial x}\right) = 0 \quad \text{in } Q \tag{1.16}$$

(N being the number of space dimensions).

Here we replace the equilibrium condition (1.13) by (1.10), joint with the following linearized kinetic condition

$$ls'(t) + \frac{\lambda}{s(t)} = \theta(s(t), t)\,, \quad \text{where } 0 < s(t) < a, \text{ in }]0, T[\,; \tag{1.17}$$

here l is a positive constant (cf. [4], pp. 222-223).

As discussed by CHALMERS in [6, p. 64], the surface tension causes the instability of the interphase S in the nucleation process; we notice that the characteristic space scale of that phenomenon is so small that the temperature can be assumed constant in space. Now we check that (1.17) accounts for the instability. Assume that at some time t_0 the equilibrium condition (1.14) holds. If later θ increases, then by (1.17) $s'(t)$ becomes positive, hence $\lambda/s(t)$ decreases; consequently, still by (1.17), $s'(t)$ increases even more and $s(t)$ becomes larger and larger. Conversely if θ decreases, then by (1.17) $s(t)$ becomes smaller and smaller and it vanishes after a finite time. For instance if for $t > 0$ the temperature at the interphase is mantained at 0, i.e. $\theta(s(t), t) = 0$, then solving (1.16) we get

$$s(t) = \sqrt{\left(s_0^2 - \frac{2\lambda t}{l}\right)^+}, \quad \forall t > 0 ,$$

hence the water phase vanishes at $t = s_0^2 l/2k$.

So far for the space scale of the nucleation process. For larger space scales, instead, the whole system (1.15), (1.3), (1.17) must be considered and it appears then that the surface tension has a stabilizing effect on planar interfaces [5].

If an ice ball surrounded by water is considered, namely if $0 \leqslant x < s(t)$ corresponds to ice and $s(t) < x \leqslant a$ to water, then the curvature of S is positive and (1.13) becomes

$$\theta(s(t), t) = -\frac{\lambda}{s(t)}, \quad \text{where } s(t) > 0, \text{ in }]0, T[. \tag{1.18}$$

The corresponding relaxation kinetics is

$$l s'(t) + \frac{\lambda}{s(t)} = -\theta(s(t), t), \quad \text{where } 0 < s(t) < a, \text{ in }]0, T[. \tag{1.19}$$

In this case in (1.3) L must be replaced with $-L$.

Both (1.17) and (1.19) are included in the following law

$$s'(t) + \frac{\tilde{\lambda}}{s(t)} = \beta\big(\theta(s(t), t)\big), \quad \text{where } 0 < s(t) < a, \text{ in }]0, T[; \tag{1.20}$$

here $\tilde{\lambda} := \lambda/l$, $\beta \in C^0(\boldsymbol{R})$ and $\beta(0) = 0$.

As pointed out by ROGERS in [16, p. 226], (1.14) is not compatible with the physical property that the temperature must be bounded from below. The kinetic condition (1.20) does not eliminate this difficulty. However, in the opinion of the present author, the latter is essentially due to the linearizations involved in the Gibbs-Thomson law, which holds just for small $|\theta|$. Hence here it should be quite convenient to have maximum and minimum principles at disposal.

In order to eliminate the degeneracy of (1.17) for $s(t) = 0$, we multiply it by $s(t)^p$ for some $p \geqslant 1$. In section 5 we shall take $p = N - 1$, getting

$$\frac{l}{N}\frac{d}{dt}[s(t)]^N + \lambda[s(t)]^{N-2} = \theta s((t), t)\cdot s(t)^{N-1}, \quad \text{where } 0 < s(t) < a, \text{ in }]0, T[; \tag{1.21}$$

we prove that the corresponding variational problem has at least one solution. Also for this problem the uniqueness of the solution is an open question.

5) In the case of several space dimensions, denoting by $\chi \in [0, 1]$ the water concentration, the analog of the kinetic condition (1.11) is

$$\frac{\partial \chi}{\partial t} + H^{-1}(\chi) \ni \beta(\theta) \quad \text{in } Q \ (H^{-1}\text{: inverse of the Heaviside graph}) \tag{1.22}$$

this was studied in [19]. As discussed in [23], even in the case of a single dimension of space, (1.11) and (1.22) correspond to two different phase transition modes. (1.11) corresponds to the movement of a sharp interface, whereas (1.22) entails the formation of mushy regions. In extending (1.11) to several dimensions of space, difficulties arise in forcing χ to attain just the values 0 and 1 a.e. in Q. However in [20] a model was proposed for phase transitions with no mushy regions in multi-dimensional homogeneous systems; this model takes also account of the surface tension effect and of metastable states.

Non-equilibrium interphase conditions for phase transitions in heterogeneous systems are dealt by the present author in [22]; the numerical aspects of a problem of that sort were studied by CROWLEY in [8].

A Stefan-type problem in one space dimension with a kinetic condition at the free boundary was proposed and studied by ASTARITA and SARTI [2, 3] as a model of some polymer phenomena; more mathematical aspects of this problem were studied by FASANO, MEYER and PRIMICERIO [10] and by COMPARINI and RICCI [7]. There a one-phase problem was considered. We notice that such an approach introduces a discontinuity for the unknown function (our θ) at the free boundary, a possibility we esclude here (see (1.10)); thus that model cannot be regarded as the one-phase problem corresponding to the two-phase problem of the present paper.

The results of the present paper were announced in [23].

2. – Problem in one space dimension.

Firstly we assume that c, L and k are positive constants. We denote by H the Heaviside function:

$$H(\xi) := \begin{cases} 0 & \text{if } \xi \leqslant 0 \\ 1 & \text{if } \xi > 0 \,, \end{cases}$$

we set $W := L^2(0, a)$, $V := H^1(0, a)$ and

$$_{V'}\langle Au, v\rangle_V := k\int_0^a u'(x)\cdot v'(x)\, dx \,, \qquad \forall u, v \in V \,.$$

We assume that

$$\beta \in C^0(\mathbf{R}) \tag{2.1}$$

$$f \in L^2(0, T; V'), \qquad \theta^0 \in V',\ s^0 \in [0, a] \tag{2.2}$$

and introduce a variational problem:

PROBLEM (P1). – *Find* $\theta \in L^2(0, T; V)$ *and* $s \in W^{1,1}(0, T)$ *such that*

$$\frac{\partial}{\partial t}[c\theta + LH(s(t) - x)] + A\theta = f \quad \text{in } V', \text{ a.e. in }]0, T[\tag{2.3}$$

$$\begin{cases} \text{a.e. in }]0, T[, \quad 0 \leqslant s(t) \leqslant a \quad \text{and} \quad \forall \xi \in [0, a] \\ \big[s'(t) - \beta\big(\theta(s(t), t)\big)\big] \cdot [\xi - s(t)] \geqslant 0 \end{cases} \tag{2.4}$$

$$\theta|_{t=0} = \theta^0 \quad \text{in } V' \tag{2.5}$$

$$s(0) = s^0 . \tag{2.6}$$

REMARKS. – (i) (2.3) yields $c\theta + LH(s(t) - x) \in H^1(0, T; V')$; moreover $H(s(t) - x) \in C^0([0, T]; W)$; hence $\theta \in C^0([0, T]; V')$ and this gives a meaning to (2.5).

(ii) For any $v \in \mathcal{D}(Q)$, setting $\mathcal{S} := \{(s(t), t) : 0 < t < T\}$, we have

$$\begin{aligned} \int_0^T {}_{V'}\Big\langle \frac{\partial}{\partial t}[c\theta + LH(s(t) - x)] + A\theta, v\Big\rangle_V \, dt = \\ = -c\iint_Q \theta \frac{\partial v}{\partial t}\, dx\, dt + L\int_{\mathcal{S}} v|_{x=s(t)}\, dx + k\iint_Q \frac{\partial \theta}{\partial x}\cdot\frac{\partial v}{\partial x}\, dx\, dt = \\ = c\iint_{Q\setminus \mathcal{S}} \frac{\partial \theta}{\partial t} v\, dx\, dt + L\int_0^T v(s(t), t)\cdot s'(t)\, dt - k\iint_{Q\setminus\mathcal{S}} \frac{\partial^2 \theta}{\partial x^2} v\, dx\, dt - \\ - k\int_Q^T \Big[\frac{\partial \theta}{\partial x}(s(t) + 0, t) - \frac{\partial \theta}{\partial x}(s(t) - 0, t)\Big]\cdot v(s(t), t)\, dt . \end{aligned} \tag{2.7}$$

Hence if

$${}_{V'}\langle f(t), v\rangle_V = g_2(t)v(a) - g_1(t)v(0), \quad \forall v \in V, \text{ a.e. in }]0, T[, \tag{2.8}$$

then (2.3) corresponds to (1.1), (1.3) and (1.10). Thus we can state the following result

PROPOSITION 1. – *If* (2.8) *holds, then* (P1) *is equivalent to the following strong formulation;*

PROBLEM ($\widetilde{\text{P1}}$). – *Find* $\theta \in C^0(\bar{Q})$ *and* $s \in W^{1,1}(0, T)$ *such that* $0 \leqslant s(t) \leqslant a$ *and* (1.1), (1.3), ..., (1.7), (1.11)′ *hold.* □

If instead distributed heat sources are present, then mushy regions may appear and consequently the variational problem (P1) is no longer equivalent to the classical formulation ($\widetilde{\text{P1}}$).

(iii) If (2.8) holds, then no maximum nor minimum can appear in the interior of any phase, if not existing for $t = 0$. Hence if (1.9) holds then the highest supercooling and superheating values are attained at the interface.

(iv) (2.3) can be rewritten in the equivalent form

$$c\frac{d}{dt}\int_0^a \theta v\,dx + Ls'(t)\cdot v(s(t)) + k\int_0^a \frac{\partial\theta}{\partial x}\cdot\frac{\partial v}{\partial x}\,dx = {}_{V'}\langle f, v\rangle_V\,, \qquad \forall v \in V, \text{ a.e. in }]0, T[\,. \tag{2.9}$$

LEMMA 1. – For any $\varepsilon > 0$ there exists a constant $C(\varepsilon) > 0$ such that, for any $\theta \in V$ and $r \in [0, a]$,

$$|\theta(r)|^2 \leqslant \int_0^a [\varepsilon\theta'(y)^2 + C(\varepsilon)\theta(y)^2]\,dy\,. \tag{2.10}$$

PROOF. – Let $\xi \in [0, a]$ be such that $\theta(\xi) = 1/a\int_0^a \theta(y)\,dy$. We have

$$\theta(r)^2 = \theta(\xi)^2 + \int_\xi^r (\theta^2(y))'\,dy \leqslant \left[\frac{1}{a}\int_0^a \theta(y)\,dy\right]^2 + 2\int_\xi^r |\theta(y)\theta'(y)|\,dy \leqslant$$
$$\leqslant \int_0^a \left[\frac{1}{a}\theta(y)^2 + \varepsilon\theta'(y)^2 + \frac{1}{\varepsilon}\theta(y)^2\right] dy\,. \qquad \square$$

Henceforth by C_i we shall denote generic positive constants.

THEOREM 1. – *Assume that* (2.1) *and* (2.2) *hold and that*

$$|\beta(\xi)| \leqslant C_1|\xi| + C_2\,, \qquad \forall \xi \in \mathbf{R} \tag{2.11}$$

$$\theta^0 \in W\,. \tag{2.12}$$

Then problem (P1) *has at least one solution such that*

$$\theta \in L^\infty(0, T; W)\,, \qquad s \in H^1(0, T)\,. \tag{2.13}$$

PROOF. – (i) *Faedo-Galerkin approximation.*

Let $\{V_m\}_{m\in N}$ be a sequence of finite dimensional subspaces filling up V and let

$$\{f_m \in C^0([0, T]; V')_{m\in N}\}\,, \qquad f_m \to f \text{ strongly in } L^2(0, T; V')$$

$$\{\theta_m^0 \in V_m\}_{m\in N}\,, \qquad \theta_m^0 \to \theta^0 \text{ strongly in } W$$

$$\Phi_m(\xi) := \begin{cases} m\xi & \text{if } \xi < 0 \\ 0 & \text{if } 0 \leqslant \xi \leqslant a \\ m(\xi - a) & \text{if } \xi > a\,. \end{cases}$$

For any m we introduce the following approximated problem:

PROBLEM $(\mathrm{P1})_m$. – *Find* θ_m: $[0, T[\to V_m$ *and* s_m: $[0, T[\to \boldsymbol{R}$ *such that, setting*

$$\tilde{s}_m(t) := \begin{cases} 0 & \text{if } s_m(t) < 0 \\ s_m(t) & \text{if } 0 \leqslant s_m(t) \leqslant a\,, \\ a & \text{if } s_m(t) > a \end{cases}$$

$$\int_0^a \left[c\frac{\partial\theta_m}{\partial t}v + k\frac{\partial\theta_m}{\partial x}\cdot\frac{\partial v}{\partial x}\right]dx + Ls'_m(t)\cdot v(\tilde{s}(t)) = {}_{V'}\langle f_m(t), v\rangle_V\,, \qquad \forall v \in V_m, \text{ in }]0, T[\tag{2.14}$$

$$s'_m(t) + \Phi_m(s_m(t)) = \beta\big(\theta_m(\tilde{s}_m(t), t)\big) \qquad \text{in }]0, T[\tag{2.15}$$

$$\theta_m(x, 0) = \theta_m^0(x) \qquad \text{a.e. in }]0, a[\tag{2.16}$$

$$s_m(0) = s^0\,. \tag{2.17}$$

This problem is equivalent to a Cauchy problem for a system of a finite number of ordinary differential equations and has at least one solution in $[0, T_m[$, for a suitable $T_m \in]0, T]$.

(ii) *A priori estimates.*

We take $v = \theta_m$ in (2.14), multiply (2.15) by $s_m(t)$, sum and integrate in $]0, \tilde{t}[$, for a generic $\tilde{t} \in]0, T_m[$. We notice that by lemma 1

$$\left|\int_0^{\tilde{t}} s'_m(t)\cdot\theta(\tilde{s}_m(t), t)\,dt\right| \leqslant \left(\int_0^{\tilde{t}} s'_m(t)^2\,dt\right)^{\frac12}\cdot\left(\int_0^{\tilde{t}}\theta_m(\tilde{s}_m(t), t)^2\,dt\right)^{\frac12} \leqslant$$
$$\leqslant \left(\int_0^{\tilde{t}} s'_m(t)_2\,dt\right)^{\frac12}\cdot\left(\int_0^{\tilde{t}}dt\int_0^a\left[\varepsilon\left(\frac{\partial\theta_m}{\partial x}\right)^2 + C(\varepsilon)\theta_m^2\right]dx\right)^{\frac12}$$

for any $\varepsilon > 0$; the term $\int_0^{\tilde{t}} \beta\big(\theta_m(\tilde{s}_m(t), t)\big)\cdot s'_m(t)\,dt$ can be estimated similarly, by (2.11). Then we get

$$(2.18)\quad \frac{c}{2}\int_0^a [\theta_m(x,\tilde{t})^2 - \theta_m(x,0)^2]\,dx + k\int_0^{\tilde{t}} dt\int_0^a \left(\frac{\partial\theta_m}{\partial x}\right)^2 dx + \int_0^{\tilde{t}} s'_m(t)^2\,dt + \int_{s^0}^{s_m(\tilde{t})} \Phi_m(\xi)\,d\xi \leqslant \|f\|_{L^2(0,T;V')}\cdot\left(\int_0^{\tilde{t}} \|\theta_m(t)\|_V^2\,dt\right)^{\frac12} + C_3\left(\int_0^{\tilde{t}} s'_m(t)^2\,dt\right)^{\frac12}\cdot\left(\int_0^{\tilde{t}} dt\int_0^a \left[\varepsilon\left(\frac{\partial\theta_m}{\partial x}\right)^2 + C(\varepsilon)\theta_m^2\right]dx\right)^{\frac12} + C_4 .$$

Applying Gronwall's lemma, we obtain $T = T_m$ for any m and

$$(2.19)\quad \|\theta_m\|_{L^\infty(0,T;W)\cap L^2(0,T;V)}, \quad \|s_m\|_{H^1(0,T)}, \quad \left\|\int_{s_0}^{s_m(t)} \Phi_m(\xi)\,d\xi\right\|_{L^\infty(0,T)} \leqslant \text{Constant} \quad (\text{independent of } m);$$

hence by comparison in (2.14) we get

$$(2.20)\quad \|\theta_m\|_{H^1(0,T;V')} \leqslant \text{Constant}.$$

Moreover (2.19) also yields

$$(2.21)\quad \big(s_m(t) - a\big)^+ - s_m(t)^- \to 0 \quad \text{a.e. in }]0,T[.$$

(iii) *Limit procedure.*

By the previous a priori estimates, there exist θ and s such that

$$(2.22)\quad \theta_m \to \theta \quad \text{weakly star in } L^\infty(0,T;W)\cap L^2(0,T;V)\cap H^1(0,T;V')$$

$$(2.23)\quad s_m \to s \quad \text{weakly in } H^1(0,T);$$

hence by Aubin's compactness lemma (see [13], p. 57)

$$\theta_m \to \theta \quad \text{strongly in } L^2\big(0,T;H^{1-\delta}(0,a)\big), \quad \forall\delta > 0;$$

then for any $\varrho \in]0,\frac12[$

$$\|\theta_m(\tilde{s}_m(t),t) - \theta(s(t),t)\|_{L^2(0,T)} \leqslant \|\theta_m(\tilde{s}_m(t),t) - \theta_m(s(t),t)\|_{L^2(0,T)} + \|\theta_m(s(t),t) - \theta(s(t),t)\|_{L^2(0,T)} \leqslant \left\|\int_{s(t)}^{\tilde{s}_m(t)} \frac{\partial\theta_m}{\partial x}(\xi,t)\,d\xi\right\|_{L^2(0,T)} + \text{Constant}\cdot\|\theta_m - \theta\|_{L^2(0,T;H^{\frac12+\varrho}(0,a))} \to 0$$

that is

$$\theta_m(\tilde{s}_m(t), t) \to \theta(s(t), t) \quad \text{strongly in } L^2(0, T) ;$$

hence

$$\beta\big(\theta_m(\tilde{s}_m(t), t)\big) \to \beta\big(\theta(s(t), t)\big) \quad \text{weakly in } L^2(0, T) .$$

Thus taking $m \to \infty$ in (2.14) we get (2.3).

Multiplying (2.15) by $\xi - s_m(t)$ for a generic $\xi \in [0, a]$, we have

$$\Big[s'_m(t) - \beta\Big(\theta_m\big(\tilde{s}_m(t), t\big)\Big)\Big]\cdot[\xi - s_m(t)] = -\,\Phi_m\big(s_m(t)\big)\cdot[\xi - s_m(t)] \geqslant 0$$

and taking $m \to \infty$ we get (2.4). □

REMARK. – Since in theorem 1 the function β is not required to be Lipschitz-continuous, it is allowed that β be very steep near $\theta = 0$; for instance

$$(2.24) \qquad \beta(\theta) := \begin{cases} \gamma \cdot \dfrac{|\theta|^\alpha}{\theta} & \text{if } \theta \neq 0 \ \ (\gamma, \alpha\text{: constants}, \gamma > 0, 1 < \alpha < 2) \\ 0 & \text{if } \theta = 0 . \end{cases}$$

In this case the supercooling and superheating amounts at the interface have a higher order of infinitesimum than the interface velocity; hence the smaller is this velocity the better is the approximation given by the usual equilibrium condition.

A model of glass formation. – « At extremely rapid cooling rates, say 10^5-10^6 °C/s rather than forming solid crystal, a glass is produced. An important consequence of this is that under these conditions no latent heat of solidification needs to be absorbed » (SZEKELY, [17]). This technique allows to produce even metal glasses.

We propose to represent this phenomenon by means of the kinetic condition (1.11), with a function β of the following form

$$(2.25) \qquad \begin{cases} \beta \in C^0(\mathbf{R}); \quad \beta(0) = 0; \quad \text{there exists } \hat{\theta} < 0 \text{ such that} \\ \beta = 0 \text{ in }]-\infty, \hat{\theta}],\ \beta(\theta) < 0 \text{ in }]\hat{\theta}, 0[,\ \beta(\theta) > 0 \text{ in } \mathbf{R}^+ \text{ (see fig. 1)} . \end{cases}$$

According to this model, there is crystallization only if the interface temperature is comprised between $\hat{\theta}$ and 0; if it drops under $\hat{\theta}$, then no latent heat is delivered and a glassy phase is formed.

Theorem 1 can be applied for a function β as in (2.25).

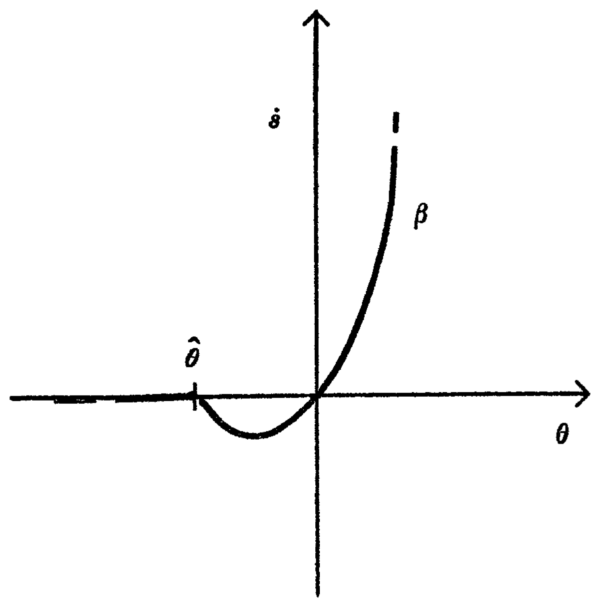

Figure 1 - Kinetic law for the glass formation model.

PROPOSITION 2 (*Maximum principle*). – *Assume that* (2.1) *and* (2.2) *hold and that there exists an* $M \in \mathbf{R}$ *such that*

(2.26) $$\beta(\xi) \geq 0\,, \quad \forall \xi \geq M$$

(2.27) $$\theta^0 \in W\,, \quad \theta^0(x) \leq M \quad \text{a.e. in }]0, a[$$

(2.28) $$f \leq 0 \qquad \text{in } \mathcal{D}'(Q)\,.$$

Thena ny solution of (P1) *fulfills the condition*

(2.29) $$\theta \leq M \quad \text{a.e. in } Q\,.$$

PROOF. – It is sufficient to take $v = (\theta - M)^+$ in (2.9) and to integrate in time. □
Similarly, a minimum principle can be established.

3. – Generalizations.

Until now we have assumed the physical coefficients c, L and k to be constant; actually these quantities depend on the temperature θ and on the phase variable χ, which represents the water concentration (thus $\chi = 0$ in the solid; $\chi = 1$ in the liquid; $0 < \chi < 1$ in mushy regions, namely mixtures of water and ice). Although in this paper we are concerned with sharp interphases, at this point it is convenient to discuss shortly the general case. The heat equation has the form

$$\hat{c}(\theta, \chi)\frac{\partial\theta}{\partial t} + \hat{L}(\theta)\frac{\partial\chi}{\partial t} - \frac{\partial}{\partial x}\left[\hat{k}(\theta, \chi)\frac{\partial\theta}{\partial x}\right] = f \quad \text{in } Q\,, \tag{3.1}$$

in the sense of distributions; of course we assume that the functions $\hat{c}$, $\hat{L}$ and $\hat{k}$ are sufficiently smooth. Since $\hat{c}(\theta, \chi)\, d\theta + \hat{L}(\theta)\, d\chi = de$ (differential of the enthalpy density), the following compatibility condition must be fulfilled

$$\frac{\partial}{\partial\chi}\hat{c}(\theta, \chi) = \frac{d}{d\theta}\hat{L}(\theta)\,, \quad \forall(\theta, \chi) \in \boldsymbol{R}\times[0, 1]\,. \tag{3.2}$$

We shall distinguish two cases:

(i) *L is constant.* – Then by (3.2) $\hat{c}$ is independent of χ and the Kirchhoff's transformation can be used. We set

$$\begin{aligned}
&\hat{\zeta}(\xi) := \int_0^\xi \hat{c}(\eta)\, d\eta && \forall \xi \in \boldsymbol{R}\\
&\tilde{\theta}(x, t) := \hat{\zeta}(\theta(x, t)) && \text{in } Q\,;\\
&\tilde{k}(v, \chi) := \frac{\hat{k}(\hat{\zeta}^{-1}(v), \chi)}{\hat{c}(\hat{\zeta}^{-1}(v))} && \forall v \in \boldsymbol{R},\ \forall \chi \in [0, 1];
\end{aligned}$$

then (3.1) becomes

$$\frac{\partial\tilde{\theta}}{\partial t} + L\frac{\partial\chi}{\partial t} - \frac{\partial}{\partial x}\left[\tilde{k}(\tilde{\theta}, \chi)\frac{\partial\tilde{\theta}}{\partial x}\right] = f \quad \text{in } Q\,, \tag{3.3}$$

in the sense of distributions. In the one-dimensional case we can formulate a problem similar to (P1) for $(\tilde{\theta}, s)$, with k replaced by $\tilde{k}(\tilde{\theta}, H(s(t) - x))$; assuming that $\tilde{k}$ is continuous and upperly and lowerly bounded by positive constants, an existence result of the type of theorem 1 can be proved.

(ii) $L = \hat{L}(\theta)$. – We also assume that this dependence is linear; then by (3.2) we have

$$\begin{cases} c = \hat{c}(\theta, \chi) = c_1(\theta) + \gamma\chi \quad (c_1 > 0,\, c_1 + \gamma > 0)\\ L = \hat{L}(\theta) = \hat{L}(0) + \gamma\theta\,. \end{cases} \tag{3.4}$$

For obvious physical reasons, it is required that $\hat{L}(\theta) \geqslant 0$; thus θ must be upperly or lowerly bounded, depending on the sign of γ. For definiteness we assume that $\gamma > 0$; then $\hat{L}(\theta) \geqslant 0$ if and only if $\theta \geqslant -\hat{L}(0)/\gamma$; hence it will be quite convenient to have a minimum principle at disposal. We set

$$\alpha(\xi) := \int_0^\xi c_1(\eta)\, d\eta\,, \qquad \forall \xi \in \boldsymbol{R}\,,$$

so that

$$de = [c_1(\theta) + \gamma\chi]\, d\theta + [\hat{L}(0) + \gamma\theta]\, d\chi = d[\alpha(\theta) + \hat{L}(\theta)\chi]\,.$$

We consider the case of a single dimension of space, with $\chi = H(s(t) - x)$, and set

$$_{V'}\langle A(\theta, \chi)u, v\rangle_V := \int_0^a \hat{k}(\theta, \chi)u' \cdot v'\, dx\,, \qquad \forall \theta \in \boldsymbol{R},\ \forall \chi \in [0, 1],\ \forall u, v \in V$$

$$\omega^0 := \alpha(\theta^0) + \gamma\theta^0 \cdot H(s^0 - x) + \hat{L}(0) \cdot H(s^0 - x) \qquad \text{in }]0, a[\,;$$

we assume that (2.1) and (2.2) hold, that $\omega^0 \in V'$ and introduce a variational problem:

PROBLEM (P2). – *Finf $\theta \in L^2(0, T; V)$ and $s \in W^{1,1}(0, T)$ such that* (2.4), (2.6) *hold and*

$$\frac{\partial}{\partial t}[\alpha(\theta) + \hat{L}(\theta) \cdot H(s(t) - x)] + A\big(\theta, H(s(t) - x)\big)\theta = f \quad \text{in } V',\ \text{a.e. in }]0, T[\tag{3.5}$$

$$[\alpha(\theta) + \hat{L}(\theta) \cdot H(s(t) - x)]_{t=0} = \omega^0 \quad \text{in } V'\,. \tag{3.6}$$

We notice that (2.4) *formally* yields

$$\int_0^a [\alpha(\theta) + \gamma H(s(t) - x)] \cdot \frac{\partial \theta}{\partial t} \cdot v\, dx + \hat{L}\big(\theta(s(t), t)\big) \cdot s'(t) \cdot v(s(t)) = + \int_0^a \hat{k}\big(\theta, H(s(t) - x)\big) \cdot \frac{\partial \theta}{\partial x} \cdot \frac{\partial v}{\partial x}\, dx = {}_{V'}\langle f, v\rangle_V\,, \qquad \forall v \in V,\ \text{a.e. in }]0, T[; \tag{3.7}$$

but this is not rigorous, as a priori $\partial\theta/\partial t$ is just a distribution.

The interpretation of (P2) as a boundary and initial value problem for an equation of the form of (3.1) is similar to that of (P1).

We prove an existence result

THEOREM 2. – *Assume that* (2.1) *holds and that*

$$|\beta(\xi)| \leq C_5\,, \qquad \forall \xi \geq -\frac{\hat{L}(0)}{\gamma} \tag{3.8}$$

$$\theta^0 \in W\,, \qquad \theta^0 \geq -\frac{\hat{L}(0)}{\gamma} \qquad \text{a.e. in }]0, a[;\ f \geq 0 \text{ in } \mathcal{D}'(Q) \tag{3.9}$$

$$\alpha \in C^1(\boldsymbol{R})\,; \qquad \alpha' \geq c_1: \quad \text{constant} > 0\,. \tag{3.10}$$

Then problem (P2) *has at least one solution such that*

$$\theta \in L^\infty(0, T; W) \cap H^{1/2-\delta}(0, T; W), \quad \forall \delta > 0; \; s \in H^1(0, T) \tag{3.11}$$

$$\hat{L}(\theta) := \hat{L}(0) + \gamma\theta \geqslant 0 \qquad \text{a.e. in } Q. \tag{3.12}$$

REMARK. - A maximum principle can be easily proven; hence (3.8) is not too restrictive.

PROOF. - At first we replace $\hat{L}(\theta)$ by $\hat{L}(\theta)^+$ in (3.5) and (3.6); this modified problem $(\widetilde{\mathrm{P}2})$ has at least one solution, as can be proved by a procedure similar to that of theorem 1; we just point out the essential modifications. We set

$$H_m(\xi) := \begin{cases} 0 & \text{if } \xi \leqslant -\dfrac{1}{m} \\[2mm] \dfrac{m}{2}\xi + \dfrac{1}{2} & \text{if } -\dfrac{1}{m} \leqslant \xi \leqslant \dfrac{1}{m} \\[2mm] 1 & \text{if } \xi \geqslant \dfrac{1}{m} \end{cases}$$

and in the approximate problem we replace (2.14) by

$$\begin{aligned} &\int_0^a [\alpha'(\theta_m) + \gamma H_m(\hat{L}(\theta_m)) \cdot H_m(s_m(t) - x)] \frac{\partial \theta_m}{\partial t} v \, dx + \\ &\quad + \hat{L}\big(\theta_m(\tilde{s}_m(t), t)\big)^+ \cdot s_m'(t) \cdot v(\tilde{s}_m(t)) + \int_0^a \hat{k}\big(\theta_m, H_m(s_m(t) - x)\big) \cdot \frac{\partial \theta_m}{\partial x} \cdot \frac{\partial v}{\partial x} \, dx = \\ &\quad = {}_{V'}\langle f_m(t), v \rangle_V, \qquad \forall v \in V, \text{ in }]0, T[\,. \end{aligned} \tag{3.13}$$

Here we take $v = \hat{L}(\theta_m)$ $(= \hat{L}(0) + \gamma\theta_m)$ and integrate in $]0, \bar{t}[$; we notice that, setting $B_m(\xi) := \int_0^{\hat{L}(\xi)} H_m(\eta)\eta \, d\eta$ for any $\xi \in \mathbf{R}$, we have

$$\begin{aligned} \gamma \int_0^{\bar{t}} dt \int_0^a H_m(\hat{L}(\theta_m)) \cdot H_m(s_m(t) - x) \cdot \frac{\partial \theta_m}{\partial t} \cdot \hat{L}(\theta_m) \, dx &= \int_0^{\bar{t}} dt \int_0^a H_m(s_m(t) - x) \cdot \frac{\partial}{\partial t} B_m(\theta_m) \, dx \geqslant \\ \geqslant \int_0^a H_m(s_m(\bar{t}) - x) \cdot B_m(\theta_m(x, \bar{t})) \, dx &- \int_0^a H_m(s^0 - x) \cdot B_m(\theta_m^0) \, dx - \\ &- \int_0^{\bar{t}} dt \int_0^a H_m'(s_m(t) - x) \cdot s_m'(t) \cdot B_m(\theta_m) \, dx \,. \end{aligned}$$

For each t, the support of $H_m'(s_m(t) - x)$ is contained in $[\lambda_m'(t), \lambda_m''(t)]$, where $\lambda_m'(t) := \max\big(s_m(t) - 1/m, 0\big)$, $\lambda_m''(t) := \min\big(s_m(t) + 1/m, 0\big)$ therefore $H_m'(s_m(t) - x)$ does not vanish identically only if $-1/m \leqslant s_m(t) \leqslant a + 1/m$ and this entails $\Phi_m(s_m(t)) = 0$. Hence using (2.15), (3.8) and noticing that $B_m(\theta_m) \neq 0$ entails $L(\theta_m) > -1/m$, we have, for a suitable $\xi_m(t) \in [\lambda'_m(t), \lambda''_m(t)]$,

$$\left|\int_0^{\tilde{t}} dt \int_0^a H'_m(s_m(t) - x) \cdot s'_m(t) \cdot B_m(\theta_m)\, dx\right| \leqslant \int_0^{\tilde{t}} dt \left|\beta\big(\theta_m(s_m(t), t)\big)\right| \cdot B_m(\xi_m(t))\, dt \leqslant$$

$$\leqslant C_5 \int_0^{\tilde{t}} B_m\big(\theta_m(\tilde{s}_m(t), t)\big)\, dt + \sigma(m) \leqslant \text{ (by lemma 1)}$$

$$\leqslant C_5 \int_0^{\tilde{t}} (\varepsilon \|L(\theta_m)^+\|_V^2 + C(\varepsilon)\|L(\theta_m)^+\|_W^2)\, dt + \tilde{\sigma}(m)\,,$$

where $\sigma(m), \tilde{\sigma}(m) \to 0$ as $m \to \infty$; moreover by (3.8) and by lemma 1

$$\left|\int_0^{\tilde{t}} \hat{L}\big(\theta_m(\tilde{s}_m(t), t)\big)^+ \cdot s'_m(t) \cdot \hat{L}\big(\theta_m(\tilde{s}_m(t), t)\big)\, dt\right| \leqslant$$

$$\leqslant \int_0^{\tilde{t}} \left|\beta\big(\theta_m(s_m(t), t)\big)\right| \{[\hat{L}(0) + \gamma\theta_m(\tilde{s}_m(t), t)]^+\}^2\, dt \leqslant$$

$$\leqslant C_5 \int_0^{\tilde{t}} [\hat{L}(0)^2 + \gamma^2(\varepsilon\|\theta_m\|_V^2 + C(\varepsilon)\|\theta_m\|_W^2)]\, dt\,.$$

Also here Gronwall's lemma can be applied, yielding the a priori esimate (2.19), whence

$$\|\hat{L}\big(\theta_m(\tilde{s}_m(t), t)\big)^+ \cdot s'_m(t)\|_{L^2(0,T)} \leqslant \text{Constant}\,. \tag{3.14}$$

Here it does not seem possible to deduce (2.20) by comparison in (3.13); we shall estimate the time regularity of θ_m by means of a technique essentially due to ALT and LUCKHAUS [1]. For any $h \in]0, T[$ we set $\theta_m^h(x, t) := \theta_m(x, t + h)$ in Q. We take $v = \theta_m^h - \theta_m$ in (3.13) and integrate in $]0, T - h[$; we notice that for any m, as $h \to 0^+$ we have

$$\sigma_{(x,t)}^m(h) := \frac{\partial \theta_m}{\partial t} - \frac{\theta_m^h - \theta_m}{h} \to 0 \quad \text{strongly in } L^2(0, T; V)\,.$$

Hence, using also (2.19), we have

$$c_1 \int_0^{T-h} dt \int_0^a \frac{(\theta_m^h - \theta_m)^2}{h}\, dx \leqslant \tag{3.15}$$

$$\leqslant \left|\int_0^{T-h} dt \int_0^a [\alpha'(\theta_m) + \gamma H_m(\hat{L}(\theta_m)) \cdot H_m(x - s_m(t))] \cdot \frac{\partial \theta_m}{\partial t} \cdot (\theta_m^h - \theta_m)\, dx + \hat{\sigma}_m(h)\right| \leqslant$$

$$\leqslant \text{Constant} \cdot \|\theta_m^h - \theta_m\|_{L^2(0,T-h;V)} \leqslant \text{Constant (independent of } h)\,;$$

here $\hat{\sigma}(h) \to 0$ as $h \to 0^+$. We also notice that for any $\delta > 0$ and for any $u \in H^{\frac{1}{2}-\delta}(\boldsymbol{R})$ one has (cf. [18, p. 190])

$$\|u\|_{H^{\frac{1}{2}-\delta}(\boldsymbol{R})} = \|u\|_{L^2(\boldsymbol{R})} + \left(\iint_{\boldsymbol{R}^2} \frac{[u(t)-u(\tau)]^2}{|t-\tau|^{2-2\delta}}\, dt\, d\tau\right)^{\frac{1}{2}} = \\ = \|u\|_{L^2(\boldsymbol{R})} + \left(2\int_{\boldsymbol{R}^+} dh\, h^{2\delta-1} \cdot \int_{\boldsymbol{R}} \frac{[u(t+h)-u(t)]^2}{h}\, dt\right)^{\frac{1}{2}}$$

(notice that $\int_{\boldsymbol{R}^+} dh\, h^{2\delta-1} < +\infty$). Thus (3.15) yields

$$\|\theta_m\|_{H^{\frac{1}{2}-\delta}(0,T;W)} \leqslant \text{Constant}\,, \quad \forall\delta > 0\,. \tag{3.16}$$

These a priori estimates allow to take the limit in the approximated problem and to get the existence of a solution (θ, s) of the modified problem $(\widetilde{\text{P2}})$. Then multiplying the θ-equation by $-\hat{L}(\theta)^-$, it is not difficult to check that $\hat{L}(\theta)^- = 0$; that is (θ, s) solves problem (P2) and (3.12) is fulfilled. □

Finally we notice that the previous developments can be extended to the case in which c, L, k and β depend explicitely on $(x, t) \in Q$, assuming that these dependences are regular enough.

4. - Vanishing relaxation time.

We assume that c, L and k are constant and that (2.1) and (2.2) hold. For any $\varepsilon > 0$ we consider the following problem

PROBLEM $(\text{P1})_\varepsilon$. - *Find* $\theta_\varepsilon \in L^2(0, T; V)$ *and* $s_\varepsilon \in W^{1,1}(0, T)$ *such that*

$$\frac{\partial}{\partial t}[c\theta_\varepsilon + LH(s_\varepsilon(t) - x)] + A\theta_\varepsilon = f \quad \text{in } V', \text{ a.e. in }]0, T[\tag{4.1}$$

$$\begin{cases} \text{a.e. in }]0, T[\,, \quad 0 \leqslant s_\varepsilon(t) \leqslant a \quad \text{and} \quad \forall \xi \in [0, a] \\ \left[\varepsilon s'_\varepsilon(t) - \beta\big(\theta_\varepsilon(s_\varepsilon(t), t)\big)\right]\cdot[\xi - s_\varepsilon(t)] \geqslant 0 \end{cases} \tag{4.2}$$

$$\theta_\varepsilon|_{t=0} = \theta^0 \quad \text{in } V' \tag{4.3}$$

$$s_\varepsilon(0) = s^0\,. \tag{4.4}$$

THEOREM 3. - *Assume that* (2.1), (2.2) *hold and that*

$$\beta(0) = 0 \tag{4.5}$$

$$\tilde{b}\xi^2 \leqslant \beta(\xi)\,\xi \leqslant b\xi^2\,, \quad \forall \xi \in \boldsymbol{R} \ (b, \tilde{b}\text{: constants} > 0) \tag{4.6}$$

$$f \in L^2(0, T; V') \cap L^1(Q)\,, \quad \theta^0 \in W\,. \tag{4.7}$$

For any set A, we denote by χ_A its characteristic function; namely $\chi_A = 1$ in A, $\chi_A = 0$ in the couplementary of A.

For any $\varepsilon > 0$, let $(\theta_\varepsilon, s_\varepsilon)$ be a solution of (P1)$_\varepsilon$ *(existing by theorem* 1*). Then as $\varepsilon \to 0^+$*

$$\|\theta_\varepsilon(s_\varepsilon(t), t)\, \chi_{\{0<s_\varepsilon(t)<a\}}\|_{L^1(0,T)} = 0(\varepsilon)\,, \tag{4.8}$$

and there exist θ and s such that, possibly taking subsequences,

$$\begin{cases} \theta_\varepsilon \to \theta \text{ weakly star in } L^\infty(0,T;W) \cap L^2(0,T;V) \cap H^{\frac{1}{2}-\delta}(0,T;V')\,, \forall\delta>0\,, \\ s_\varepsilon \to s \text{ weakly star in } BV(0,T)\,. \end{cases} \tag{4.9}$$

Moreover (θ, s) solves the reduced problem (P1)$_0$:

PROBLEM (P1)$_0$. – *Find $\theta \in L^2(0,T;V)$ and $s \in BV(0,T)$, such that $0 \leqslant s(t) \leqslant a$ in $]0, T[$ and*

$$\frac{\partial}{\partial t}[c\theta + LH(s(t)-x)] + A\theta = f \quad \text{in } V', \text{ in } \mathcal{D}'(]0,T[) \tag{4.10}$$

$$\theta(s(t), t)\cdot[s(t) - \xi] \geqslant 0\,, \quad \forall \xi \in [0, a], \text{ a.e. in }]0, T[\tag{4.11}$$

$$[c\theta + LH(s(t)-x)]_{t=0} = c\theta^0 + LH(s^0 - x) \quad \text{in } V'\,. \tag{4.12}$$

REMARK. – If (2.8) and (1.9) hold, then neither superheated nor supercoooled regions appear; then problem (P1)$_0$ coincides with the standard two-phase Stefan problem (1.1), ..., (1.8) and has a unique solution; consequently the whole sequence of solutions $(\theta_\varepsilon, s_\varepsilon)$ converges to (θ, s).

PROOF. – (i) *Estimates.*

We notice that (4.2) yields

$$\varepsilon s_\varepsilon'(t) = \beta\big(\theta_\varepsilon(s_\varepsilon(t), t)\big)\, \chi_{\{0<s_\varepsilon(t)<a\}} \quad \text{a.e. in }]0, T[\,. \tag{4.13}$$

For any $j \in \mathbf{N}$, we set

$$\sigma_j(\xi) := \begin{cases} -1 & \text{if } \xi \leqslant -\frac{1}{j} \\ j\xi & \text{if } -\frac{1}{j} < \xi < \frac{1}{j}\,; \\ 1 & \text{if } \xi \geqslant \frac{1}{j} \end{cases}$$

we also set $m_j(\xi) = \int\limits_0^\xi \sigma_j(\varrho)\, d\varrho$, $\forall \xi \in \mathbf{R}$. We multiply (4.1) by $\sigma_j(\theta_\varepsilon)$ and integrate in $]0, \bar{t}[$, for a generic $\bar{t} \in]0, T[$; thus we get

$$(4.14)\qquad c\int\limits_0^a [m_j(\theta_\varepsilon(x, \bar{t})) - m_j(\theta^0(x))]\, dx + L\int\limits_0^{\bar{t}} s'_\varepsilon(t)\cdot\sigma_j\big(\theta_\varepsilon(s_\varepsilon(t), t)\big)\, dt + \\ + k\int\limits_0^{\bar{t}} dt\int\limits_0^a \sigma'_j(\theta_\varepsilon)|\overline{\nabla}\theta_\varepsilon|^2\, dx \leqslant \int\limits_0^{\bar{t}} dt\int\limits_0^a |f|\, dx\,.$$

By (4.13) and (4.6) we have

$$(4.15)\qquad L\int\limits_0^{\bar{t}} s'_\varepsilon(t)\cdot\sigma_j\big(\theta_\varepsilon(s_\varepsilon(t), t)\big)\, dt = \frac{L}{\varepsilon}\int\limits_0^{\bar{t}} \beta\big(\theta_\varepsilon(s_\varepsilon(t), t)\big)\cdot\sigma_j\big(\theta_\varepsilon(s_\varepsilon(t), t)\big)\cdot\chi_{\{0<s_\varepsilon(t)<a\}}\, dt \geqslant \\ \geqslant \frac{L}{\varepsilon}\int\limits_0^{\bar{t}} \left|\beta\big(\theta_\varepsilon(s_\varepsilon(t), t)\big)\right|\cdot\chi_{\{|\theta_\varepsilon(s_\varepsilon(t),t)|\geqslant 1/j\}}\cdot\chi_{\{0<s_\varepsilon(t)<a\}}\, dt \geqslant L\int\limits_0^{\bar{t}} |s'_\varepsilon(t)|\cdot\chi_{\{|\beta(\theta_\varepsilon(s_\varepsilon(t),t))|\geqslant b/j\}}\, dt = \\ = L\int\limits_0^{\bar{t}} |s'(t)|\cdot\chi_{\{|s'_\varepsilon(t)|\geqslant b/\varepsilon j\}}\, dt \geqslant L\int\limits_0^{\bar{t}} |s'_\varepsilon(t)|\, dt - \frac{Lb\bar{t}}{\varepsilon j}\,.$$

We also notice that the first and the third integrals in (4.14) are non-negative; thus taking $j \to \infty$ in (4.14), by (4.15) we get

$$(4.16)\qquad \|s'_\varepsilon\|_{L^1(0,T)} \leqslant \text{Constant} \quad (\text{independent of } \varepsilon)\,,$$

which yields (4.8), by (4.2) and (4.6).

Now we multiply (4.13) by θ_ε and integrate in $]0, \bar{t}[$, for a generic $\bar{t} \in]0, T[$. We notice that by (4.2), (4.6) and (4.13) we have

$$(4.17)\qquad L\int\limits_0^{\bar{t}} s'_\varepsilon(t)\cdot\theta_\varepsilon\big(s_\varepsilon(t), t\big)\, dt = \frac{L}{\varepsilon}\int\limits_0^{\bar{t}} \beta\big(\theta_\varepsilon(s_\varepsilon(t), t)\big)\cdot\chi_{\{0<s_\varepsilon(t)<a\}}\cdot\theta_\varepsilon\big(s_\varepsilon(t), t\big)\, dt \geqslant \\ \geqslant \frac{L}{b\varepsilon}\int\limits_0^{\bar{t}} \beta\big(\theta_\varepsilon(s_\varepsilon(t), t)\big)^2\cdot\chi_{\{0<s_\varepsilon(t)<a\}}\, dt = \frac{L\varepsilon}{b}\int\limits_0^{\bar{t}} s'_\varepsilon(t)^2\, dt\,;$$

thus, by calculations similar to those of section 1, we get

$$(4.18)\qquad \|\theta_\varepsilon\|_{L^\infty(0,T;W)\cap L^2(0,T;V)}\,, \quad \sqrt{\varepsilon}\|s'_\varepsilon\|_{L^2(0,T)} \leqslant \text{Constant} \quad (\text{independent of } \varepsilon)\,.$$

For any $v \in L^\infty(0, T; V)$ by (4.16) we have

$$\left|\int\limits_0^T {}_{V'}\!\left\langle\frac{\partial}{\partial t}H(s_\varepsilon(t) - x), v\right\rangle_V dt\right| = \left|\int\limits_0^T s'_\varepsilon(t)\cdot v\big(s_\varepsilon(t), t\big)\, dt\right| \leqslant \|s'_\varepsilon\|_{L^1(0,T)}\cdot\left\|v\big(s_\varepsilon(t), t\big)\right\|_{L^\infty(0,T)} \leqslant \\ \leqslant \text{Constant}\cdot\|s'_\varepsilon\|_{L^1(0,T)}\cdot\|v\|_{L^\infty(0,T;V)}\,,$$

hence

$$\left\|\frac{\partial}{\partial t}H(s_\varepsilon(t)-x)\right\|_{L^\infty(0,T;V)'}\leqslant \text{Constant}\,,$$

whence, as for any $\delta>0$ $\{v\in L^2(0,T)\colon v'\in L^\infty(0,T)'\}\subset W^{1-\delta,1}(0,T)\subset H^{\frac12-\delta}(0,T)$ with continuous injections, we have

$$\|H(s_\varepsilon(t)-x)\|_{H^{\frac12-\delta}(0,T;V')}\leqslant \text{Constant}\,,\qquad \forall\delta>0\,;$$

by comparison in (4.1) we also have

$$\|c\theta_\varepsilon+LH(s_\varepsilon(t)-x))\|_{H^1(0,T;V')}\leqslant \text{Constant}\,;$$

thus we get

$$\|\theta_\varepsilon\|_{H^{\frac12-\delta}(0,T;V')}\leqslant \text{Constant}\,,\qquad \forall\delta>0\,. \tag{4.19}$$

(ii) *Limit procedure.*

By (4.16), (4.18) and (4.19), there exist θ and s such that, possibly taking subsequences, (4.9) holds; then by compactness, in particular by Aubin's lemma (see [13, p. 57]), we have

$$\begin{aligned}&\theta_\varepsilon\to\theta \quad \text{strongly in } L^2(0,T;H^{1-\delta}(0,a)),\ \forall\delta>0\\ &s_\varepsilon\to s \quad \text{strongly in } L^p(0,T),\ \forall p\in[1,+\infty[\,;\end{aligned}$$

hence

$$\begin{aligned}&H(s_\varepsilon(t)-x)\to H(s(t)-x) && \text{weakly star in } L^\infty(Q) \text{ and a.e. in } Q\\ &\theta_\varepsilon(s_\varepsilon(t),t)\to\theta(s(t),s) && \text{strongly in } L^2(0,T)\\ &\beta\big(\theta_\varepsilon(s_\varepsilon(t),t)\big)\to\beta\big(\theta(s(t),t)\big) && \text{strongly in } L^2(0,T)\,.\end{aligned}$$

Moreover (4.18) yields

$$\varepsilon s'_\varepsilon\to 0 \quad \text{strongly in } L^2(0,T)\,;$$

hence taking $\varepsilon\to0$ in (4.2) we get

$$-\beta\big(\theta(s(t),t)\big)\cdot[\xi-s(t)]\geqslant0\,,\quad \forall\xi\in[0,a]\,,\quad \text{a.e. in }]0,T[\,,$$

whence (4.11), by (4.5) and (4.6). □

REMARKS. – (i) In general $s(t)$ cannot be expected to be continuous. For instance in the Stefan problem for a supercooled liquid, at a certain finite time $s(t)$ jumps to 0 [12].

(ii) (4.12) does not entail

$$\theta|_{t=0} = \theta^0 , \qquad H(s(t) - x)|_{t=0} = H(s^0 - x) \qquad \text{in }]0, a[;$$

neither θ nor $H(s(t) - x)$ have a trace for $t = 0$, a priori.

(iii) In [8] CROWLEY studied a problem of phase transition in a heterogeneous system with a kinetic condition at the interface. There the supercooling is so small that it can be neglected. In the case of a homogeneous system, such a condition has the form

$$\theta(s(t), t) = -\gamma[s'(t)]^- , \quad \text{where } 0 < s(t) < a , \quad \text{in }]0, T[, \tag{4.20}$$

with γ: constant > 0; namely

$$s'(t) \in \beta\big(\theta(s(t), t)\big) , \quad \text{where } 0 < s(t) < a , \quad \text{in }]0, T[; \tag{4.21}$$

here β is a maximal monotone graph with domain $\boldsymbol{R}^-$: $\beta(\xi) = \{\xi/\gamma\}$ if $\xi < 0$, $\beta(0) = \boldsymbol{R}^+$, (4.21) can be rewritten in the form

$$\left\{\begin{array}{l} \theta(s(t), t) \leqslant 0 ; \quad \forall v \leqslant 0 , \\ s'(t)\cdot[\theta(s(t), t) - v] \geqslant \dfrac{\gamma}{2}[\theta(s(t), t)^2 - v^2] \end{array}\right\} \quad \text{where } 0 < s(t) < a, \text{ in }]0, T[, \tag{4.22}$$

A result similar to theorem 3 can be proved also in this case: thus the phase-transition problem corresponding to (4.20) has at least one solution, which can be obtained as the limit of a subsequence of solutions $(\theta_\varepsilon, s_\varepsilon)$ corresponding to inserting a superheating term vanishing with ε:

$$s'_\varepsilon(t) = \beta_\varepsilon\big(\theta_\varepsilon(s_\varepsilon(t), t)\big) := \frac{1}{\varepsilon}[\theta_\varepsilon(s_\varepsilon(t), t)]^+ - \frac{1}{\gamma}[\theta_\varepsilon(s_\varepsilon(t), t)]^- , \tag{4.23}$$

$$\text{where } 0 < s_\varepsilon(t) < a, \text{ a.e. in }]0, T[.$$

5. – Several dimensions of space with radial symmetry.

We take into account a radially symmetric system constituted by a water ball surrounded by ice. Let $N \geqslant 2$ be the number of space dimensions; we denote the radial coordinate by ϱ; the space domain is $\Omega = \{(x_1, \dots, x_N) \in \boldsymbol{R}^N : \varrho < a\}$ and the interphase S is characterized by the condition $\varrho = s(t)$. The energy balance yields

$$\frac{\partial}{\partial t}[c\theta + LH(s(t)-\varrho)] - \bar{\nabla}\cdot(k\bar{\nabla}\theta) = 0 \quad \text{in } \Omega\times]0,T[\tag{5.1}$$

($\nabla := (\partial/\partial x_1, \dots, \partial/\partial x_N)$); (5.1) corresponds to (1.15), (1.3) and (1.10). We consider the boundary condition

$$k\frac{\partial\theta}{\partial\nu} = g(t) \quad \text{on } \partial\Omega\times]0,T[\,, \tag{5.2}$$

where $\partial/\partial\nu$ denotes the exterior normal derivative. Because of the radial symmetry, (5.1) and (5.2) yield

$$\omega_N c\frac{d}{dt}\int_0^a \theta v\varrho^{N-1}\,d\varrho + \omega_N k\int_0^a \frac{\partial\theta}{\partial\varrho}\cdot v'(\varrho)\,\varrho^{N-1}\,d\varrho + \omega_N L s'(t)\cdot v(s(t))\cdot s(t)^{N-1} = \\ = \omega_N a^{N-1} g(t)\cdot v(a)\,, \quad \forall v\in C^1([0,a]),\ \text{in }]0,T[\tag{5.3}$$

where ω_N is the area of the $(N-1)$-dimensional sphere of radius 1.

Taking account of the surface tension effect, we shall use the kinetic condition (1.16).

Henceforth we shall replace ϱ by x. We introduce

$$\tilde{W} := \left\{\text{measurable } v\colon]0,a[\,\to \mathbf{R}\colon \int_0^a v(x)^2 x^{N-1}\,dx < +\infty\right\}$$

$$\tilde{V} := \{v\in\tilde{W}\colon v'\in\tilde{W}\}\,, \quad \tilde{Z} := \tilde{V}\cap C^0([0,a])\,,$$

Hilbert and Banach spaces endowed with the norms

$$\|v\|_{\tilde{W}} = \left[\int_0^a v(x)^2 x^{N-1}\,dx\right]^{\frac12}$$

$$\|v\|_{\tilde{V}} = \left\{\int_0^a [v(x)^2 + v'(x)^2]x^{N-1}\,dx\right\}^{\frac12}$$

$$\|v\|_{\tilde{Z}} = \|v\|_{\tilde{V}} + \max_{[0,a]}|v|\,.$$

We assume that

$$f\in L^2(0,T;\tilde{V})\,, \quad \theta^0\in\tilde{V}'\,, \quad s^0\in[0,a] \tag{5.4}$$

and introduce a variational problem:

PROBLEM (P3). – *Find* $\theta \in L^2(0, T; \tilde{V})$ *and* $s \in L^\infty(0, T)$ *such that* $s^N \in W^{1,1}(0, T)$ *and*

(5.5) $$\theta(s(t), t) \cdot s(t)^{N-1} \in L^1(0, T)$$

(5.6) $$c \frac{d}{dt} \int_0^a \theta v x^{N-1}\, dx + k \int_0^a \frac{\partial \theta}{\partial x} \cdot v'(x) x^{N-1}\, dx + \frac{L}{N} \frac{d}{dt}[s(t)^N] \cdot v(s(t)) = {}_{\tilde{V}'}\langle f(t), v \rangle_{\tilde{V}}, \quad \forall v \in \tilde{Z}, \text{ a.e. in }]0, T[$$

(5.7) $$\begin{cases} \text{a.e. in }]0, T[, \quad 0 \leqslant s(t) \leqslant a \quad \text{and} \quad \forall \xi \in [0, a] \\ \left\{ \dfrac{l}{N} \dfrac{d}{dt}[s(t)^N] + \lambda s(t)^{N-2} - \theta(s(t), t) \cdot s(t)^{N-1} \right\} \cdot [\xi - s(t)] \geqslant 0 \end{cases}$$

(5.8) $$\theta|_{t=0} = \theta^0 \quad \text{in } \tilde{Z}'$$

(5.9) $$s(0) = s^0 .$$

REMARK. – By comparison in (5.6) we have $\theta \in H^1(0, T; \tilde{Z}')$; this gives a meaning to (5.8). (5.6) corresponds to (5.3), setting

$$_{V'}\langle f(t), v \rangle_V := a^{N-1} g(t) \cdot v(a), \quad \forall v \in V .$$

THEOREM 4. – *Let* $N \geqslant 3$. *Assume that* (5.4) *holds and that*

(5.10) $$\theta^0 \in \tilde{W} .$$

Then there exists at least one solution of problem (P3) *such that*

(5.11) $$\theta \in L^\infty(0, T; \tilde{W}), \quad s^N \in H^1(0, T) .$$

PROOF. – (i) *Faedo-Galerkin approximation.*

We introduce $\tilde{V}_m$, f_m, θ_m^0 and Φ_m as in the proof of theorem 1; here we also require that $\tilde{V}_m \subset C^0([0, a])$. For any m we consider the following approximated problem

PROBLEM $(\text{P3})_m$: – *Find* θ_m: $[0, T[\to \tilde{V}_m$ *and* s_m: $[0, T[\to \mathbf{R}$ *such that, setting*

$$\tilde{s}_m(t) = \begin{cases} 0 & \text{if } s_m(t) \leqslant 0 \\ s_m(t) & \text{if } 0 < s_m(t) < a , \\ a & \text{if } s_m(t) \geqslant a \end{cases}$$

$$(5.12)\qquad \int_0^a \left(c\frac{\partial\theta_m}{\partial t}\cdot v + k\frac{\partial\theta_m}{\partial x}\cdot v'(x)\right)x^{N-1}\,dx + \frac{L}{N}\frac{d}{dt}[s_m(t)^N]\cdot v(\tilde{s}_m(t)) = {}_{\tilde{V}'}\langle f_m(t), v\rangle_{\tilde{V}}, \quad \forall v\in V_m, \text{ in }]0,T[$$

$$(5.13)\qquad \frac{l}{N}\frac{d}{dt}[s_m(t)^N] + \Phi_m(s_m(t)) + \lambda s_m(t)^{N-2} = \theta_m(\tilde{s}_m(t),t)\cdot s_m(t)^{N-1}, \quad \text{in }]0,T[$$

$$(5.14)\qquad \theta_m(x,0) = \theta_m^0(x) \quad \text{in }]0,a[$$

$$(5.15)\qquad s_m(0) = s^0.$$

This problem is equivalent to a Cauchy problem for a system of a finite number of ordinary differential equations and has at least one solution in $[0, T_m[$, for a suitable $T_m \in]0, T]$.

(ii) *A priori estimates.*

We take $v = \theta_m$ in (5.12), multiply (5.13) by $Ls_m'(t)$, sum and integrate in $]0, \tilde{t}[$, for a generic $\tilde{t}\in]0, T_m[$. Thus we get

$$\frac{c}{2}\int_0^a [\theta_m(x,\tilde{t})^2 - \theta_m^0(x)^2]x^{N-1}\,dx + k\int_0^{\tilde{t}} dt\int_0^a\left(\frac{\partial\theta_m}{\partial x}\right)^2 x^{N-1}\,dx + \frac{4Ll}{(N+1)^2}\int_0^{\tilde{t}}\left(\frac{d}{dt}[s(t)^{(N+1)/2}]\right)^2 dt + \frac{L\lambda}{N-1}[s_m(t)^{N-1} - (s^0)^{N-1}] + L\int_{s^0}^{s_m(\tilde{t})}\Phi_m(\xi)\,d\xi \leqslant \|f_m\|_{L^2(0,T;\tilde{V}')}\cdot\left(\int_0^T \|\theta_m(t)\|_{\tilde{V}}^2\,dt\right)^{\frac{1}{2}}.$$

Then by Gronwall's lemma we get $T_m = T$ for any m and

$$(5.16)\qquad \|\theta_m\|_{L^\infty(0,T;\tilde{W})\cap L^2(0,T;\tilde{V})}, \quad \|s_m^{(N+1)/2}\|_{H^1(0,T)}, \quad \left\|\int_0^{s_m(\tilde{t})}\Phi_m(\xi)\,\xi\right\|_{L^\infty(,T)} \leqslant \text{Constant} \quad (\text{independent of } m).$$

We notice that for any $v\in\tilde{Z}$

$$\frac{L}{N}\left|\int_0^T \frac{d}{dt}[s_m(t)^N]\cdot v(\tilde{s}_m(t))\,dt\right| \leqslant \frac{2L}{(N+1)}\left|\int_0^T\frac{d}{dt}[s_m(t)^{(N+1)/2}]\cdot s_m(t)^{(N-1)/2}\cdot v(\tilde{s}(t))\,dt\right| \leqslant \text{Constant}\,\|s_m(t)^{(N+1)/2}\|_{H^1(0,T)}\cdot\|v\|_{C^0([0,a])} \leqslant \text{Constant}$$

then by comparison in (5.12) we have

$$(5.17)\qquad \|\theta_m\|_{H^1(0,T;\tilde{Z}')} \leqslant \text{Constant}.$$

Finally, multiplying (5.13) by $(d/dt)[s_m(t)^N]$ we get

$$(5.18)\quad l\left\|\frac{d}{dt}[s_m(t)^N]\right\|_{L^2(0,T)} \leqslant \|\theta_m(\tilde{s}_m(t),t)\cdot s_m(t)^{N-1}\|_{L^2(0,T)} \leqslant C\|\theta_m(x,t)x^{N-1}\|_{L^2(0,T;H^1(0,a))} \leqslant$$
$$\leqslant C\cdot\left\{\|\theta_m x^{N-1}\|_{L^2(Q)} + \left\|\frac{\partial\theta_m}{\partial x}x^{N-1} + (N-1)\theta_m x^{N-2}\right\|_{L^2(Q)}\right\} \leqslant$$
$$\left(\text{as } N-2 \geqslant \frac{N-1}{2}\right) \leqslant C\cdot\|\theta_m\|_{L^2(0,T;\tilde{V})} \leqslant \text{Constant}.$$

(iii) *Limit procedure.*

By the previous a priori estimates, there exist θ and r such that

$$(5.19)\quad \theta_m \to \theta \quad \text{weakly star in } L^\infty(0,T;\tilde{W}) \cap (L^2(0,T;\tilde{V}) \cap H^1(0,T;\tilde{Z}'))$$
$$(5.20)\quad s_m^N \to r \quad \text{weakly in } H^1(0,T),$$

with $0 \leqslant r \leqslant a^N$ in $]0,T[$; hence

$$(5.21)\qquad s_m \to s := r^{1/N} \quad \text{uniformly in } [0,T].$$

By Aubin's lemma (see [13], p. 57), (5.19) yields

$$\theta_m x^{N-1} \to \theta x^{N-1} \quad \text{strongly in } L^2(0,T;H^{1-\delta}(0,a)),\ \forall\delta>0,$$

whence

$$\theta_m(s(t),t)\cdot s(t)^{N-1} \to \theta(s(t),t)\cdot s(t)^{N-1} \quad \text{strongly in } L^2(0,T)$$

then

$$|\theta_m(\tilde{s}_m(t),t)\cdot\tilde{s}_m(t)^{N-1} - \theta(s(t),t)\cdot s(t)^{N-1}| \leqslant |\theta_m(\tilde{s}_m(t),t)\cdot\tilde{s}_m(t)^{N-1} - \theta_m(s(t),t)\cdot s(t)^{N-1}| +$$
$$+ |\theta_m(s(t),t)\cdot s(t)^{N-1} - \theta(s(t),t)\cdot s(t)^{N-1}| \leqslant \left|\int\limits_{s(t)}^{\tilde{s}_m(t)}\frac{\partial}{\partial x}[\beta_m(\theta_m(x,t))\cdot x^{N-1}]\,dx\right| +$$
$$+ |\theta_m(s(t),t) - \theta(s(t),t)|\cdot s(t)^{N-1} \leqslant \|\theta_m x^{N-1}\|_{H^1(0,a)} + |\theta_m(s(t),t) - \theta(s(t),t)|\cdot s(t)^{N-1} \to 0$$

strongly in $L^2(0,T)$.

Taking $m\to\infty$ in (5.12) we obtain (5.6). Multiplying (5.13) by $\xi - s_m(t)$, for a generic $\xi \in [0,a]$, and taking $m\to\infty$ we get (5.7). □

REMARK. – In the case of an ice ball surrounded by water, L is replaced by $-L$ in (5.6) and $\theta(s(t),t)$ by $-\theta(s(t),t)$ in (5.7). Theorem 4 holds also there.

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