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# Phase Transition with Supercooling.

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**Sunto.** – *L'articolo riassume il quadro dei risultati noti circa il cosiddetto problema di Stefan con sopraraffreddamento. Con ciò si intende in senso lato l'estensione del modello di Stefan a quei casi in cui la temperatura della fase liquida (solida) non è confinata al di sopra (sotto) di quella di cambiamento di fase, supposta costante. La nostra discussione è prevalentemente rivolta allo sviluppo di singolarità (non limitatezza della velocità dell'interfaccia, ecc.), al modo di prevederle, di prevenirle (regolarizzazione), alla loro interpretazione termodinamica e alla descrizione del comportamento delle soluzioni in vicinanza dei punti singolari.*

## Introduction.

The paper by A. Visintin published in this same issue provides a rather exhaustive description of the complex and diversified world of the mathematical models describing phase change processes. His recent monograph [27] is an excellent and comprehensive review of classical and modern approaches to the problem.

Here we want to deal more specifically with some aspects of phase change in the presence of undercooling. Roughly speaking we can distinguish several classes of problems. Undercooling due to surface tension as well as kinetic undercooling and phase relaxation have been discussed at length in Visintin's paper. Also in nucleation driven phase change processes the formation of crystals occurs in the presence of substantial undercooling. In such processes phase change takes place not at a sharp interface but in a region where the temperature ranges in an interval depending on the physical system and on the pressure. We still refer to Visintin's paper for some general remarks about the complexity of nucleation. The dominant effect of nucleation is particularly evident in many polymers in which the kinetics of the formation of nuclei and of crystal growth is still a subject of intensive theoretical and experimental investigation. We refer to [8] and to the recent survey paper [2] for a description of various mathematical models and for the relevant literature, as well as for a discussion on the so-called additivity rules [11] and on classes of travelling wave solutions [13].

The specific aim of this paper is the decription of the so-called supercooled Stefan problem (SSP), mainly in one space dimension and in one phase. SSP differs from the ordinary Stefan problem in the only fact that the temperature in the heat conducting phase, here specified as the *liquid*, is below the melting point.

We will illustrate the main results known in the literature, referring for simplicity of exposition to the 1-dimensional model problem stated in Section 1. First of all we will recall the general properties concerning existence and the possible development of a singularity (Sect. 2) [16]. Then we consider the critical influence of initial data not matching the melting temperature at the interface [12], a question which is crucial in understanding the possibility of continuing the solution after the occurrence of a blow-up point (a singular point of the free boundary accompained by a discontinuity of the temperature). Continuation beyond blow-up and regularization procedures to prevent it are discussed in Sect. 4 [15, 14]. The following two sections present a discussion of blow-up on a thermodynamical basis, addressing the concept of bulk nucleation according to M. Gurtin's theory [18] (Sect. 5) and the way it can be obtained as a limit case of kinetic undercooling (Sect. 6), the basic reference being [17].

Finally, Sect. 7 is devoted to the study of the way blowing-up solutions approach their singularity. Besides the 1-D case [20], we discuss very briefly also the 2-D and 3-D cases [25], emphasizing the fact that they can exhibit a qualitative behaviour substantially different from the one-dimensional case as it was already conjectured long ago in [22].

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## 1. – The one phase one-dimensional Stefan problem.

In 1970 B. Sherman [24] showed that the one-phase one- dimensional Stefan problem with supercooling may have solutions which blow up in a finite time. About ten years later Fasano and Primicerio performed a more systematic analysis of the problem with the aim of characterizing the occurrence of singularities [16] and of investigating the criticality of initial discontinuities at the interface for the existence of solutions [12]. The question of the development of a singularity has been analyzed under various points of views: possible thermodynamical interpretations [18, 17], possible continuation of the solutions and alternative regularized models in which the singularity is prevented [15, 14], a finer description of the solutions when the singularity is approached [20, 25].

We will touch very briefly these subjects.

## 2. – Characterization of finite time extinction, blow up and global existence

Let us summarize some of the results of [16], referring to the following one-phase model problem for the solidification of a liquid:

$$\frac{\partial^2 \theta}{\partial x^2} - \frac{\partial \theta}{\partial t} = 0 \qquad \text{in } D_T := \{(x, t): 0 < x < s(t), \ 0 < t < T\}, \tag{2.1}$$

$$s(0)=1\,, \tag{2.2}$$

$$\theta(x,0)=h(x)\,, \qquad 0<x<1\,, \tag{2.3}$$

$$\left.\frac{\partial\theta}{\partial x}\right|_{x=0}=0\,, \tag{2.4}$$

$$\theta(s(t),t)=0\,, \qquad 0<t<T\,, \tag{2.5}$$

$$\left.\frac{\partial\theta}{\partial x}\right|_{x=s(t)}=-\,\dot{s}(t)\,, \quad 0<t<T\,, \tag{2.6}$$

in its strong formulation, where $h(x)$ is a given continuous function in $[0,1]$. Of course we are interested in the case in which the initial data are negative, at least in part of the interval $(0,1)$. In (2.1)-(2.6) we use nondimensional and normalized variables. Therefore the quantity

$$Q=1+\int_0^1 h(x)\,dx \tag{2.7}$$

can be interpreted as the total thermal «energy» stored in the system for $t=0$ (the term 1 being the normalized latent heat). Such a quantity plays a crucial role in discriminating among the following cases:

($A$) the problem is solvable for arbitrarily large $T$,

($B$) there exists a finite extinction time $T_0$ such that $\lim_{t\uparrow T_0} s(t)=0$,

($C$) there exists a blow up time $T^*$ such that

$$\inf_{t\in(0,T^*)} s(t)>0\,, \qquad \lim_{t\uparrow T^*}\dot{s}(T)=-\infty\,.$$

The fact that a singularity can occur only in the way described under ($C$) was pointed out in [24].

Leaving aside for the moment the question of existence of solutions to (2.1)-(2.6), we state a theorem establishing a 1-1 correspondence between the values of $Q$ and the occurrence of the cases above.

THEOREM 2.1. – *Let $h$ verify the following assumptions*:

(H1) *there exists a positive constant $H$ such that*

$$h(x)\geqslant -H(1-x)\,, \tag{2.8}$$

(H2) *the equation $h(x)=-1$ has at most one root in* $[0,1]$.

*Then for any solution of* (2.1)-(2.6) *we have*

$$(A)\Leftrightarrow Q>0\,, \tag{2.9}$$

$$(B)\Leftrightarrow Q=0\,, \tag{2.10}$$

$$(C)\Leftrightarrow Q<0\,. \tag{2.11}$$

The proof goes through the following lemmas.

LEMMA 2.1. – *For any solution of* (2.1)-(2.6)

$$s(t) = Q - \int_0^{s(t)} \theta(x, t)\, dx, \qquad \forall\, t \in (0, T). \tag{2.12}$$

This is nothing but energy balance.

LEMMA 2.2. – *Assume* (H1) *and let* $(T, s, \theta)$ *be a solution of* (2.1)-(2.6) *such that*

$$\text{(i)} \qquad S_T = \inf_{t \in (0, T)} s(t) > 0\,, \tag{2.13}$$

(ii) *there are two constants* $d \in (0, s_T)$ *and* $\theta_0 \in (0, 1)$ *such that*

$$\theta(s(t) - d, t) > -\theta_0, \qquad t \in (0, T). \tag{2.14}$$

*Then*

$$\dot{s}(t) \geqslant \min\left\{ -\frac{H}{\theta_0}, \frac{\ln(1-\theta_0)}{d} \right\}, \qquad t \in (0, T). \tag{2.15}$$

PROOF. – The proof consists in showing that the function

$$w(x, t) = -\theta_0 (1 - e^{-ad})^{-1} \{1 - \exp[a(x - s(t))]\}$$

for a suitable choice of the constant $a$ is a barrier in the domain $\Omega_d := \{(x, t)\colon s(t) - d < x < s(t),\ 0 < t < T\}$. Indeed if $a \geqslant H/\theta_0$ we have $w \leqslant \theta$ on the parabolic boundary of $\Omega_d$. If in addition $a$ is such that $a + \dot{s}(t) \geqslant 0$ in $(0, T)$, then $\omega_{xx} - \omega_t \geqslant 0$ in $\Omega_d$. Therefore $\theta(x, t) \geqslant \omega(x, t)$ in $\Omega_d$ and $|\dot{s}(t)| \leqslant \omega_x(s(t), t)$. Thus either $\dot{s} > -H/\theta_0$, and (2.15) is satisfied, or we put $a = -\inf_{t \in (0, T - \varepsilon)} \dot{s}(t)$ (to avoid a possible singularity at $T$) and we conclude that $a \leqslant \theta_0 a (1 - e^{-ad})^{-1}$, i.e. $a \leqslant (1/d) \log|1 - \theta_0|$, which again leads to (2.15). Finally, let $\varepsilon \to 0$. ■

LEMMA 2.3. – *Suppose* $h(x)$ *satisfies* (H2) *and that it takes the value* $-1$ *once in* (0,1). *Then* $\theta(0, t) < -1$ *and if* $Q \geqslant 0$ *the level curve* $\theta = -1$ *is separated by a positive distance from the free boundary at all points such that* $s(t) > 0$.

PROOF. – The proof is based on the fact that the level curve $\theta = -1$ is unique and cannot meet the axis $x = 0$ before extinction, nor the free boundary before blow up. Moreover if the curve $\theta = -1$ approaches the free boundary as $t \uparrow T^*$ we can see that this is consistent with (2.12) only if $Q < 0$. ■

Next we introduce the quantity

$$S_0 = 1 + \int_0^1 \max[0, h(x)]\, dx$$

and the solution $Z(x, t)$ of

$$\begin{aligned}
&\frac{\partial^2 Z}{\partial x^2} - \frac{\partial Z}{\partial t} = 0\,, && 0 < x < S_0, \quad t > 0\,,\\
&Z(x, 0) = |h(x)|\,, && 0 < x < 1\,,\\
&Z(x, 0) = 0\,, && 1 \leqslant x < S_0 \ \ (\text{if } S_0 > 1)\,,\\
&Z_x(0, t) = 0\,, \quad Z(S_0, t) = 0\,, && t > 0\,,
\end{aligned}$$

which provide more comparison elements for the solutions of our free boundary problem:

LEMMA 2.4. – *For any solution* $(T, s, \theta)$ *of* (2.1)-(2.6) we have

$$s(t) \leqslant S_0, \qquad t \in (0, T)\,, \tag{2.16}$$

$$|\theta(x, t)| < Z(x, t) \textit{ in } D_T. \tag{2.17}$$

The proof is omitted.

PROOF OF THEOREM 2.1. – The proof is rather straightforward with the help of the lemmas above. First we observe that when for some $T_0 > 0$ $\inf\limits_{t \in (0, T_0)} s(t) = 0$ then $\lim\limits_{t \uparrow T_0} s(t)$ exists (and is zero). If $s(t)$ had no limit, then it would be nonmonotone in any interval $(T_0 - \varepsilon, T_0)$, implying that $\dot{s}$ changes its sign infinitely many times. It is not difficult to realize with the use of the maximum principle that in that case the domain $D_T$ is crossed by an infinite number of zero level curves of $\theta(x, t)$, which is not permitted for the solutions of the heat equation [hint: two distinct zero level curves starting from the free boundary cannot hit $x = 0$, nor converge to the point $(0, T_0)$; a zero level curve cannot touch the free boundary twice, ...].

Now we see that the implication $(B) \Rightarrow Q = 0$ is a trivial consequence of (2.12). In order to obtain the reverse implication $Q = 0 \Rightarrow (B)$ remark that $Z(x, t) \to 0$ as $t \to \infty$ uniformly w.r.t. $x$, implying in particular (Lemma 2.4) that if $(A)$ occurs then $\theta(0, t) \to 0$ as $t \to \infty$, which contradicts Lemma 2.3 (note that $Q = 0$ requires $h + 1$ vanishing somewhere). Case $(C)$ is likewise excluded because of Lemmas 2.2, 2.3.

Showing that $(A) \Rightarrow Q > 0$ is easy: Lemma 1.4 implies $\theta(x, t) \to 0$ as $t \to +\infty$ uniformly and Lemma 2.1 that $s \to Q$, which cannot be zero (we already know that $Q = 0 \Rightarrow (B)$).

The converse $Q > 0 \Rightarrow (A)$ is obtained by excluding $(C)$, that is possible on the basis of Lemmas 2.2, 2.3.

The equivalence $(C) \Leftrightarrow Q < 0$ is now proved automatically. ■

REMARK 2.1. – Note from the proof of Theorem 2.1 that the implications

$$(A) \Rightarrow Q \geqslant 0\,, \qquad \lim_{t\to\infty} s(t) = Q\,,$$

$$(B) \Rightarrow Q = 0\,,$$

$$Q < 0 \Rightarrow (C)$$

do not require any additional assumption beside continuity for $h$.

In the same paper [16] there are several extensions of this theorem, which we do not describe. More cases are illustrated in the papers by D. Andreucci [1].

## 3. – The largest admissible discontinuity for the initial data.

It is well known [9, 23] that in the one-dimensional case there is a strict relationship between the one-phase supercooled Stefan problem and the so-called oxygen diffusion-consumption problem, first introduced by Crank and Gupta [7] (for the multidimensional case see [25]). If $c(x, t)$ denotes the concentration of a diffusing substance which is consumed by a chemical reaction at a constant rate and uniformly throughout the region in which the substance is present, then the problem can be put in the following nondimensional form

$$\frac{\partial^2 c}{\partial x^2} - \frac{\partial c}{\partial t} = 1\,, \qquad 0 < x < s(t)\,, \quad 0 < t < T\,, \tag{3.1}$$

$$s(0) = 1\,, \tag{3.2}$$

$$c(x, 0) = c_0(x)\,, \qquad 0 < x < 1\,, \tag{3.3}$$

$$c(0, t) = F(t)\,, \qquad 0 < t < T\,, \tag{3.4}$$

$$c(s(t), t) = 0\,, \qquad 0 < t < T\,, \tag{3.5}$$

$$\left.\frac{\partial c}{\partial x}\right|_{x = s(t)} = 0\,, \qquad 0 < t < T\,, \tag{3.6}$$

or with (3.4) replaced by a flux condition

$$\left.\frac{\partial c}{\partial x}\right|_{x = 0} = G(t)\,, \quad 0 < t < T\,. \tag{3.4$'$}$$

By a solution of (3.1)-(3.6) we mean a classical solution, whose definition is evident. Assuming that $c(x, t)$ is sufficiently regular at the boundary, setting $\theta = \partial c/\partial t$, we see that the triple $(T, s, \theta)$ satisfies (2.1), (2.2), (2.3), (2.5), (2.6) and a boundary condition of the type

$$\theta(0, t) = \dot{F}(t), \qquad 0 < t < T, \tag{3.7}$$

or of the type

$$\left.\frac{\partial \theta}{\partial x}\right|_{x=0} = \dot{G}(t), \qquad 0 < t < T. \tag{3.7$'$}$$

Conversely if we start from a solution $(T, s, \theta)$ of (2.1), (2.2), (2.3), (2.5), (2.6) and

$$\theta(0, t) = f(t), \qquad 0 < t < T, \tag{3.8}$$

or

$$\left.\frac{\partial \theta}{\partial x}\right|_{x=0} = g(t), \qquad 0 < t < T, \tag{3.9}$$

the transformation

$$c(x, t) = \int_x^1 s(t)\, d\xi \int_\xi^{s(t)} d\eta \{\theta(\eta, t) + 1\} \tag{3.10}$$

leads to the system (3.1)-(3.6) with

$$F(t) = \int_0^t f(\tau)\, d\tau \tag{3.11}$$

if (3.8) is the boundary condition for $\theta$, while if (3.9) is prescribed, the corresponding boundary condition for $c$ is of the form (3.4$'$) with

$$G(t) = \int_0^t g(\tau)\, d\tau. \tag{3.12}$$

This equivalence was first observed by Schatz [23] and further investigated in [9, 10] and [16] for a case of non-compatible data for $c$ (namely $G(0) \neq c_0'(0)$). The oxygen diffusion-consumption problem has been extensively treated in many papers (see e.g. [7], [6]).

The equivalent form (3.1)-(3.6) of the supercooled one- phase Stefan problem can be conveniently exploited in order to prove a number of properties. For instance the following non-existence theorem [12].

THEOREM 3.1. – *If in a left neighbourhood of* $x = 1$ *the function* $c_0(x)$ *does not take positive values, the problem* (3.1)-(3.6) *has no solutions.*

PROOF. – Let $c_0 \leqslant 0$ in $(1-\varepsilon, 1)$ and take $x_0 \in (1-\varepsilon, 1)$. Then if a solution $(T, s, c)$ of (3.1)-(3.6) exists we can find some time $t_0$ such that $s(t) > x_0$ in $[0, t_0]$ and $c(x, t) < 0$ for $x_0 \leqslant x < s(t)$, $0 < t \leqslant t_0$. Indeed, either $c_0$ takes some negative value in $(1-\varepsilon, 1)$, or, if $c_0 \equiv 0$ in this same interval, then $\partial c/\partial t = -1$ for $t = 0$ in $(1-\varepsilon, 1)$. In such a case there exists some interval $(0, t_0)$ in which $c(x_0, t) < 0$ and the negativity of $c(x, t)$ for $x_0 \leqslant x < s(t)$, $0 < t \leqslant t_0$ is then obvious. Hence, by standard arguments we conclude that $\partial c/\partial x$ is positive on the free boundary for $0 < t \leqslant t_0$, thus contradicting (3.6). ■

REMARK 3.1. – Although this theorem is physically intuitive, we can indeed construct solutions of (3.1)-(3.6), whose initial data are negative somewhere in $(0, 1-\varepsilon)$, or which start positive and take negative values at later times. As we shall see this behaviour is crucially connected with the development of singularities. ■

Clearly the theorem above implies that problem (2.1)-(2.6) has no solutions if $h(x) \leqslant -1$ in a left neighbourhood of $x = 1$.

On the contrary, assume that

$$h(x) \geqslant -1, \qquad h(x) \not\equiv -1 \text{ in } (1-\varepsilon, 1) \text{ for some } \varepsilon \in (0, 1), \tag{3.13}$$

then we can prove uniqueness [12]:

THEOREM 3.2. – *If $h(x)$ satisfies* (3.13) *problem* (2.1)-(2.6) *has at most one solution.*

PROOF. – Taken two solutions $(T_i, s_i, \theta_i)$, $i = 1, 2$ of (2.1)-(2.6) and the corresponding solutions $(T_i, s_i, c_i)$ of (3.1)-(3.6), we define the curves $x = \gamma_i(t)$ setting $\gamma_i(t) = 0$ if $\theta_i(x, t) > -1$, $\forall\, x \in (0, s(t))$, and $\gamma_i(t) = \sup \{x \in (0, s(t)) : \theta(x, t) = -1\}$ otherwise. In this way we define two domains $D_i^+$, $i = 1, 2$ in which $\theta_i > -1$. It is an easy consequence of the maximum principle and of (3.13) that the curves $\gamma_i$ must keep a positive distance from each point of the interval $(1-\varepsilon, 1)$ on $t = 0$. Thus the intersection $D_1^+ \cap D_2^+$ must have a connected component $\widehat{D}$ confined by this same interval. The right hand boundary of such a domain is the curve $x = \min(s_1(t), s_2(t)) := \alpha(t)$. We note that in $D_i^+$ both the associated functions $c_i$ are positive, so that on $x = \alpha(t)$ either $c_1 > 0$ and $c_2 = 0$ or viceversa, at least as long as $x = \alpha(t)$ is part of $\partial\widehat{D}$. Moreover we can also say that $\partial c_i/\partial x$ are negative in $D_i^+$. At this point we remark that $w(x, t) = c_1(x, t) - c_2(x, t)$ satisfies the heat equation in $0 < x < \alpha(t)$, $0 < t < \hat{t}$ for some $\hat{t}$ and the conditions $w(0, t) = 0$ (or the zero Neumann condition), $w(x, 0) = 0$ in $(0, 1)$. If $(\alpha(t_0), t_0)$ is a point of positive maximum for $w$, it means that $w(\alpha(t_0), t_0) = c_1(\alpha(t_0), t_0)$, $\alpha(t_0) = s_2(t_0)$ and that $\partial w/\partial x > 0$ at this point. However $\partial w/\partial x = \partial c_1/\partial x < 0$ because of (3.6) and we have a contradiction. ■

Note that the proof makes no use of the «physical» condition $c \geqslant 0$, which is not imposed to the solution.

In [12] the following existence theorem is proved

THEOREM 3.3. – *A sufficient condition for the (local) existence of a classical solution is that*

$$h(x) > -1 \ \text{in some interval}\ (1-\varepsilon, 1)\,. \tag{3.14}$$

The proof is quite long and is omitted. Theorems 3.1 and 3.3 point out that, in the adopted normalization, $-1$ is the lowest allowable value for the critical temperatures in the vicinity of the initial interface. On the contrary it is well known that there is no bound to admissible positive values for $h(1)$, the corresponding behaviour of the free boundary near $t=0$ being of the type $\alpha\sqrt{t}$ with $\alpha>0$. In the supercooled case a discontinuity of the temperature at $x=1$, $t=0$ will again produce a singularity of the free boundary of type $\alpha\sqrt{t}$ (with $\alpha<0$) as long as $\liminf h(x) > -1$ and a singularity of higher order in the critical limit case.

## 4. – The nature of blow up points. Regularization procedures monitored by the mean energy.

In the previous section we have mentioned the equivalence between problem (2.1)-(2.6) and problem (3.1)-(3.6) under suitable regularity assumptions. The latter problem is usually associated to the simultaneous diffusion and consumption (at a constant rate) of a substance whose (normalized) concentration is denoted by $c$. However, if we want to keep such an equivalence, we must allow $c$ to take negative (i.e. unphysical) values. The real diffusion-consumption problem is instead formulated with the addition of the constraint

$$c \geqslant 0\,. \tag{4.1}$$

In [15, 14] Fasano, Howison, Ockendon, Primicerio proved that the onset of a singularity for the supercooled one-phase Stefan problem is related to the violation of the constraint (4.1) for the corresponding diffusion-consumption problem. They also proved that there are limit cases of singular solutions having a natural continuation beyond the blow up point.

The specific boundary condition (2.4) (zero flux) was considered, with the corresponding data

$$c_0(x) = \int_x^t d\xi \int_\xi^1 [\theta_0(\eta)+1]\, d\eta \tag{4.2}$$

$$\left.\frac{\partial c}{\partial x}\right|_{x=0} = c_0'(0) = -\int_0^1 [\theta_0(\eta)+1]\, d\eta = -Q\,. \tag{4.3}$$

Using the notation of [14], we refer to problem (2.1)-(2.6) as (SSP) and to problem (3.1)-(3.6) as (UDCP), U standing for «unconstrained», while (CDCP) is the diffusion-consumption problem with the constraint (4.1), which is the solution of a variational inequality.

REMARK 4.1. – The transition from (UDCP) to (CDCP) must be introduced artificially at the first time instant (if it exists) at which (UDCP) develops a negativity set. The latter is replaced in (CDCP) by the appearance of a dead core confined between two free boundaries carrying zero Cauchy data.

In order to state the main result of [15, 14] we discriminate between *essential* and *non-essential* blow-up points.

DEFINITION 4.1. – *A solution of* (SSP) *or* (UDCP) *is said to have an essential* (*or proper*) *blow-up at* $t = t^* > 0$ *if* $s(t^*) > 0$, $\liminf_{t \uparrow t^*} \dot{s}(t) = -\infty$, *and it cannot be continued beyond* $t^*$.

*If the solution can be continued beyond the blow-up point we say that it has a non-essential blow-up.*

By continuation we mean that $t^*$ is an isolated singularity of the free boundary and that for $t > t^*$ (SSP) has a solution with the data inherited as limits for $t \uparrow t^*$.

The analysis of [14] is based on the study of the negativity set of the solution $c(x, t)$ of (UDCP).

THEOREM 4.1. – *Let* $c(x, t)$ *be the solution of (UDCP) and*

$$N(t) := \{x\colon 0 \leqslant x < s(t), \quad c(x, t) < 0\}. \tag{4.4}$$

*If for some* $t_1 \geqslant 0$ $\quad N(t_1) \neq \emptyset$, *then*

(i) $N(t_1)$ *is strictly contained in* $N(t)$ *for* $t \in (t_1, T)$, *i.e. the negativity set expands*,

(ii) *if for some* $t^* > t_1$ *the boundary* $\partial N(t^*)$ *touches the free boundary, then* $\lim_{t \uparrow t^*} \dot{s}(t) = -\infty$

(iii) *the time instant* $t^*$ *must exist.*

On the basis of this theorem the following result is proved

THEOREM 4.2. – *The appearance of a negativity set for* (UDCP) *is a necessary and sufficient condition for the occurrence of essential blow-up.*

We omit proofs for the sake of brevity. It is interesting to comment on the relationship between the appearance of the negativity set for (UDCP) and the presence of the curve $\theta = -1$ for (SSP), which we know from [16] to generate a singularity when it approaches the free boundary.

PROPOSITION 4.1. – *Let $t$ be such that $N(t) \neq \emptyset$ and define $\widehat{x}(t) := \sup\{x \in N(t)\}$. If $\widehat{x}(t) < s(t)$, then there exists at least one point $x_0(t) \in (\widehat{x}(t), s(t))$ such that $\theta(x_0(t), t) = -1$.*

PROOF. – The proof is elementary since $x_0(t)$ is nothing but an inflection point for the function $c(x, t)$. ■

Thus the expansion of $N(t)$ pushes the level curve $\theta = -1$ towards the free boundary. The intersection of $\overline{N}(t)$, of $\{\theta = -1\}$ and of $x = s(t)$ occurs at the essential blow-up point.

However one can conjecture that even if the set $N(t)$ is always empty, the level curve $\theta = -1$ exists and meets the free boundary at some time $t^*$. This event will produce a singularity of the free boundary, but the solution will exist also for $t > t^*$, i.e. we have a non- essential blow- up.

In [14] using piecewise constant initial data $\theta_0(x)$ it is shown that such a case is possible:

THEOREM 4.3. – (UDCP) *admits global classical solutions with a singular free boundary.*

We remark that a classical solution of (UDCP) need not have a continuously differentiable free boundary. In the case described by Theorem 4.3 we mean that the free boundary is continuous for all $t > 0$ (and continuously differentiable for almost all $t > 0$), but there exists at least one time $t_0$ such that $\lim_{t \to t_0} \dot{s}(t) = -\infty$.

Therefore, the basic distinction between essential and non-essential blow-up is the behaviour of $\theta(x, t)$ [and of $c(x, t)$] near the singularity: in the essentially singular case we have $\theta(x, t^*) \leqslant -1$ [$c(x, t^*) < 0$] in a neighbourhood of the point $x = s(t^*)$, $t^*$ being the blow-up time; in the other case we find $\theta(x, t^*) > -1$ near the blow-up point and Theorem 3.1 allows to continue the solution for $t > t^*$.

On the basis of the results above it has been suggested that (SSP) can be regularized just shifting from the corresponding (UDCP) to (CDCP), i.e. letting a dead core appear any time that (UDCP) would develop a negativity set. Is is worth noting that the sign of $c(x, t)$ coincides with the sign of the «average energy» contained in the interval $(x, s(t))$ at time $t$. The regularization procedure suggested amounts in preventing such a quantity to take negative values.

In [15] an extension to the two-phase problem is considered. However suggestive, regularization is not the only option. We may pose the question to provide a physical interpretation of blow up and to formulate a more general approach in which the free boundary is allowed to be discontinuous, thus accounting for instantaneous solidification of a whole layer of supercooled liquid. We will discuss briefly these more recent developments in the next sections.

## 5. – Supercooled and super-supercooled liquids. Bulk nucleation.

Here we summarize some aspects of an interesting theory due to M. E. Gurtin [18]. Gurtin's theory is rich and elegant, but for the necessity of being concise we extract just the remarks concerning the one-dimensional one-phase supercooled Stefan problem. Using the symbols (and the pictures) of [18], we consider the constitutive equations for the solid (index $i = 1$) and for the liquid (index $i = 2$)

$$\eta = \widehat{\eta}_i(\varepsilon), \qquad \theta = \widehat{\theta}_i(\varepsilon) = [\widehat{\eta}_i'(\varepsilon)]^{-1}, \qquad i = 1, 2 \tag{5.1}$$

$\varepsilon$ being the thermal energy, $\eta$ the entropy and $\theta$ the temperature, to which the usual Fourier law has to be added.

The functions $\widehat{\eta}_1(\varepsilon), \widehat{\eta}_2(\varepsilon)$ are assumed as in fig. 5.1, i.e. having negative second derivatives and one unique intersection at some energy $\varepsilon^*$. The common tangent line $\mathscr{L}$ defines two energies $\varepsilon_1$ (for the solid) and $\varepsilon_2$ (for the liquid) such that

$$\widehat{\theta}_1(\varepsilon_1) = \widehat{\theta}_2(\varepsilon_2) := \theta_0 \tag{5.2}$$

which is the transition temperature, while $\varepsilon_2 - \varepsilon_1$ is the latent heat.

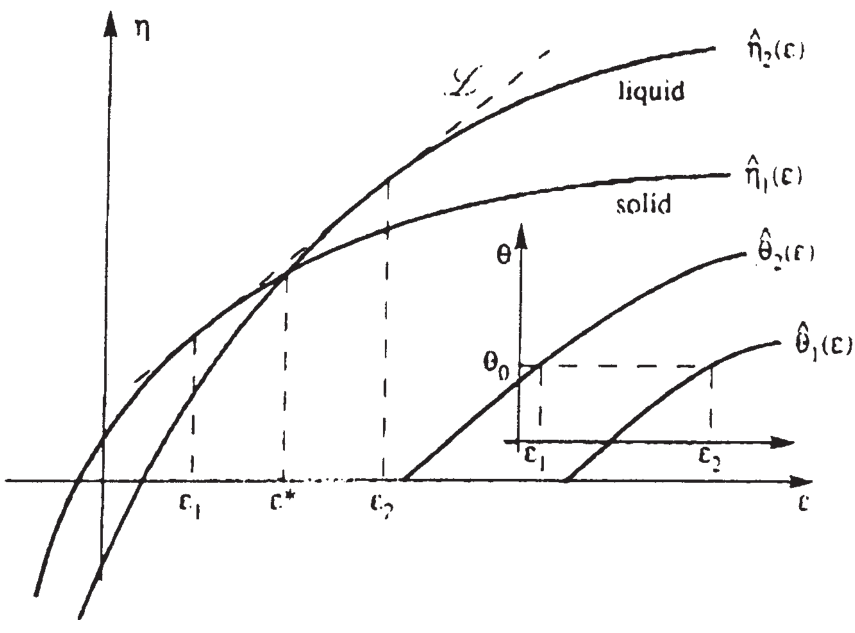


Figure 5.1. – entropy and temperature vs. internal energy.

The free energy in each phase is defined by

$$\widehat{\psi}_i(\varepsilon) = \varepsilon - \widehat{\theta}_i(\varepsilon)\, \widehat{\eta}_i(\varepsilon) \tag{5.3}$$

and it is easy to check that

$$\widehat{\psi}_1(\varepsilon_1) = \widehat{\psi}_2(\varepsilon_2) \tag{5.4}$$

and that the simultaneous coincidence of temperatures and free energies of the two phases occurs only at the phase transition temperature.

The crossing energy $\varepsilon^*$ marks a stability change of the phases: if the liquid finds itself at an energy below $\varepsilon^*$ then its entropy is less than the corresponding entropy of the solid, thus favouring isoenergetic phase change. Then we say that the liquid is not just supercooled ($\varepsilon < \varepsilon_2$) but *super-supercooled* ($\varepsilon < \varepsilon^*$).

We can also introduce the Gibbs functions for the two phases

$$\varphi_i = \widehat{\varphi}_i(\varepsilon) = \varepsilon - \theta_0 \widehat{\eta}_i(\varepsilon), \qquad i = 1, 2 \tag{5.5}$$

and the corresponding temperature deviations ($u = \theta - \theta_0/\theta$)

$$u = \widehat{u}_i(\varepsilon) = \widehat{\varphi}_i'(\varepsilon), \qquad i = 1, 2, \tag{5.6}$$

for which we have

$$\widehat{u}_1(\varepsilon_1) = \widehat{u}_2(\varepsilon_2) = 0 .$$

Consistently with the assumptions on the entropy functions $\widehat{\eta}(\varepsilon)$, we see that $\widehat{\varphi}_1(\varepsilon)$, $\widehat{\varphi}_2(\varepsilon)$ are strictly convex, that they cross only at $\varepsilon = \varepsilon^*$ and that take equal minimum values for $\varepsilon = \varepsilon_1$, $\varepsilon = \varepsilon_2$ respectively (we can take $\widehat{\varphi}_i(\varepsilon_i) = 0$).

For a super-supercooled liquid $\widehat{\varphi}_2(\varepsilon) > \widehat{\varphi}_1(\varepsilon)$ (see fig. 5.2, which refers to quadratic Gibbs functions).

Starting from this thermodynamical setting, Gurtin derives the Stefan problem on the basis of the so-called local equilibrium hypothesis ($u$ continuous in space for almost all times) and then he discusses with some detail the question of «nucleation» with specific reference to the blow-up case (case ($C$)), here described in section 2.

By nucleation he means a bulk phase-change of a super-supercooled liquid occurring instantaneously and in which energy does not change, thus increasing entropy and decreasing the Gibbs function. As a consequence there will be a sudden increase of temperature. According to this model, considering precisely problem (2.1)-(2.6) with initial data such that $Q < 0$ (see (2.7)), it is suggested that at the blow-up there is an instantaneous solidification isoenergetic over the entire neighbourhood of the free boundary in which the temperature is below the critical value $-1$. Indeed in this model problem we may select the physical constants so that $-1$ represents the limit temperature between super and super-super-

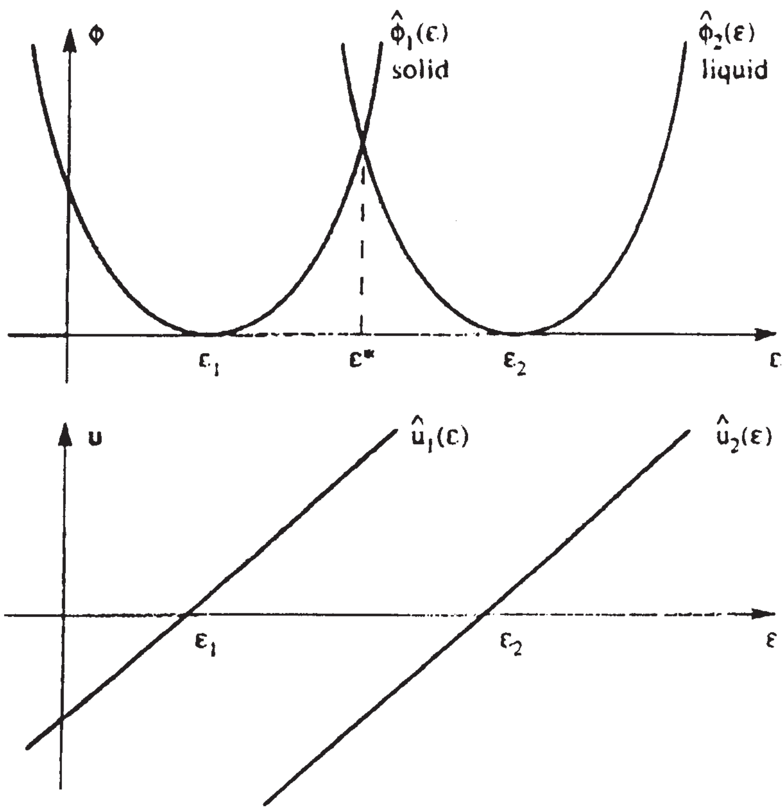


Figure 5.2. – Gibbs function and temperature deviations vs. internal energy.

cooled liquid. The corresponding temperature increase is 1. In this way after blow-up the new data for the temperature are no longer incompatible for continuation (in the sense of the non-existence Theorem 3), but the free boundary experiences a jump.

I repeat that this section has a very limited aim and does not render justice to Gurtin's paper which is much more extended and profound.

## 6. – Bulk nucleation as the limit of kinetic undercooling.

Concluding his discussion on bulk nucleation Gurtin conjectures that the solution he proposed should also be obtained from the kinetic undercooling scheme (see Sect. II.2 of Visintin's paper) in the limit that takes it back to the Stefan problem. In a note added in proof he quotes a preprint by Götz and Zaltzman [17] in which precisely that procedure had been investigated.

In [17] the authors consider the two-phase problem (here we set all the coefficients equal to 1)

$$\theta_t = \theta_{xx} \qquad \text{in } Q_T^- \cup Q_T^+ , \tag{6.1}$$

$$\theta(x, 0) = \theta_0(x), \qquad 0 < x < 1 , \tag{6.2}$$

$$\theta(i, t) = \theta^i(t), \qquad 0 < t < T, \quad i = 0, 1 , \tag{6.3}$$

$$\dot{s}(t) = \theta_x(s(t)^-, t) - \theta_x(s(t)^+, t) , \tag{6.4}$$

$$s(0) = s_0, \qquad 0 < s_0 < 1 , \tag{6.5}$$

$$\theta(s(t), t) = 0 , \qquad 0 < t < T, \tag{6.6}$$

where $Q_T^{\pm} := \{(x, t): \pm(x - s(t)) > 0, \ 0 < t < T, \ 0 < x < 1\}$ denote the solid ($Q_T^-$) and the liquid ($Q_T^+$) regions, together with the family of problems obtained by replacing (6.6) with

$$\theta^\varepsilon(s^\varepsilon(t), t) = -\varepsilon \dot{s}^\varepsilon(t), \qquad 0 < t < T \tag{6.7}$$

(kinetic undercooling). Problem (6.1)-(6.6) is formulated in a weak form introducing the functions

$$U = \theta + H(x - s(t)) ,$$

$$U_0 = \theta + H(x - s_0),$$

$H$ being the Heaviside function, and saying that $s \in BV(0, T)$, $\theta \in L_2(0, T; H^1(0, 1)) \cap L_\infty(Q_T)$ be such that (6.3) is satisfied, $\theta(x, t) \to 0$ as $x \to s(t)$ for a.a. $t \in (0, T)$, and

$$\iint_{Q_T} U(x, t)\, \psi_t(x, t)\, dx\, dt + \iint_{Q_T} \theta_x(x, t)\, \psi_x(x, t)\, dx\, dt = \int_0^1 U_0(x)\, \psi(x, 0)\, dx$$

$\forall\ \psi \in W_2^{1,1}(Q_T)$, $\psi(i, t) = 0$, $i = 0, 1$, $t \geqslant 0$, $\psi(x, t) = 0$, $0 < x < 1$.

The question of the existence of weak solutions $(s^\varepsilon, \theta^\varepsilon)$ and the analysis of the limit $(s^\varepsilon, \theta^\varepsilon) \to (s, \theta)$ as $\varepsilon \to 0$ was performed (in a slightly different context) by Visintin [26]. Götz and Zaltzman perform a deeper investigation of the limit $\varepsilon \to 0$, obtaining several interesting qualitative results for the weak solutions of (6.1)-(6.6), particularly in the presence of supercooling.

For instance the following global existence result.

THEOREM 6.1. – *If $\theta_0 \in C^1[0, s_0] \cap C^1[s_0, 1] \cap C[0, 1]$ and $\theta^i$ are $C^1$ and bounded for $t > 0$, satisfying compatibility conditions for $t = 0$ and moreover $\theta^0 < -\gamma$, $\theta^1 > \gamma$ for some $\gamma > 0$, then both Stefan problem and the kinetic undercooled problem have global weak solutions with the free boundary strictly separated from the lateral boundary.*

Concerning regularity, we have the following theorem.

THEOREM 6.2. – *Under the same assumptions as in Theorem* 6.1 *the free boundary of the Stefan problem can have at most a countable set of isolated singularities.*

Another interesting result for the Stefan problem concerns the disappearance of the supercooled liquid in a finite time.

THEOREM 6.3. – *Adding to the previous hypotheses the assumption that for* $t=0$ *the solid region is not supercooled and* $\theta_0(x)$ *in the interval* $(s_0, 1)$ *is such that* $\theta_0 < 0$ *in* $(s_0, \sigma_0)$, $\theta_0 > 0$ *in* $(\sigma_0, 1)$ *for some* $\sigma_0 \in (s_0, 1)$ (*the liquid is supercooled near the interface and not supercooled near the external wall*), *then there exists a time* $t^*$ *beyond which* $\theta < 0$ *and* $\theta > 0$ *a.e. in the solid and in the liquid region, respectively. Moreover the free boundary is nondecreasing up to* $t = t^*$.

The proofs are based on uniform estimates obtained for the pairs $(s^\varepsilon, \theta^\varepsilon)$. Next they come to the question of bulk nucleation, introducing the further assumption that the interval $(s_0, 1)$ contains an interval $(r_0^-, r_0^+)$ with $s_0 < r_0^- < r_0^+ < 1$, in which $\theta_0(x) < -1$. Then they prove the following theorem.

THEOREM 6.4. – *Under all the assumptions stated above the free boundary of the Stefan problem has at most one isolated singularity which occurs at some time* $\bar{t}$ *between 0 and the disappearance time* $t^*$. *Moreover*

(6.8) $$s(\bar{t}^{\,+}) \geqslant s(\bar{t}^{\,-}),$$

(6.9) $$\theta(x, \bar{t}^{\,-}) \leqslant -1 \qquad \textit{for } x \in (s(\bar{t}^{\,-}), s(\bar{t}^{\,+}))\,,$$

(6.10) $$\theta(x, \bar{t}) > -1 \qquad \textit{for } x \in (s(\bar{t}^{\,+}), 1)\,.$$

Thus the theorem states that at $t = \bar{t}$ the free boundary jumps exactly across the interval over which $\theta(x, \bar{t}^{\,-}) \leqslant -1$, meaning that bulk nucleation has occurred.

A basic point in the proof of Theorem 6.4 is the study of the critical set $M := \{(x, t) \colon \theta(x, t) < -1\}$, which is shown to be bounded by two curves $x = r^-(t)$, $x = r^+(t)$. The curve $x = r^-(t)$ necessarily meets the free boundary at its singular point.

As a byproduct of the proof of Theorem 6.4 it comes out that the function $U(x, t) = \theta(x, t) + H(x - s(t))$ is actually continuous across the nucleation interval, meaning that

(6.11) $$\theta(x, \bar{t}^{+}) = \theta(x, \bar{t}^{-}) + 1\,,$$

thus confirming Gurtin's conjecture.

## 7. – The behaviour of solutions near blow-up points.

In the preceding two sections we have illustrated some attempts to interpret blow-up on a physical basis. Now we go back to the investigation of the blow-up points with the aim of describing the admissible singularities of a blowing-up solution.

The reference paper is M. A. Herrero and J. L. Velázques [20], where problem (2.1)-(2.6) is considered with the following conditions on the initial data: $h(x) \leqslant 0$, $h \in C^1[0, 1]$, $h'(0) = 0$.

The study performed there is heavily technical in its details, but very appropriately the authors point out that the underlying philosophy is transparent. Therefore we confine ourselves to summarizing the main ideas (as the authors did in the preliminary sections), emphasizing the conceptual simplicity and the ingenuity of their approach.

Assuming that blow-up occurs at $t = T$ and $x_0 = s(T) > 0$, the following theorem provides a complete classification of the blow-up profiles.

THEOREM 7.1. – *If* $(x_0, T)$, $x_0 > 0$, *is a blow-up point for* (2.1)-(2.6) *the pair* $(s, u)$ *behaves in one of the following ways*

(i) *logarithmic behaviour*

$$u(x, T) \approx -1 - \frac{1}{2 \log|\log|x - x_0||} \tag{7.1}$$

*for* $x$ *approaching* $x_0$, *and*

$$s(t) - s(T) = 2[(T-t)\log|\log(T-t)|]^{1/2} + o(1) \tag{7.2}$$

*for* $t$ *approaching* $T$;

(ii) *for some integer* $k \geqslant 3$ *there exist positive constants* $C, K$ *such that*

$$u(x, T) \approx -1 - C(x - x_0)^{k-2} \tag{7.3}$$

*in a left neighborhood of* $x_0$, *and*

$$s(t) - s(T) = K(T-t)^{1-1/k} + o(1) \tag{7.4}$$

as $t \uparrow T$.

REMARK 7.1. – Formulas (7.1), (7.3) are clearly consistent with the theory illustrated in Sections 2,4 according to which blow-up is characterized by the fact the the level set $u = -1$ approaches the free boundary. In addition, in view of the results of Section 3 it is clear that the solutions behaving as in (7.1) cannot be continued, and that the same is true for the case (7.3) with $k$ *even* (see Theorem 3.3).

REMARK 7.2 (again from [20]). – A small refinement of (7.3), (7.4) is needed when $x_0 = 0$, namely $k$ has to be even.

On the line of the discussion made in Sect. 4 about the relationship between the supercooled Stefan problem (SSP) and the oxygen diffusion-consumption problem (with (CDCP) or without (UDCP) the positivity constraint) another result is proved for (CDCP), concerning *extinction points*. If $T$ is the extinction time (the inf of times for which $c(x, t)$ vanishes identically for $x \in [0, 1]$), then $x_0 \in [0, 1)$ is an extinction point if $(x_0, T)$ is the limit of a sequence $(x_n, t_n)$ such that $c(x_n, t_n) > 0$. Such a result describes the structure of the positivity set of $c$ near the extinction point.

THEOREM 7.2. – *Let* $(x_0, T)$ *be an extinction point for* (CDCP), $x_0 > 0$. *For* $t$ *close enough to* $T$ *there exist two continuous functions* $x = \xi_1(t)$, $x = \xi_2(t)$ *such that* $c > 0$ *in* $(x_0 - \xi_1(t), x_0 + \xi_2(t))$ *and* $c$ *vanishes in a left and in a right neighbourhood of the same interval. Moreover either*

$$\lim_{t \uparrow T} \xi_i(t)[2(T-t)\log|\log(T-t)|]^{1/2} = 1, \qquad i = 1, 2, \tag{7.5}$$

*or*

$$\lim_{t \uparrow T} \xi_i(t)[C(T-t)^{1-1/k}]^{-1} = 1, \qquad i = 1, 2 \tag{7.6}$$

*for some* $C > 0$ *and some integer* $k > 3$ *and even.*

*Finally, if* $x_0 = 0$ *we just have the right hand side interface.*

Let us now describe the main ideas of the proofs. For Theorem 7.1 the starting point is to consider the (UCDP) version of (SSP), namely (3.1)-(3.6), denoting as usual its solution by $(s, c)$. Next a smooth function $\eta(x)$ is introduced such that $\eta = 0$ for $x < (1/4)\, x_0$, $\eta = 1$ for $x > (1/2)\, x_0$, $\eta' \geqslant 0$, and a Cauchy problem is considered for the function

$$w(x, t) = c(x, t)\, \eta(x) \tag{7.7}$$

with zero extension outside the domain of definition of $c$. The further change of variables

$$w(x, t) = (T-t)\, \phi(y, \tau), \qquad y = (x - x_0)(T-t)^{-1/2}, \qquad \tau = \log(T-t), \tag{7.8}$$

and

$$\lambda(\tau) = (s(t) - x_0)(T-t)^{-1/2} \tag{7.9}$$

leads to the following equation for $\phi$

$$\frac{\partial \phi}{\partial \tau} = A\phi - \chi_{\lambda(\tau)} + f(y, \tau), \tag{7.10}$$

where

$$A\phi = \frac{\partial^2 \phi}{\partial y^2} - \frac{1}{2} y \frac{\partial \phi}{\partial y} + \phi \,, \tag{7.11}$$

$\chi_{\lambda(\tau)} = 1$ for $y < \lambda(\tau)$ and zero elsewhere, and $f$ is a bounded function.

Thus the analysis of the solution near the blow-up point is reduced to the study of the asymptotic behaviour of the pair $(\lambda, \phi)$ as $\tau \to \infty$.

Noting that the operator $A$ in (7.11) is self-adjoint in a suitable weighted space (1), the function

$$\psi(y, \tau) = \phi(y, \tau) - 1$$

is represented in the form

$$\psi(y, \tau) = \sum_{k=0}^{\infty} b_k(\tau)\, H_k(\tau) \,, \tag{7.12}$$

where $H_k(\tau)$ is the normalized $k$-th Hermite polynomial. Indeed the $H_k$ are the eigenfunctions of $A$ with the corresponding eigenvalues

$$\lambda_k = 1 - \frac{k}{2} \,, \qquad k = 0, 1, 2, \dots \,. \tag{7.13}$$

It is proved that asymptotically only one of the modes in (7.12) dominates. The modes $k = 0$, $k = 1$ are not candidates for becoming dominant, because it is not difficult to see that they produce a behaviour for the pair $(s, c)$ contrasting with the occurrence of blow-up. At this point a finer analysis of $\lambda(\tau)$, $\phi(y, \tau)$ and of $\partial^2 \phi / \partial y^2$ for $\tau \gg 1$ leads exactly to the conclusions of Theorem 7.1.

The proof of Theorem 7.2 goes along the same lines. Here the odd values of $k$ are ruled out by imposing that the asymptotic solution satisfies the additional constraint

$$c(x, t) \leqslant C(T - t) \tag{7.14}$$

for some $C > 0$, which has been proved for (CDCP) by the same authors in [19].

What is particularly remarkable in the paper so shortly summarized so far is that results of the kind presented were indeed expected at least since the appearance of [16], but the proof came only after some fifteen years: this is an indirect evidence of how non-trivial the whole question is. The authors made use of the large experience accumulated in the study of singular problems such as the rate of collapse of a melting ice ball [21] or degeneracies in mean curvature flow (see [4] and the corresponding literature and [5] in which the scaling (7.2) appears for the first time), or blow-up in reaction-diffusion system (see e.g. [3] and the quoted literature).

(1) A key point is the choice of the weight $\exp(-y^2/4)$, which is crucial in determining the length scale (7.2).

Soon after [20] another paper appeared by J. J. Velázques [25] in which singularities of SSP in two and three space dimensions are studied. Although the asymptotic techniques are similar to the 1-D case the extension is far from being trivial since the qualitative behaviour of the solutions is different. For instance, while in the 1-D (SSP) (in normalized variables) the undercooling at a blow-up point must be 1 (blow-up occurs when the level curve $u = -1$ hits the free boundary), in the multidimensional case the development of a cusp may be accompanied by an undercooling which can be anywhere in $(0, 1)$. Cusps profiles are obtained in the 2-D and 3-D case, again making use of the relationship between (SSP) and (UDCP). However such a relation is no longer obvious as in the 1-D case and is discussed at length, providing basically an alternative proof of the existence of regular solutions to (SSP) in more than one space dimension.

The typical cusp profile in 2-D is

$$|x_2| \approx k(c)(x_1) + [\log|\log|x_1||]^{-1/2} \qquad \text{as} \;\; |x_1| \to 0 \tag{7.15}$$

where $c$ is a constant varying in $(0, 2\sqrt{2\pi})$ and determining the degree of supercooling at the cusp, while $k(c)$ is a function increasing from 0 to $\infty$ in the same interval.

The behaviour of the free boundary in the vicinity of the cusp can be estimated by

$$|x_2| \leq k(c)\,\frac{|x_1|}{2\sqrt{|\log(T-t)|}} \tag{7.16}$$

where $T$ is the time of cusp formation.

In the 3-D case $|x_2|$ is replaced by $\sqrt{x_2^2 + x_3^2}$.

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