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Introduction to the Models of Phase Transitions.

A. VISINTIN

Sunto. – *Le transizioni di fase si presentano in svariati processi fisici: un esempio tipico è la transizione solido-liquido. Il classico modello matematico, noto come* problema di Stefan, *tiene conto solo dello scambio del calore latente e della diffusione termica nelle fasi. Si tratta di un* problema di frontiera libera, *poiché l'evoluzione dell'interfaccia solido liquido è una delle incognite. In questo articolo si rivedono le formulazioni forte e debole di tale problema, e quindi si considerano alcune generalizzazioni fisicamente motivate. In particolare si presenta un modello su scala mesoscopica per la* tensione superficiale, *il* superraffreddamento *e la* nucleazione.

Introduction.

Phase transitions occur in many relevant processes: metal casting, steel annealing, crystal growth, thermal welding, freezing of soil, food conservation, and so on. The *Stefan problem* is the classical analytical model of the temperature evolution in solid-liquid systems. It is a *free boundary problem*, as the evolution of the interface between the phases is a priori unknown.

The Stefan model represents phase transitions in a rather simplified way, and leaves several open questions to modelling and analysis. In this survey we introduce the basic Stefan problem and some of its physically justified generalizations; we then deal with a fine-scale model which also accounts for *undercooling, superheating, surface tension*, and *phase nucleation*. This presentation is based on the recent monograph [233]. We refer to the parallel papers of Fasano, Magenes and Verdi for the analysis of phase transitions in polymers, in concentrated capacities, and for the numerical aspects.

Note. The paper consists of five sections, labelled by roman numbers, which are divided in subsections. Formulae are labelled indicating the number of the subsection, not that of the section.

I. – The plain Stefan problem.

We outline and shortly discuss the strong and weak formulations of the basic Stefan model in several dimensions of space.

I.1. *Strong formulation.*

SOME DEFINITIONS. – We deal with a system composed of a homogeneous and isotropic material, capable of attaining two phases, liquid and solid, say. We label quantities relative to the liquid and solid phases by 1 and 2, respectively. We denote by Ω a bounded domain of $\boldsymbol{R}^3$ occupied by this material, fix any constant $T > 0$, set $Q := \Omega \times]0, T[$, and use the following notation:

Q_i: open subset of Q corresponding to the phase i,

$\mathcal{S} := \partial Q_1 \cap \partial Q_2$: (possibly disconnected) space-time manifold representing the evolution of the *interface* which separates the phases,

$\mathcal{S}_t := \mathcal{S} \cap (\Omega \times \{t\})$: configuration of the interface at a generic instant $t \in [0, T]$,

u: density of internal energy (namely, internal energy per unit volume),

θ: relative temperature (namely, the difference between the actual absolute temperature τ and the value τ_E at which a planar solid–liquid interface is at equilibrium),

$\vec{q}$: heat flux (per unit surface),

$C_{Vi}(\theta)$: heat capacity per unit volume (namely, the heat needed to increase the temperature of a unit volume by one degree),

$k_i(\theta)$: thermal conductivity,

$L(\theta)$: density of *latent heat* of phase transition (namely, the heat needed to melt a unit volume of crystal),

g: intensity of a distributed heat source (or sink) (namely, the heat either produced or absorbed per unit volume).

ENERGY BALANCE. – We assume that the solid that is initially present and that which is formed in the process are in the crystalline state, so that they contain no latent heat ([1]). We neglect convection, and assume that both phases are incompressible, so that processes occur at constant volume ([2]). In each phase the en-

([1]) At variance with amorphous solids, like glasses.

([2]) In practice it is more usual (and easier) to keep the pressure constant rather than the volume. However most of our developments hold also for systems at constant pressure, just with minor changes in the terminology. For instance in this case one should use the term *enthalpy* instead of internal energy.

ergy balance reads $\partial u/\partial t = -\nabla\cdot\vec{q} + g$; u can be regarded as a function of θ, and $C_{Vi}(\theta) := du/d\theta$. By the classical Fourier conduction law $\vec{q} = -k_i(\theta)\,\nabla\theta$ (which defines k_i), we then get the heat equation

$$C_{Vi}(\theta)\,\frac{\partial\theta}{\partial t} - \nabla\cdot[k_i(\theta)\nabla\theta] = g \quad \text{in } Q_i \ (i=1,2). \tag{1.1}$$

THE STEFAN CONDITION. – The temperature θ is continuous across $\mathcal{S}$. We assume that $\mathcal{S}$ is sufficiently regular, denote by $\vec{\nu} \in \boldsymbol{R}^3$ a unit vector field normal to $\mathcal{S}_t$ oriented from the liquid to the solid, by $\vec{q}_1$ ($\vec{q}_2$, resp.) the heat flux per unit surface contributed by the liquid phase (absorbed by the solid phase, resp.) through $\mathcal{S}_t$. For instance let us assume that in a small time interval dt an element dS of interface moves with normal velocity $\vec{v}$ through the solid phase ([3]). This melting process transforms the net heat flux absorbed at the interface by conduction into an amount of latent heat proportional to the volume spanned by dS in dt. Thus $\vec{q}_1\cdot\vec{\nu} - \vec{q}_2\cdot\vec{\nu} = L(\theta)\,\vec{v}\cdot\vec{\nu}$ on $\mathcal{S}$. This equality also holds in case of freezing; in that case the same quantities are negative, and represent the heat released at the interface. In either case, by the Fourier law this yields the classical *Stefan condition*

$$k_1(\theta)\,\frac{\partial\theta_1}{\partial\nu} - k_2(\theta)\,\frac{\partial\theta_2}{\partial\nu} = -L(\theta)\,\vec{v}\cdot\vec{\nu} \quad \text{on } \mathcal{S}, \tag{1.2}$$

where we denote by $\partial\theta_i/\partial\nu$ the normal derivative of θ relative to the phase labelled by i. If $g \in C^1(Q)$ is such that $\mathcal{S} = \{(x, y, z, t) \in Q\colon\ g(x, y, z, t) = 0\}$, then $\nabla g\cdot\vec{v} + \partial g/\partial t = 0$ on $\mathcal{S}$. Hence (1.2) is equivalent to $[k_1(\theta)\nabla\theta_1 - k_2(\theta)\nabla\theta_2]\cdot\nabla g = L(\theta)\,\partial g/\partial t$ on $\mathcal{S}$.

LOCAL THERMODYNAMICAL EQUILIBRIUM. – Although the heat equation describes nonequilibrium, here we assume *local* thermodynamical equilibrium; by this we mean that in a neighbourhood of each point the system is close to equilibrium, and that we can apply the same constitutive relations as at equilibrium.

Here we need this assumption only at the interface. For a homogeneous material, neglecting surface tension effects we have

$$\theta = 0 \quad \text{on } \mathcal{S}. \tag{1.3}$$

(Hence in (1.2) we might replace $L(\theta)$ by $L(0)$ and $k_i(\theta)$ by $k_i(0)$ $(i=1,2)$.) In Sect. III.1 we shall see that (1.3) can be derived from the minimization of the free energy.

The evolution of the solid–liquid interface is unknown. In principle, this lack

([3]) The moving interface is not a material surface, hence only the normal component of its velocity has a physical meaning.

of information is compensated by *two* quantitative conditions at the *free boundary* S, namely, (1.2) and (1.3). Appropriate conditions on the initial value of θ and on the initial phase configuration must also be provided, as well as boundary conditions. For instance, one may choose a partition $\{\Gamma', \Gamma''\}$ of the boundary Γ of Ω, and prescribe θ on $\Gamma' \times]0, T[$, $\partial\theta/\partial\nu$ on $\Gamma'' \times]0, T[$. As an example we consider the following model problem, under natural smoothness assumptions on the data.

PROBLEM 1.1 (Strong formulation of the three-dimensional two-phase Stefan problem). – *To find* $\theta \in C^0(\overline{Q})$ *and a partition* $\{Q_1, Q_2, S\}$ *of* Q *such that:*

(i) Q_1 *and* Q_2 *are open sets*;

(ii) $S \subset Q$ *is a smooth 3-dimensional manifold, and* $S_t := S \cap (\Omega \times \{t\})$ *is a (possibly disconnected) smooth surface, for any* $t \in]0, T[$;

(iii) θ *is smooth in* Q_1 *and in* Q_2, *and* $\partial\theta/\partial\nu$ *exists on both sides of* S;

(iv) *the equations* (1.1), (1.2), (1.3) *are fulfilled*;

(v) $\partial\theta/\partial\nu$ *equals a given field on* $\Gamma'' \times]0, T[$;

(vi) θ *equals a given field on* $\Omega \times \{0\}$ *and on* $\Gamma' \times]0, T[$;

(vii) $S \cap (\Omega \times \{0\})$ *is prescribed.*

If the temperature vanishes identically in one of the phases, one often speaks of a *one-phase* Stefan problem ([4]).

Problem 1.1 can also be formulated in presence of either *undercooled* or *superheated* regions, which are respectively characterized by liquid at $\theta < 0$ or solid at $\theta > 0$. These states are labelled as *metastable,* and can be excluded by assuming natural sign conditions on the initial and boundary data, because of the maximum and minimum principles.

ONE-DIMENSIONAL STEFAN PROBLEM. – Now we assume that $\Omega :=]a, b[$. Let $a < s^0 < b$, and let the interval $]a, s^0[$ ($]s^0, b[$, resp.) represent the solid (liquid, resp.) phase at $t = 0$. If we exclude the formation of new phases, the phase interface S coincides with the graph of a function $s: [0, T] \to [a, b]$ such that $s(0) = s^0$. Hence $x > s(t)$ in Q_1 and $x < s(t)$ in Q_2. We assume that

$$
\text{(1.4)} \qquad \begin{cases} C_{Vi} \in C^0(\boldsymbol{R}), \quad k_i \in C^1(\boldsymbol{R}), \quad C_{Vi}, k_i > 0 \quad (i = 1, 2), \\ g \in C^0(\overline{Q}), \quad \theta_a, \theta_b \in C^0([0, T]), \quad \theta_a < 0, \quad \theta_b > 0, \\ \theta^0 \in C^0([a, b]), \quad \theta^0 < 0 \text{ in }]a, s^0[, \quad \theta^0 > 0 \text{ in }]s^0, b[. \end{cases}
$$

The previous equations coupled with natural initial and boundary conditions yield the following problem; cf. Fig. I.1.

([4]) This somehow misleading terminology is traditional.

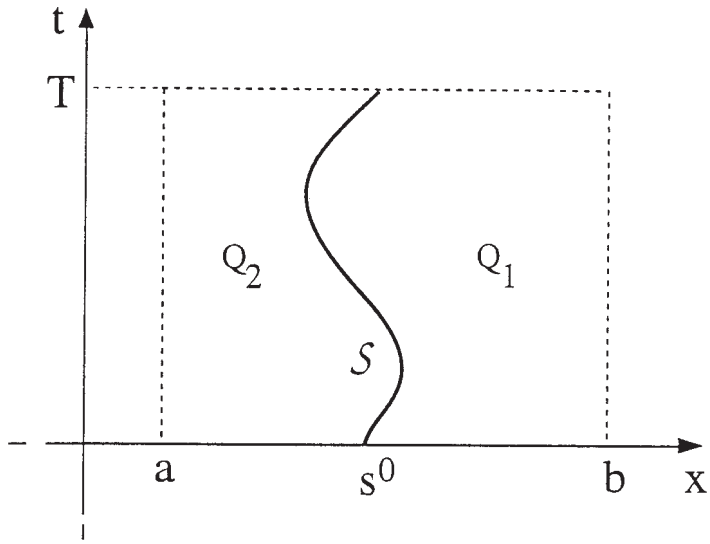

Figure I.1. – One-dimensional two-phase Stefan problem.

PROBLEM 1.2 (Strong formulation of the one-dimensional two-phase Stefan problem). – *To find* $s \in C^0([0, T]) \cap C^1(]0, T[)$ *and* $\theta \in C^0(\overline{Q})$ *such that, setting*

$$Q_1 := \{(x, t) \in Q\colon\ x > s(t)\}, \qquad Q_2 := \{(x, t) \in Q\colon\ x < s(t)\},$$

$\partial\theta/\partial t$, $\partial^2\theta/\partial x^2 \in C^0(Q_i)$ $(i = 1, 2)$, *the limits* $[k_i(\theta)\partial\theta/\partial x](s(t) \pm 0, t)$ *exist for any* $t \in]0, T[$, *and*

$$C_{Vi}(\theta)\frac{\partial\theta}{\partial t} - \frac{\partial}{\partial x}\left[k_i(\theta)\frac{\partial\theta}{\partial x}\right] = g \quad \text{in } Q_i \ (i = 1, 2), \tag{1.5}$$

$$\left(k_1(\theta)\frac{\partial\theta}{\partial x}\right)(s(t) + 0, t) - \left(k_2(\theta)\frac{\partial\theta}{\partial x}\right)(s(t) - 0, t) = -L(\theta)\frac{ds}{dt}(t) \tag{1.6}$$

$$\text{for } 0 < t < T,$$

$$\theta(s(t), t) = 0 \quad \text{for } 0 < t < T, \tag{1.7}$$

$$\theta(a, t) = \theta_a(t), \qquad \theta(b, t) = \theta_b(t) \quad \text{for } 0 < t < T, \tag{1.8}$$

$$s(0) = s^0, \qquad \theta(x, 0) = \theta^0(x) \quad \text{for } a < x < b. \tag{1.9}$$

By the maximum principle, here the occurrence of metastable states is excluded.

HISTORICAL NOTE. – The classical mathematical model of phase transitions is named after the Austrian physicist Josef Stefan, who in 1889 proposed a model

for melting of the polar ices. In a series of papers [211], he dealt with several aspects of the one- and two-phase problems in a single dimension of space. However the archaeology of phase transitions dates the first model back to Lamé and Clayperon [150] in 1831.

In 1947, Rubinstein [196] formulated the one-dimensional two-phase Stefan problem in terms of a system of integral equations, and proved existence and uniqueness of a solution in a small time interval. Apparently this was the first result of existence of a solution (for a *large* class of data).

Other formulations of the one-dimensional Stefan problem via various integral equations were then considered by several authors: G. W. Evans [91], Sestini [204], Friedman [109], Kolodner [148], Jiang [141], and others. The well-posedness for large time was proved in several ways, jointly with approximation, regularity results, information on the asymptotic behaviour, and other properties; see e.g. Cannon and Hill [49], Friedman [110; Chap. 8], [111, 112, 113], Fasano and Primicerio [95, 96], Schaeffer [203], Fasano, Primicerio and Kamin [102], and Rubinstein, Fasano and Primicerio [201]. Physically motivated generalizations of the problem were also studied in the one-dimensional setting; see, for example, Fasano and Primicerio [96] for a rather general result.

I.2. *Weak formulation.*

ILL-POSEDNESS. – The early research on the Stefan problem concentrated on the one-dimensional model. This is just natural, since in general the multidimensional Problem 1.1 is ill-posed for large times. In particular its solution may be nonunique: for instance, if a negative temperature is imposed on a part of the fixed boundary in contact with the liquid phase, this model allows for undercooling of the liquid as well as nucleation of a new solid phase.

Although a solution exists in a small time interval under fairly natural assumptions, Problem 1.1 may also have no global-in-time solution. In fact it does not account for possible discontinuities in the evolution of the solid–liquid interface, which may occur in several ways, as we shall see in Sect. IV.3. This induces us to consider a weak formulation.

MUSHY REGION AND TWO-SCALE MODEL. – We define the *phase function*

$$\chi := 1 \quad \text{in } Q_1, \qquad \chi := -1 \quad \text{in } Q_2, \tag{2.1}$$

drop the requirement that the phases be separated by a sharp interface $\mathcal{S}$, and allow χ to attain intermediate values between -1 and 1.

This can be interpreted according to the following *two-scale model.* It is assumed that at a *mesoscopic* length-scale (namely, a scale intermediate between that of laboratory experiments and that of molecular phenomena) just pure phases (either liquid or solid) can be observed, that is, $\chi = \pm 1$. However fine solid–liquid mixtures may appear. At the macroscopic scale, a set where this oc-

curs is called a *mushy region;* it is characterized by $-1 < \chi < 1$, which corresponds to a liquid concentration $0 < (\chi + 1)/2 < 1$. For instance this may occur if there is a distributed heat source, or if the latent heat depends on the space variable.

AN EQUATION IN THE SENSE OF DISTRIBUTIONS. – We define $C_V(\theta, \chi)$ and $k(\theta, \chi)$ as follows:

$$(2.2)\qquad \begin{cases} C_V(\theta, \chi) := C_{V1}(\theta)\,\dfrac{1+\chi}{2} + C_{V2}(\theta)\,\dfrac{1-\chi}{2}\,, \\ k(\theta, \chi) := k_1(\theta)\,\dfrac{1+\chi}{2} + k_2(\theta)\,\dfrac{1-\chi}{2}\,, \qquad \forall \theta \in \boldsymbol{R}\,, \quad \forall \chi \in [-1, 1]\,. \end{cases}$$

(It is immaterial how these functions are defined for $-1 < \chi < 1$, since mushy regions are isothermal, and so no heat diffusion can occur there.)

PROPOSITION 2.1. – *Let χ be defined as in* (2.1). *If θ is continuous across $\mathcal{S}$, then the system* (1.1), (1.2) *is formally equivalent to the equation*

$$(2.3)\qquad C_V(\theta, \chi)\,\frac{\partial \theta}{\partial t} + \frac{L(\theta)}{2}\,\frac{\partial \chi}{\partial t} - \nabla \cdot [k(\theta, \chi) \nabla \theta] = g \qquad \textit{in } \mathcal{D}'(Q)\,.$$

PROOF. – Let us denote by $\vec{n} := (\vec{n}_x, n_t) \in \boldsymbol{R}^4$ the unit vector field normal to $\mathcal{S}$, oriented towards Q_2. As $n_t = -\vec{v} \cdot \vec{n}_x$, the Stefan condition (1.2) can be written in the form

$$(2.4)\qquad [k_1(\theta) \nabla \theta_1 - k_2(\theta) \nabla \theta_2] \cdot \vec{n}_x = L(\theta) n_t \qquad \text{on } \mathcal{S}\,.$$

Let us denote the duality pairing between $\mathcal{D}'(Q)$ and $\mathcal{D}(Q)$ by $\langle \cdot, \cdot \rangle$. A simple calculation yields

$$(2.5)\qquad \left\langle C_V(\theta, \chi)\,\frac{\partial \theta}{\partial t} + \frac{L(\theta)}{2}\,\frac{\partial \chi}{\partial t} - \nabla \cdot [k(\theta, \chi) \nabla \theta],\, \varphi \right\rangle =$$

$$\iint_Q \left\{ C_V(\theta, \chi)\,\frac{\partial \theta}{\partial t}\,\varphi - \chi\,\frac{\partial}{\partial t}\,\frac{L(\theta)\varphi}{2} + k(\theta, \chi)\,\nabla \theta \cdot \nabla \varphi \right\} dx\,dt =$$

$$\iint_{Q \setminus \mathcal{S}} \left\{ C_V(\theta, \chi)\,\frac{\partial \theta}{\partial t} - \nabla \cdot [k(\theta, \chi)\,\nabla \theta] \right\} \varphi\,dx\,dt +$$

$$\int_{\mathcal{S}} \{ -L(\theta)\,n_t + \vec{n}_x \cdot [k_1(\theta)\,\nabla \theta_1 - k_2(\theta)\,\nabla \theta_2] \}\,\varphi\,d\mathcal{S}\,, \qquad \forall \varphi \in \mathcal{D}(Q)\,.$$

Notice that $\partial\theta/\partial t$ and $\nabla\theta$ are locally integrable: unlike $\partial\chi/\partial t$, these derivatives cannot exhibit any *Dirac-type* measure on $\mathcal{S}$.

The last two integrals of (2.5) vanish for any test function φ iff the heat equation (1.1) and Stefan condition (2.4) are fulfilled. ■

Loosely speaking, at the moving boundary the Dirac-type measure due to the discontinuity of χ balances with that due to the discontinuity of the normal heat flux.

GLOBAL ENERGY BALANCE. – The weak equation (2.3) can be derived directly from physical principles, independently of the strong formulation and without assuming any regularity property for the interface $\mathcal{S}$, actually even if a *mushy region* is present.

We assume that the density of internal energy u is a known differentiable function of the state variables θ and χ, $u = \widehat{u}(\theta, \chi)$, which is characteristic of the material. Thus $u(x, t) = \widehat{u}(\theta(x, t), \chi(x, t))$. Setting $C_V := \partial\widehat{u}/\partial\theta$ and $L := 2\,\partial\widehat{u}/\partial\chi$ (the factor 2 is due to the fact that $\chi = \pm 1$), for any process at constant volume we have

$$\frac{\partial u}{\partial t} = C_V(\theta, \chi)\,\frac{\partial\theta}{\partial t} + \frac{L(\theta, \chi)}{2}\,\frac{\partial\chi}{\partial t} \quad \text{in } \mathcal{D}'(Q). \tag{2.6}$$

In presence of a distributed heat source g and of interfaces, the *global energy balance* reads

$$\frac{\partial u}{\partial t} + \nabla\cdot\vec{q} = g \quad \text{in } \mathcal{D}'(Q). \tag{2.7}$$

These equations and the Fourier law yield (2.3) (here with $L(\theta, \chi)$ in place of $L(\theta)$).

THE TEMPERATURE-PHASE RULE. – In the absence of internal sources, assuming obvious sign conditions on the initial and boundary data, by the maximum principle (1.1) and (1.3) yield the *temperature-phase rule:* $\theta \geq 0$ in Q_1, $\theta \leq 0$ in Q_2. Setting

$$\operatorname{sign}(x) := \{-1\} \quad \text{if } x < 0, \qquad \operatorname{sign}(0) := [-1, 1], \qquad \operatorname{sign}(x) := \{1\} \quad \text{if } x > 0,$$

these conditions read

$$\chi \in \operatorname{sign}(\theta) \quad \text{in } Q. \tag{2.8}$$

So here *undercooling* and *superheating* effects are excluded, and new phases can be nucleated at the interior of those initially present.

The system (2.3), (2.8) must be coupled with an initial condition for u and with boundary conditions either for θ or for its normal derivative. This constitutes the *weak formulation* of the *two-phase Stefan problem* in several space dimensions,

which was proposed and studied around 1960 by Kamenomostskaya [142] and Oleĭnik [176].

REFORMULATION OF THE PROBLEM. – By (2.8), phase transition only occurs at $\theta = 0$; hence we can replace $L(\theta)$ by $L(0)$ in (2.3), and the *Kirchhoff transformations*

$$v(\xi) := \int_0^\xi C_V(\eta, \, sign(\eta))\, d\eta\,, \qquad \psi(\xi) := \int_0^\xi k(\eta, \, sign(\eta))\, d\eta\,, \qquad \forall \xi \in \boldsymbol{R}\,, \tag{2.9}$$

allow to rewrite (2.3) in the form

$$\frac{\partial}{\partial t}\varphi(\theta) + \frac{L(0)}{2}\,\frac{\partial \chi}{\partial t} - \Delta\psi(\theta) = g \quad \text{ in } \mathcal{D}'(Q)\,. \tag{2.10}$$

Note that φ and ψ can be inverted, as $C_V > 0$ and $k > 0$, and $\operatorname{sign}(\theta) = \operatorname{sign}(\psi(\theta))$. Setting $\tilde{\theta} := \psi(\theta)$, the system (2.8), (2.10) is then equivalent to

$$\begin{cases} \dfrac{\partial \tilde{u}}{\partial t} - \Delta\tilde{\theta} = g \quad \text{ in } \mathcal{D}'(Q)\,, \\ \tilde{u} \in \alpha(\tilde{\theta}) := \varphi(\psi^{-1}(\tilde{\theta})) + \dfrac{L(0)}{2}\operatorname{sign}(\tilde{\theta}) \quad \text{ in } Q\,. \end{cases} \tag{2.11}$$

This system can be coupled with an initial condition for $\tilde{u}$ and boundary conditions for $\tilde{\theta}$.

THE QUASI-STEADY STEFAN PROBLEM AND THE HELE-SHAW PROBLEM. – If the heat capacity C_V is very small, one can replace the heat equation by the quasi-stationary equation

$$-\nabla\cdot[k(\theta, \chi)\nabla\theta] = g \quad \text{ in } Q_i \ \ (i = 1, 2)\,. \tag{2.12}$$

In the weak formulation one then gets

$$\frac{L(\theta)}{2}\,\frac{\partial \chi}{\partial t} - \nabla\cdot[k(\theta, \chi)\nabla\theta] = g \quad \text{ in } \mathcal{D}'(Q) \tag{2.13}$$

in place of (2.3). (2.13) can then be coupled with (2.8). As an initial condition here one must specify $\chi(\cdot, 0)$.

This setting is also known as the *Hele-Shaw problem*, since in the two-dimensional case it represents the evolution of a *Hele-Shaw cell*, which consists of two slightly separated parallel plates partially filled with a viscous fluid. If some fluid is injected into the cell with a syringe the fluid expands, and the evolution of the pressure can be represented by an equation like (2.13); see e.g. DiBenedetto and Friedman [78], Elliott and Janovsky [88], Richardson [188, 1892], Rodrigues [191; Sect. 9.5], Saffman and Taylor [202].

Table 1. – Schematic comparison between the strong and weak formulation of the basic Stefan model.

	Strong formulation	Weak formulation
Energy balance	Heat equation in Q_i Stefan condition on S	Equation in $D'(Q)$
Local equilibrium condition	$\theta = 0$ on S	$\chi \in \text{sign}(\theta)$in Q
Phase characterization	Global, via S	Local, via sign (θ)
Mushy regions	Excluded	Allowed
Metastable states	Allowed	Excluded
Analytical features	Free boundary problem	Degenerate P.D.E.

This model can also represent the industrial process of *electro-chemical machining,* by which a metal body is either machined or formed by using it as an anode in an electrolytic cell; see e.g. McGeough [161], McGeough and Rasmussen [162], Elliott [86], Alt and Caffarelli [3].

I.3. *Comparison between strong and weak formulations.*

Despite of the terminology, in general the *strong* formulation of the Stefan problem (S.S.P.) and the *weak* formulation of the Stefan problem (W.S.P.) are not different formulations of the same problem. In particular in the former it is assumed that the phases are separated by a (*smooth*) interface, whereas in the latter the interface is not supposed to exist. Moreover these problems differ as for the phase characterization:

in the S.S.P. the phases are *globally* determined by the interface;

in the W.S.P. the phases are *pointwise* characterized by the sign of θ.

The solution of the S.S.P. can exhibit undercooling and superheating, but no mushy region; on the other hand, the W.S.P. can represent the occurrence of a mushy region, but neither undercooling nor superheating. See table I. As we saw, the W.S.P. can be derived from the S.S.P. whenever metastability is excluded; the converse holds under regularity properties and in the absence of mushy region. This raises at least two questions, concerning possible entensions of the previous formulations:

(i) is it possible to account for the mushy region in the S.S.P.?

(ii) is it possible to include undercooling and superheating in the W.S.P.?

The first question leads to the formulation of a *three-phase problem,* with solid, liquid and mushy phases. This has been studied in the one-dimensional setting, see e.g. Meirmanov [165], Primicerio [1862], Fasano and Primice-

rio [100, 101]. In this respect see also Atthey [12]. The second issue is crucial for most of the physically justified extensions of the Stefan model, see e.g. V. [231, 232].

A HIGHLY IRREGULAR PHASE INTERFACE. – In presence of heat-distributed sources, in the W.S.P. the interface can degenerate in a three-dimensional region, as it appears in the following example.

Let us consider a solid system initially at a uniform temperature $\theta(\cdot, 0) = \theta^0 < 0$, that evolves under the action of a uniform heat source of intensity $g = 1$ (this can be accomplished by infrared radiation, for instance), with no heat flux across the fixed boundary. Then the temperature remains uniform in Ω, and the equation (2.3) is reduced to the O.D.E.

$$C_V(\theta, \chi)\frac{d\theta}{dt} + \frac{L(\theta)}{2}\frac{d\chi}{dt} = 1 \qquad \text{in } [0, T], \tag{3.1}$$

coupled with (2.8). As θ vanishes, melting starts and χ increases smoothly from -1 to 1, uniformly in Ω. Thus the whole Ω becomes a mushy region. As χ reaches the value 1, the whole mushy region becomes liquid; then the temperature increases again.

Thus, according to the W.S.P., for some time there is no phase interface; at some instant the interface appears in a highly degenerate form, invading the whole system; after some more time the interface disappears instantaneously. The S.S.P. provides a different picture: here no mushy region can appear, θ becomes positive and increases indefinitely, yielding a superheated solid.

COMPARISON OF ANALYTICAL PROPERTIES. – The S.S.P. consists of nondegenerate equations set in unknown domains, hence it is a genuine *free boundary problem.* On the other hand in the W.S.P. the domain is fixed but the equation is degenerate.

The one-dimensional S.S.P. is well-posed, under natural assumptions. In several space dimensions in general the S.S.P. has a solution only in a *small* time interval, which depends on the data. As we said, the solution of the S.S.P. may fail after some time, even if the heat source term g vanishes identically. On the other hand the W.S.P. is well-posed, and can be solved numerically by means of standard techniques.

THE CHOICE. – Which one of the two models makes more sense?

This depends on the nucleation behaviour of the specific material. If solid nucleation occurs with negligible undercooling, a mushy region is formed consistently with the W.S.P. On the other hand, if nucleation requires some undercooling, the temperature behaves as predicted by the S.S.P., until the nucleation threshold is attained. But for later times the physical evolution diverges from that prescribed by this model. Thus the two models represent extreme nucleation

behaviours, and a more sound model should be based on the analysis of nucleation.

HISTORICAL NOTE. – The onset of weak formulations stimulated investigations about the regularity of the weak solution of the multi-dimensional Stefan problem. Results on the regularity of the free boundary for the multi-dimensional one-phase Stefan problem were obtained by using a variational inequality formulation (which we outline in the next section) by Friedman and Kinderlehrer [116] and Caffarelli [35, 36]. Kinderlehrer and Nirenberg [145, 146] were then able to prove that the weak solution is also strong, under appropriate restrictions. Continuity of the temperature was proved by Caffarelli and Friedman [38] for the one-phase problem, and by DiBenedetto [76, 77], Ziemer [241], Caffarelli and L. C. Evans [37] for the two-phase problem.

To the surprise of many, in 1979 Meirmanov [163, 164] proved existence of the strong solution of the multi-dimensional two-phase Stefan problem in a small time interval. This stimulated the study of *mushy regions;* see Meirmanov [165], Primicerio [186], Showalter [206]. On the other hand, Berger and Rogers [18] proved that no mushy region is formed in several dimensions, in the absence of any distributed heat source and in case of constant coefficients. Götz and Zaltzman [120] showed that under natural conditions the mushy region cannot expand. Other results were then obtained, for example, by Fasano and Primicerio [186, 100, 101]; see also the survey [94] of Fasano.

Recent studies on the regularity are due to DiBenedetto and Vespri [80], Athanassopoulos, Caffarelli and Salsa [9, 10, 11], and others.

I.4. *On the analysis of the weak formulation.*

A MODEL PROBLEM. – We assume that

$$u^0 \in L^2(\Omega), \qquad f \in L^2(Q), \tag{4.1}$$

and couple the system (2.11) (which we shall write omitting the tilde) with the following initial and (simplified) boundary conditions

$$u = u^0 \quad \text{in } \Omega \times \{0\}, \qquad \theta = 0 \text{ on } \partial\Omega \times]0, T[\,. \tag{4.2}$$

In the framework of Sobolev spaces this can be formulated as follows.

PROBLEM 4.1. – *To find* $\theta \in L^2\big(0, T; H_0^1(\Omega)\big)$ *and* $u \in L^2(Q)$ *such that*

$$\int\!\!\int_Q \left[(u^0 - u) \frac{\partial v}{\partial t} + \nabla\theta \cdot \nabla v - fv \right] dx\, dt = 0 \tag{4.3}$$

$$\forall v \in H^1(Q) \text{ such that } v = 0 \text{ on } (\partial\Omega \times]0, T[) \cup (\Omega \times \{0\}),$$

$$u \in \alpha(\theta) \quad \text{a. e. in } Q\,. \tag{4.4}$$

As α is a *maximal monotone graph,* a standard theory can be applied to this problem; see e.g. Brézis [31]. For instance, one can approximate the equation by implicit time discretization; at any time step the approximate problem is then equivalent to the minimization of a coercive, convex and semicontinuous functional. Multiplying the discretized equation by the approximate solution, one can then derive standard L^2-type estimate, which allow one to pass to the limit on a subsequence, via standard compactness and monotonicity techniques. Regularity results can also be obtained, for instance multiplying the discretized equation by the time incremental ratio of the approximate solution.
Here is a simplified statement.

THEOREM 4.1. – *Assume that* (4.1) *is satisfied and that*

$$\exists L, M > 0 : \ \forall (\theta, u) \in \mathrm{graph}\,(\alpha), \ |u| \leqslant L|\theta| + M\,, \tag{4.5}$$

$$B(u^0) \in L^1(\Omega) \qquad (B' := \alpha^{-1})\,. \tag{4.6}$$

Then Problem 4.1 *has one and only one solution, and* $u \in L^\infty(0, T; L^2(\Omega))$.
If moreover

$$\exists c > 0 : \ \forall (\theta_i, u_i) \in \mathrm{graph}\,(\alpha) \quad (i = 1, 2), \quad (u_1 - u_2)(\theta_1 - \theta_2) \geqslant c(\theta_1 - \theta_2)^2, \tag{4.7}$$

$$\alpha^{-1}(u^0) \in H_0^1(\Omega)\,, \tag{4.8}$$

then

$$\theta \in H^1(0, T; L^2(\Omega)) \cap L^\infty(0, T; H_0^1(\Omega))\,, \qquad u \in L^\infty(0, T; L^2(\Omega))\,. \tag{4.9}$$

One can derive L^1-type estimates, multiplying the time incremental ratio of the discretized equation by the sign of the time incremental ratio of the approximate solution. Maximum and minimum principles also hold.

As α is nonlinear, the operator $A : \ v \mapsto -\Delta\alpha^{-1}(v)$ is not monotone in $L^2(\Omega)$. Nevertheless one can apply the operator $-\Delta^{-1}$ (associated with the homogeneous Dirichlet condition, for instance) to the equation, and then profit of the maximal monotonicity of α. This is equivalent to regarding A as a maximal monotone operator in $H^{-1}(\Omega)$, cf. Brézis [30]. This procedure can also be interpreted as a change of *pivot space,* cf. Lions [152; Sect. 2.3].

The operator A is also *m-accretive* in $L^1(\Omega)$. One can then derive the well-posedness of an especially weak formulation of the problem, by means of the theory of *semigroups of nonlinear contractions* in $L^1(\Omega)$; see e.g. Bénilan [16].

THE BAIOCCHI-DUVAUT TRANSFORMATION. – In several parabolic problems the inversion of the Laplace operator Δ and the time integration play similar roles.

This suggests to set

$$z(x,t) := \int_0^t \tilde{\theta}(x,\tau)\,d\tau\,, \quad G(x,t) := \int_0^t g(x,\tau)\,d\tau + \tilde{u}(x,0)\,, \quad \forall (x,t) \in Q\,, \tag{4.10}$$

and, assuming that C_V, L and k are (positive) constants, to write the system (2.3), (2.8) in the equivalent form

$$\begin{cases} C_V \dfrac{\partial z}{\partial t} + \dfrac{L}{2}\chi - k\Delta z = G\,, \\ \chi \in \operatorname{sign}\left(\dfrac{\partial z}{\partial t}\right), \end{cases} \quad \text{in } Q\,. \tag{4.11}$$

As the *sign* graph is the *subdifferential* of the absolute value function, this is also equivalent to the following *variational inequality*:

$$\int\int_Q \left[\left(C_V \frac{\partial z}{\partial t} - k\Delta z - G\right)\left(\frac{\partial z}{\partial t} - v\right) + \frac{L}{2}\left(\left|\frac{\partial z}{\partial t}\right| - |v|\right)\right] dx\,dt \leqslant 0 \tag{4.12}$$

$$v\colon Q \to \boldsymbol{R}\,.$$

This can be coupled with the initial condition «$z = 0$ in Ω» and with appropriate boundary conditions. This leads to results similar to those mentioned above.

Let us now consider the case of the one-phase problem, in which the temperature identically vanishes in one of the two phases (the solid, say). If $g \geqslant 0$ in Q and the initial and boundary data fulfil obvious sign conditions, solidification can then be excluded, and we have $\partial z/\partial t = \tilde{\theta} > 0$ in Q_1, $\partial z/\partial t = \tilde{\theta} = 0$ in Q_2. This entails that the interface is monotone, whence $z > 0$ in Q_1 and $z = 0$ in Q_2; that is, $\chi \in \operatorname{sign}(z)$ in Q. Therefore (4.11) is equivalent to

$$\begin{cases} C_V \dfrac{\partial z}{\partial t} + \dfrac{L}{2}\chi - k\Delta z = G\,, \\ \chi \in \operatorname{sign}(z)\,, \end{cases} \quad \text{in } Q\,, \tag{4.13}$$

which can also be written as a variational inequality. As $z \geqslant 0$, this problem can also be formulated as an *obstacle problem*.

All these problems are well-posed in Sobolev spaces of Hilbert type; see e.g. Rodrigues [194].

HISTORICAL NOTE. – The transformation by time integration was independently introduced by Duvaut [84, 85] and Frémond [107] for the *Stefan problem*. This technique was inspired by an integral transformation which was successfully used by Baiocchi [13] to solve a free boundary problem

representing porous medium filtration, the so-called *dam problem*, see also Baiocchi and Capelo [14; Chap. 13].

I.5. *Comments.*

We represented phase transitions in an extremely simplified way, neglecting physically relevant aspects like stress and deformation in the solid, convection in the liquid, change of density, and so on. Convection in phase transitions has been studied, e.g., by Cannon and DiBenedetto [48], DiBenedetto and Friedman [79], Rodrigues [194].

In most of the mathematical literature on phase transitions, solidification and melting are described as qualitatively similar phenomena, and are represented in a *symmetrical* form. This is not completely consistent with the evidence: melting is a rather regularizing process, whereas solidification may yield a variety of morphologies. This is especially evident at the *mesoscopic* length-scale, and is largely related to *metastability;* see Sect. IV. On the contrary, the traditional Stefan model deals with the macroscopic scale, and assumes local stability.

II. – Generalizations of the Stefan problem.

Here we outline some physically justified generalizations of the Stefan model.

II.1. *Surface tension.*

UNDERCOOLING AND SUPERHEATING. – So far we dealt with phase transitions in pure materials, assumed local equilibrium, and neglected surface tension. If we drop these restrictions, then (I.1.2) must be replaced by a law of the form

$$\theta = \theta_{\text{s.t.}} + \theta_{\text{n.e.}} + \theta_{\text{imp.}} \qquad \text{on } \mathcal{S}\,. \tag{1.1}$$

The term $\theta_{\text{s.t.}}$ accounts for *surface tension*, and is proportional to the mean curvature of the interface; $\theta_{\text{n.e.}}$ is related to *nonequilibrium*, and depends on the rate of phase transition; $\theta_{\text{imp.}}$ is due to the presence of other components (so-called *impurities*).

By the continuity of the temperature at the interface, (1.1) entails the occurrence of undercooling and/or superheating in the interior of the phases, so that here the temperature-phase rule (I.2.8) does not hold.

THE GIBBS-THOMSON LAW. – Here we just deal with the term $\theta_{\text{s.t.}}$. We assume that at any instant t the interface $\mathcal{S}_t$ is of class C^2, denote by κ its *mean curvature* (assumed positive for a convex solid phase), and replace the condition (I.1.3) by

the classical *Gibbs-Thomson law*

$$\theta = -\frac{2\sigma\tau_E}{L}\kappa \quad \text{on } \mathcal{S}, \tag{1.2}$$

where σ is the surface tension coefficient, which is here supposed to be constant, like L.

For water at atmospheric pressure at about 0 °C, $2\sigma\tau_E/L$ is about 1.2×10^{-5} cm. Hence the right side of (1.2) is only significant for curvature radii of the order of 10^{-5} cm, namely, at a *mesoscopic* length-scale. Nevertheless, as we shall see, this term accounts for quantitatively relevant effects, like the undercooling prior to solid nucleation.

CONTACT ANGLE CONDITION. – For any $(x, t) \in \mathcal{S} \cap (\Gamma \times]0, T[)$, let us denote by $\omega(x, t)$ the angle formed by the normal to $\mathcal{S}_t$, oriented towards the liquid phase $\Omega_1(t)$, and the outward normal to Ω at x. We then impose the *contact angle condition*

$$\cos\omega = h \quad \text{on } \mathcal{S} \cap (\Gamma \times]0, T[), \tag{1.3}$$

where $h \in [-1, 1]$ depends on the external material the system is in contact with. In particular, $h = 0$ if Ω is surrounded by the vacuum.

(1.2) and (1.3) can be derived by minimizing the free energy potential, cf. Sect. III.2.

The surface tension has important consequences far from solid-liquid interfaces. In particular, it is responsible for the high undercooling which is required for solid *nucleation* (about $400K$ for platinum!). See e.g. Chalmers [53; Chap. 3], Flemings [106; Chap. 9], Woodruff [240; Chap. 2].

PROBLEM 1.1 (Stefan-Gibbs-Thomson problem, or Stefan problem with surface tension). – *To find* $\theta \in C^0(\overline{Q})$ *and a partition* $\{Q_1, Q_2, \mathcal{S}\}$ *of* Q *such that*

(i) Q_1 *and* Q_2 *are open sets*;

(ii) $\mathcal{S} \subset Q$ *is a smooth* 3*-dimensional manifold, and* $\mathcal{S}_t := \mathcal{S} \cap (\Omega \times \{t\})$ *is a* (*possibly disconnected*) *smooth surface, for any* $t \in]0, T[$;

(iii) θ *is smooth in* Q_1 *and in* Q_2, *and* $\partial\theta/\partial\nu$ *exists on both sides of* $\mathcal{S}$;

(iv) *the equations* (I.1.1), (I.1.2), (1.2) *and* (1.3) *are fulfilled*;

(v) $\partial\theta/\partial\vec{\nu}$ *equals a given field on* $\Gamma'' \times]0, T[$;

(vi) θ *equals a given field on* $\Omega \times \{0\}$ *and on* $\Gamma' \times]0, T[$;

(vii) $\overline{\mathcal{S}} \cap (\Omega \times \{0\})$ *is prescribed.*

This setting will be studied in Sect. III.1.

II.2. *Kinetic undercooling and phase relaxation.*

In this section we amend the classical Stefan problem, and replace the local equilibrium condition (I.1.3) by a dynamical law.

FIRST MODE: DIRECTIONAL SOLIDIFICATION (OR COLUMNAR GROWTH OR KINETIC UNDERCOOLING). – Phase transition is driven either by *undercooling* or by *superheating.* In a one-dimensional system we replace (I.1.7) by the *kinetic law*

$$\dot{s}(t) + \gamma(\theta(s(t), t)) = 0; \tag{2.1}$$

cf. Fig. II.1. The *kinetic function* γ depends on the material. In several cases one can assume that $\gamma\colon \boldsymbol{R} \to \boldsymbol{R}$ is continuous and strictly increasing, and $\gamma(0) = 0$. Often one can also deal with the corresponding linearized law $\dot{s}(t) + c\theta(s(t), t) = 0$, where c is a positive constant. By replacing (I.1.7) with (2.1) in Problem I.1.2, one gets the *one-dimensional two-phase Stefan problem with kinetic law.*

In the metallurgical literature, this mode of solidification is named *directional solidification,* and the corresponding undercooling is often referred to as *kinetic undercooling.*

SECOND MODE: EQUIAXED SOLIDIFICATION (OR PHASE RELAXATION). – Dealing with the weak formulation of the Stefan problem, we replace (I.1.3) by a nonequilibrium condition written in terms of the phase function χ. As the condition (I.2.8) can be written in the equivalent form $\mathrm{sign}^{-1}(\chi) \ni \theta$ in Q, it is natural to consider

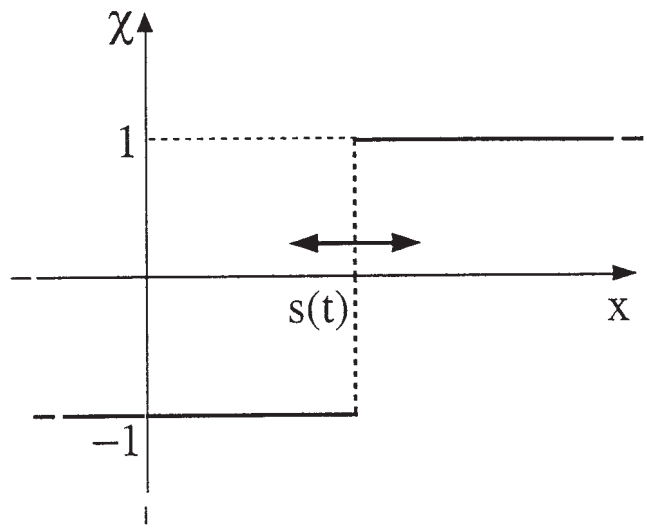

Figure II.1. – Kinetic undercooling *or* directional solidification *for a one-dimensional system.*

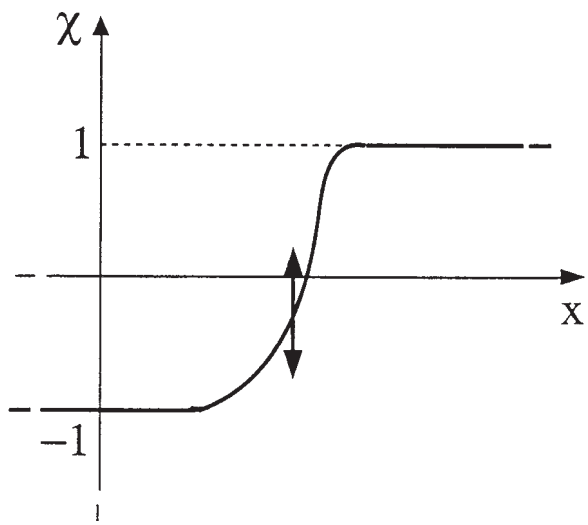

Figure II.2. – Phase relaxation, *or* equiaxed solidification, *for a one-dimensional system.*

the relaxation law

$$a\frac{\partial\chi}{\partial t} + \mathrm{sign}^{-1}(\chi) \ni \theta \quad \text{in } Q\,, \tag{2.2}$$

where a is a positive coefficient; cf. Fig. II.2. More generally, we can replace the right hand side by $\gamma(\theta)$, where the function γ is as above.

The inclusion (2.2) is equivalent to the following variational inequality:

$$\begin{cases} -1 \leqslant \chi \leqslant 1 \quad \text{in } Q\,, \\ \left(a\frac{\partial\chi}{\partial t} - \theta\right)(\chi - v) \leqslant 0 \quad \forall v \in [-1, 1], \ \text{in } Q\,, \end{cases} \tag{2.3}$$

In the metallurgical literature, this mode of phase transition is called *equiaxed solidification.*

COMPARISON OF THE FIRST AND SECOND MODE. – The laws (2.1) and (2.2) describe different evolution modes, although both represent relaxation towards (local) equilibrium. The equation (2.1) describes motion of the interface separating two pure phases, without formation of any mushy region. On the other hand, the second mode represents phase transition by formation of a mushy region, and (2.2) describes the evolution of the liquid concentration in that zone. Thus these two modes are naturally associated with the strong and the weak formulation of the Stefan problem, respectively.

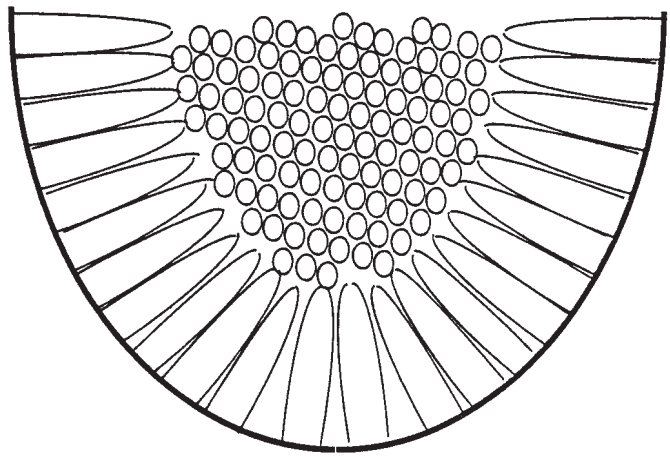

Figure II.3. – Schematic representation of a crystal grown from an undercooled liquid in a vessel: the solid columns advanced from the border, and impinged on the equiaxed grains which formed in the bulk.

Directional and equiaxed growth are the basic modes of solidification of a pure material. For instance, in casting metal at first an equiaxed zone is formed in contact with the wall of the mould. Then a columnar region moves towards the interior, while in the remainder of the liquid, nucleation occurs and an equiaxed solid phase grows, until the two solid phases impinge on and eventually occupy the whole volume; see Fig. II.3. For the physical aspects see, e.g., Flemings [106; Chap. 5], Kurz and Fisher [149; Sect. 1.1.2]; for the analysis see, e.g., Kenmochi [143], V. [221, 223, 224].

GLASS FORMATION. – A glass is an undercooled liquid, which retains a large part of the latent heat of phase transition. The solid behaviour is caused by high viscosity, which in turn is due to the undercooling. A glass is *amorphous:* despite of the low temperature, its crystal structure is not complete, since the viscosity reduces the mobility of particles in their migration to reach the crystal sites. Glass formation can be represented by means of a nonlinear kinetic law of the form (2.1), with a nonnmonotone function γ as outlined in Fig. II.4.

II.3. *Phase transition in two-component systems.*

In this section we extend the Stefan model to phase transitions in heterogeneous materials.

THE MASS DIFFUSION EQUATION. – We consider a *binary alloy;* that is, a homogeneous mixture of two components, which are soluble in each other in all proportions in both phases, outside a critical range of temperature. Here *homogeneity*

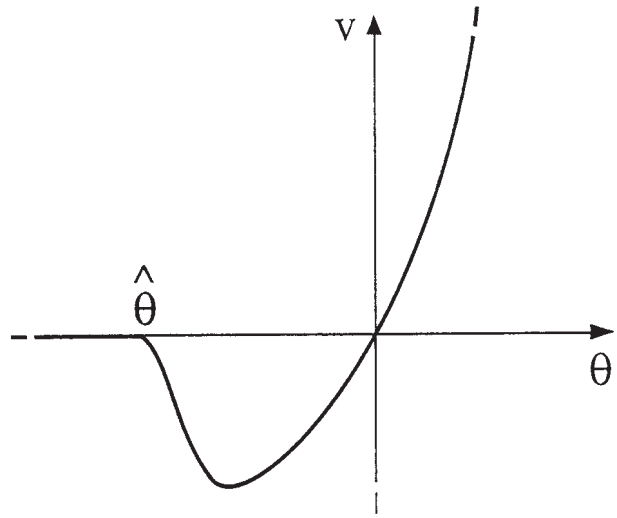

Figure II.4. – Kinetic function for glasses.

means that the constituents are intermixed on the atomic length-scale to form a single phase, either solid or liquid. We regard one of the two components as the *solute*, for instance that with the lower solid–liquid equilibrium temperature.

We label by 1 and 2 quantities relative to the liquid and solid phases, respectively, denote by c the concentration of the solute, by $\vec{j}$ the flux of solute (per unit surface), and by $D_i(c)$ the *mass diffusivity* in the phase i. In the solid the latter coefficient is rather small, but does not vanish.

The principle of mass conservation, $\partial c/\partial t = -\nabla\cdot\vec{j}$, and the *Fick law*, $\vec{j} = -D_i(c)\nabla c$, yield the *mass diffusion equation* in the interior of each phase:

$$\frac{\partial c}{\partial t} - \nabla\cdot[D_i(c)\nabla c] = 0 \quad \text{in } Q_i \ (i = 1, 2). \tag{3.1}$$

We denote by $\vec{j}_i$ the mass flux (per unit surface) through $\mathcal{S}$ contributed by the phase i, by c_i the limit of c on $\mathcal{S}$ from the phase i, by $\vec{v}$ the (normal) velocity of $\mathcal{S}_t$, by $\vec{\nu} \in \boldsymbol{R}^3$ a unit vector normal to $\mathcal{S}_t$. By mass conservation we have $\vec{j}_2\cdot\vec{\nu} - \vec{j}_1\cdot\vec{\nu} = (c_2 - c_1)\,\vec{v}\cdot\vec{\nu}$ on $\mathcal{S}$. The Fick law then yields the following discontinuity condition:

$$D_1(c_1)\frac{\partial c_1}{\partial \nu} - D_2(c_2)\frac{\partial c_2}{\partial \nu} = (c_2 - c_1)\,\vec{v}\cdot\vec{\nu} \quad \text{on } \mathcal{S}. \tag{3.2}$$

Notice the (partial) analogy between the balance laws (I.1.1) and (3.1) in the interior of the phases, and between the discontinuity conditions (I.1.2) and (3.2) at the interface. However θ is continuous across $\mathcal{S}$, whereas c is not.

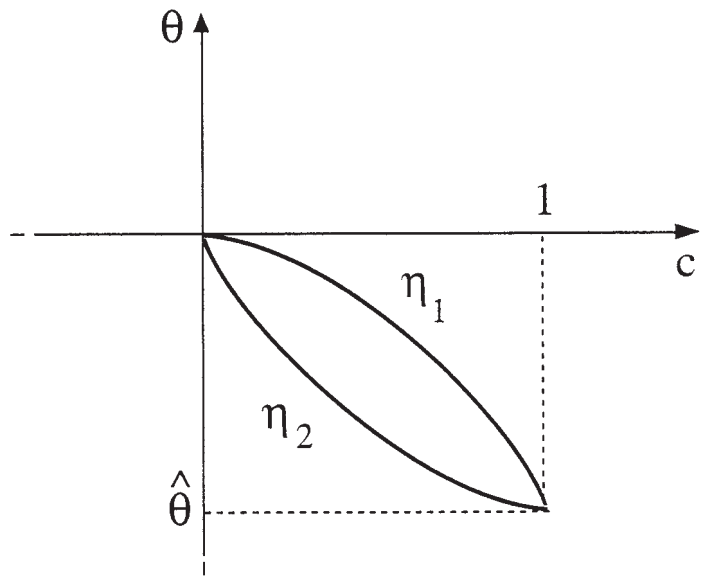

Figure II.5. – Constitutive law relating temperature and concentration of the interface at local equilibrium. The region between the two graphs represents either metastable or unstable states. In this model these states are not accessible, because of the assumption of (stable) equilibrium.

TEMPERATURE *VERSUS* CONCENTRATION DIAGRAMS. – Since the two components have different phase transition temperatures, the transition temperature of the mixture depends on the concentration, and here (I.1.7) is not fulfilled.

On $\mathcal{S}$, the temperature and the two limits c_1 and c_2 of the concentration from either phase are related as follows

$$\theta = \eta_1(c_1) = \eta_2(c_2) \quad \text{on } \mathcal{S}\,, \tag{3.3}$$

where η_1 and η_2 are known functions such that (cf. Fig. II.5)

$$\begin{cases} \eta_i \in C^1([0,1]), \quad \eta_i' < 0 \ (i=1,2), \quad \eta_2 \leqslant \eta_1\,, \\ \eta_1(0) = \eta_2(0) = 0\,, \quad \eta_1(1) = \eta_2(1) = \widehat{\theta}(= \text{constant} < 0)\,. \end{cases} \tag{3.4}$$

At local equilibrium, we have

$$\theta \geqslant \eta_1(c) \quad \text{in } Q_1\,, \qquad \theta \leqslant \eta_2(c) \quad \text{in } Q_2\,. \tag{3.5}$$

The states characterized by $\eta_2(c) \leqslant \theta \leqslant \eta_1(c)$ are not stable. If in a single phase system the variables are forced to attain such values (e.g., by rapid cooling), then a secondary phase nucleates and grows, until the two phases reach the respective concentrations $c_i = \eta_i^{-1}(\theta)$ $(i=1,2)$. This process of *phase separation* in binary alloys is also known as *spinodal decomposition*, and

is described by the classical *Cahn-Hilliard equation;* see, e.g., Cahn [43, 44], Cahn and Hilliard [45].

PROBLEM 3.1 (Strong formulation of the three-dimensional problem of phase transition in binary mixtures). – *To find* θ, $c \in C^0(\overline{Q})$ *and a partition* $\{Q_1, Q_2, S\}$ *of* Q *such that:*

(i) Q_1 *and* Q_2 *are open sets*;

(ii) $S \subset Q$ *is a smooth* 3*-dimensional manifold, and* $S_t := S \cap (\Omega \times \{t\})$ *is a* (*possibly disconnected*) *smooth surface, for any* $t \in]0, T[$;

(iii) θ *and* c *are smooth in* Q_1 *and* Q_2;

(iv) *the equations* (3.1) *through* (3.5) *are fulfilled*;

(v) θ *and* c *attain given values on* $\Omega \times \{0\}$ *and on* $\partial\Omega \times]0, T[$;

(vi) $\overline{S} \cap (\Omega \times \{0\})$ *is prescribed.*

Models of this sort have extensively been used by material scientists, and their numerical approximation has provided quantitatively acceptable results; see e.g. Bermudez and Saguez [19], Crowley [65], Crowley and Ockendon [66], Fix [103], Mullins and Sekerka [170, 171], Rubinstein [199], Wilson, Solomon and Alexiades [237]. Nevertheless, as far as this author knows, no result of existence of a solution has yet been proved for this problem in the multidimensional setting. This may be ascribed to the fact that physically this approach is not completely satisfactory, since it neglects cross effects between heat and mass diffusion: indeed a temperature gradient also induces a mass flux, and a concentration gradient also causes a heat flux. On the other hand, in practice the omitted terms do not seem to be quantitatively very significant.

A different approach issued in the framework of so-called *nonequilibrium thermodynamics* has been applied to phase transitions in multi-component systems by Donnelly [82], Luckhaus and V. [157]. It is based on:

(i) a constitutive relation for the entropy density (the *Gibbs formula*),

(ii) a system of balance laws which include the first principle of thermodynamics,

(iii) a set of *phenomenological laws* consistent with a local formulation of the second principle of thermodynamics.

The latter accounts for dissipation, which in analytical terms corresponds to the forward parabolicity of the resulting second order system of P.D.E.s.

II.4. *Other generalizations.*

THE HYPERBOLIC STEFAN PROBLEM. – One can replace the Fourier conduction law $\vec{q} = -k(\theta, \chi)\nabla\theta$ by the *Cattaneo law* $a\partial\vec{q}/\partial t + \vec{q} = -k(\theta, \chi)\nabla\theta$, where a is

a positive relaxation constant. The parabolic problem (I.2.11) is then replaced by the quasilinear hyperbolic system

$$\text{(4.1)}\qquad \begin{cases} a\dfrac{\partial^2 \tilde{u}}{\partial t^2} + \dfrac{\partial \tilde{u}}{\partial t} - \nabla\cdot[k(\theta,\chi)\nabla\theta]\,\tilde{\theta} = f & \text{in } \mathcal{D}'(Q), \\ \tilde{u} \in \alpha(\tilde{\theta}) & \text{in } Q\,. \end{cases}$$

with α as in $(\text{I.2.11})_2$. The analysis of the corresponding initial and boundary value problem is still open, even for k constant, as far as this author knows. However, usually a is very small, and in most applications the Fourier law is an acceptable approximation, although it represents instantaneous heat diffusion, at variance with Cattaneo's law.

In this respect, see e.g. Showalter and Walkington [207] and references therein.

A VECTORIAL STEFAN-TYPE PROBLEM IN FERROMAGNETISM. – Ferromagnetic processes without hysteresis exhibit several analogies with phase transitions in solid-liquid systems.

In a linearly conducting material, the *Maxwell equations* without *displacement current* term yield the equation

$$\text{(4.2)}\qquad 4\pi\sigma\frac{\partial \boldsymbol{B}}{\partial t} + c^2\nabla\times\nabla\times\vec{H} = \vec{0} \qquad \text{in } Q\,,$$

in *Gauss units* and with standard notation (e.g., here σ represents the electrical conductivity). Let us assume that the fields $\vec{B}$ and $\vec{H}$ are related by a maximal monotone graph. For instance, the behaviour of soft iron for high field saturation can be represented by

$$\text{(4.3)}\qquad \vec{B} \in \vec{H} + 4\pi\mathfrak{M}\,\vec{\beta}(\vec{H}), \qquad \text{in } Q\,,$$

where $\mathfrak{M}$ is a positive constant and $\vec{\beta}$ is the subdifferential of the modulus function (a natural extension of the sign graph to the vectorial setting). *Formally* the system (4.2) and (4.3) is the weak formulation of a vectorial free boundary problem. Its well-posedness can be proved by the methods mentioned in Sect. I.4. $\vec{B} = \vec{0}$ and $|\vec{B}| \geqslant 4\pi\mathfrak{M}$ correspond to the unmagnetized and magnetically saturated phases, respectively. However the existence of an interface between the two phases is not obvious a priori, even under regularity hypotheses, and the occurrence of a *mixed phase* characterized by $0 < |\vec{B}| < 4\pi\mathfrak{M}$ (a sort of *magnetical mushy region*) is not excluded a priori.

Surprisingly enough, apparently this problem has not yet received the attention that it certainly deserves because of its applicative relevance. In particular, this author is not aware of any result concerning the existence of an interface between the magnetically saturated and unsaturated phases. For related problems,

see, for example, Bossavit [22-25], Bossavit and Damlamian [26], Bossavit and Vérité [69], Damlamian [69], Visintin [222, 225].

OTHER RELATED PROBLEMS. – Phase transitions occur in several processes of physical, engineerical and industrial interest, which can be represented by models that are more or less closely related to the Stefan problem. See e.g. Elliott and Ockendon [89], Crank [63; Sect. 2.12], Friedman [115], and the proceedings of the many meetings on free boundary problems held in the last twenty years. These processes include:

(i) Monocrystal growth; see e.g. Almgren, Taylor and Wang [6], Almgren and Wang [6], Cahn and Taylor [46], Crank and Ockendon [64], Dobrushin, Kotecký and Shlosman [81], Langer [151], Rubinstein [198-200], Taylor [216], Taylor and Cahn [217].

(ii) Continuous casting; see e.g. Rodrigues [190], [191; Sect. 9.4].

(iii) Soil freezing; see e.g. Frémond [107], Fasano and Primicerio [98], Talamucci [212].

(iv) Solid-solid phase transitions; see e.g. Brokate and Sprekels [33; Chap. 8], Hömberg [138], Verdi and Visintin [220], [227].

(v) Phase transitions in polymers (see the parallel paper of Fasano).

(vi) Phase transitions in systems with *concentrated capacities* (see the parallel paper of Magenes).

(vii) Memory effects in phase transitions; see e.g. Colli and Grasselli [60], Colli, Gilardi and Grasselli [57-59].

III. – The Gibbs-Thomson law.

The fine length-scale (or *mesoscopic*) structure of two-phase systems is characterized by nonconvexity and surface tension. The latter is at the basis of the *Gibbs-Thomson law*.

III.1. *The free energy*.

Under stationary conditions, the heat equation (I.1.1) reduces to $-\nabla\cdot[k(\theta,\chi)\nabla\theta]=g$ in $\mathcal{D}'(\Omega)$. For the sake of simplicity, here we assume that k does not depend on χ, so that the temperature is uncoupled from the phase, and can be determined once appropriate boundary conditions have been prescribed. So the system can be stationary outside (global) thermodynamical equilibrium. Henceforth we assume that θ is just any function of $L^\infty(\Omega)$.

THE FREE ENERGY FUNCTIONAL. At prescribed (nonnecessarily uniform) tem-

perature, stationary states minimize the (*Helmholtz*) free energy. At variance with single phase systems, in solid-liquid systems the free energy is represented by a *nonconvex* functional.

We assume that Ω is a bounded domain of $\boldsymbol{R}^3$ having a Lipschitz boundary Γ, and introduce the perimeter functional $P: L^1(\Omega) \to \boldsymbol{R} \cup \{+\infty\}$:

$$P(\chi) := \begin{cases} \frac{1}{2}\int_\Omega |\nabla\chi| \ (\leqslant +\infty) & \text{if } |\chi| = 1 \text{ a.e. in } \Omega, \\ +\infty & \text{otherwise;} \end{cases} \tag{1.1}$$

here $\int_\Omega |\nabla\chi| := \sup\left\{\int_\Omega \chi \nabla\cdot\vec{\eta}:\ \vec{\eta} \in C_0^1(\Omega)^N,\ |\vec{\eta}| \leqslant 1 \text{ in } \Omega\right\}$.

We denote by σ the surface density of free energy at the solid-liquid interface, by σ_L (σ_S, resp.) the surface density of free energy relative to a surface separating the liquid phase (solid phase, resp.) from an external material. The functional

$$F_\theta(\chi) := \sigma P(\chi) + \frac{\sigma_L - \sigma_S}{2}\int_\Gamma \chi\, d\Gamma - \frac{L}{2\tau_E}\int_\Omega \theta\chi\, dx, \qquad \forall \chi \in \mathrm{Dom}(P) \tag{1.2}$$

represents the total phase contribution to the free energy, but for an additive constant that is independent of χ. Notice that $F_\theta(\chi) < +\infty$ only if $|\chi| = 1$ a.e. in Ω; hence by minimizing F_θ the constraint «$|\chi| = 1$ a.e. in Ω» is automatically imposed.

Crystals are anisotropic, and indeed the isotropy assumption is more appropriate for liquid-vapour than for solid-liquid system. However, a large part of our discussion might be extended to heterogeneous and anisotropic materials, by replacing $\sigma\int_\Omega |\nabla\chi|$ by $\int_\Omega |\sigma\cdot\nabla\chi|$, here with $\sigma = \sigma(x)$ a positive definite 3×3-tensor.

THEOREM 1.2 (Existence). – *If* $\theta \in L^\infty(\Omega)$ *and*

$$|\sigma_L - \sigma_S| \leqslant \sigma, \tag{1.3}$$

then the functional F_θ *has an* (*absolute*) *minimizer.*

In general the minimizer of F_θ is not unique since this functional is nonconvex.

PROOF. – After Massari and Pepe [160], F_θ is lower semicontinuous with respect to the strong topology of $L^1(\Omega)$ if and only if (1.3) is fulfilled. It then suffices to apply the direct method of the calculus of variations. ■

LIMIT AS $\sigma \to 0$. – On the macroscopic length-scale, $\sigma = 0$. It is not difficult to show that, as $\sigma \to 0$ (and σ_L, $\sigma_S \to 0$), F_θ Γ-converges (in the sense of De Giorgi)

to the *macroscopic free energy* functional

$$F_\theta^0(\chi) := \begin{cases} -\dfrac{L}{2\tau_E}\displaystyle\int_\Omega \theta\chi\,dx & \text{if } |\chi| \leq 1 \text{ a.e. in } \Omega, \\ +\infty & \text{otherwise}. \end{cases} \tag{1.4}$$

Notice that χ is a minimum point of F_θ^0 iff $\chi \in \mathrm{sign}(\theta)$ a.e. in Ω, cf. (I.2.8).

III.2. *The Gibbs-Thomson law.*

ABSOLUTE AND RELATIVE MINIMIZERS. – We say that $\chi \in L^1(\Omega)$ is a *relative minimizer* of F_θ if it is not an absolute minimizer and there exists $K(\chi) > 0$ such that

$$F_\theta(\chi) \leq F_\theta(v),\ \forall v \in L^1(\Omega) \text{ such that } \|v - \chi\|_{L^1(\Omega)} \leq K(\chi). \tag{2.1}$$

The existence of relative minimizers is made possible by the nonconvexity of the potential, and by the presence of a (convex and coercive) higher order term like the surface tension term $\sigma P(\chi)$.

PROPOSITION 2.1 (Existence of relative minimizers). – (i) *For any* $\theta \in L^\infty(\Omega)$, *if* $\theta \leq 0$ *and* $\theta \not\equiv 0$ *in* Ω, *then* $\chi \equiv 1$ *is a relative minimizer* (*and similarly for* $\theta \geq 0$ *and* $\chi \equiv -1$).

(ii) *If in* (1.2) *the* σ*-term were dropped, then* F_θ *would have no relative minimizer for any* $\theta \in L^\infty(\Omega)$.

(Obviously an analogous result holds for $\theta \geq 0$ and $\chi = -1$.)

PROOF. (i) If we modify the field $\chi \equiv 1$ by setting $\chi = -1$ in a ball $A \subset \Omega$, then the bulk term of (1.2) decreases at most proportionally to $\|\theta\|_{L^\infty(\Omega)} |A|$, whereas the perimeter increases proportionally to the area of the surface of A. For small balls the surface contribution prevails over the bulk one. By the isoperimetric property of the sphere, the same holds *a fortiori* for shapes different from a ball.

(ii) Let A be any measurable subset of Ω in which the temperature-phase rule does not hold. If we modify χ by imposing that rule also in A, then F_θ decreases, as $\sigma = 0$. ■

At constant temperature (states represented by) absolute minimizers of the free energy persist for any time. On the other hand, relative minimizers may persist for some time, but eventually are destined to decay because of *fluctuations*. By the same token, relative maximizers and saddle points decay instantaneously.

THEOREM 2.1 (Gibbs-Thomson law and contact angle condition). – *Let* $\theta \in W^{1,1}(\Omega)$, $\chi \in L^1(\Omega)$, *and the boundary* S *of the set* $\Omega^+ := \{x \in \Omega : \chi(x) = 1\}$ *in* Ω *be of class* C^1. *Let us denote by* $\vec{n}$ *the unit normal vector to* S *oriented towards* Ω^+, *and set* $\kappa := \nabla_S \cdot \vec{n}/2$. *If*

$$\liminf \frac{F_\theta(v) - F_\theta(\chi)}{\|v - \chi\|_{L^1(\Omega)}} \geqslant 0 \qquad \text{as } v \to \chi \text{ strongly in } L^1(\Omega), \tag{2.2}$$

then $\kappa \in L^1(S)$ *and*

$$\gamma_0 \theta = -\frac{2\sigma\tau_E}{L}\kappa \qquad \text{a.e. on } S. \tag{2.3}$$

Moreover,

$$\cos\omega = \frac{\sigma_S - \sigma_L}{\sigma} \qquad \text{a.e. on } S \cap \Gamma, \tag{2.4}$$

where ω *is the angle between* $\vec{n}$ *and the outward normal vector to* Γ, *and* $S \cap \Gamma$ *is endowed with the one-dimensional Hausdorff measure.*

The simple argument is based on the local representation of S as a Cartesian graph.

In particular (2.2) holds for any either relative or absolute minimizer of F_θ.

Whenever $\theta \in L^p(\Omega)$ with $p > 3$, by a classical result of Almgren [4] $\partial\Omega^+$ is a manifold of class $C^{1,(p-3)/2p}$. This allows to apply the latter result.

III.3. *Phase-field model.*

DOUBLE WELLS. – Let us consider a so-called *double well* potential, e.g., $W_1(v) := (1 - v^2)^2$ for any $v \in \boldsymbol{R}$, fix two positive parameters a and ε, and consider a free energy functional of the form

$$F_\theta^\varepsilon(\chi) := \int_\Omega \left(\frac{\varepsilon a}{2} |\nabla\chi|^2 + \frac{1}{\varepsilon} W(\chi) - \frac{L}{2\tau_E}\theta\chi \right) dx + \frac{\sigma_L - \sigma_S}{2} \int_\Gamma \chi \, d\Gamma, \tag{3.1}$$

$$\forall \chi \in H^1(\Omega).$$

If χ is nonuniform, the first two terms are in competition: $(1/\varepsilon)\, W(\chi)$ penalizes deviations from $|\chi| = 1$, whereas $(\varepsilon a/2)\, |\nabla\chi|^2$ penalizes the high gradients that are induced by sharp variations of χ. For small ε, any relative minimizer of F_θ^ε attains values close to ± 1 in the whole Ω, but for *thin* transition layers which represent neighbourhoods of the phase interfaces. The coefficients a, ε are so small that the layer thickness is typically of the order of 10^{-7} cm. This length-scale is so close to that of molecular phenomena, that the use of a continuous model might be questioned.

DYNAMICS. – Generally speaking, if Ψ is a functional defined in a Banach space B with dual B', by *gradient flow* with respect to Ψ one means a law of the form $c du/dt + \nabla\Psi(u) \ni 0$ in B'. Here $c = c(u) > 0$ and ∇ is an appropriate differential operator (it might be the subdifferential of *convex analysis,* the subdifferential of Clarke, and so on).

We denote by $F_\theta^{\varepsilon\prime}$ the *Fréchet differential* of F_θ^ε, and consider the *gradient flow* $c\partial\chi/\partial t + F_\theta^{\varepsilon\prime}(\chi) = 0$. This is tantamount to the *Allen-Cahn* (or *Landau-Ginzburg*) *equation*

$$c\frac{\partial\chi}{\partial t} - \varepsilon a\Delta\chi + \frac{4}{\varepsilon}\chi(\chi^2 - 1) = \frac{L\theta}{2\tau_E} \quad \text{in } Q\,, \tag{3.2}$$

where c is a positive coefficient. See, e.g., Allen and Cahn [3].

The so-called *phase-field* model consists in coupling (3.2) with the energy balance equation (II.2.3); see e.g. Fix [104, 105], Caginalp [39-41], and for a related model Penrose and Fife [180, 181], Colli and Sprekels [61, 62], Sprekels and Zheng [210], and so on.

THEOREM 3.1 (Γ-limit). – *Let $\theta \in L^\infty(\Omega)$ and $a := 9\sigma^2/128$. As $\varepsilon \to 0$ the family of functionals $\{F_\theta^\varepsilon\}$ $\Gamma(L^1(\Omega)^-)$-converges to F_θ, that is:*

(i) *for any $\chi \in L^1(\Omega)$ and any sequence $\{\chi_\varepsilon\}$ such that $\chi_\varepsilon \to \chi$ strongly in $L^1(\Omega)$, $\liminf_{\varepsilon\to 0} F_\theta^\varepsilon(\chi_\varepsilon) \geq F_\theta(\chi)$;*

(ii) *for any $\chi \in L^1(\Omega)$, there exists a sequence $\{\chi_\varepsilon\}$ such that $\chi_\varepsilon \to \chi$ strongly in $L^1(\Omega)$ and $\lim_{\varepsilon\to 0} F_\theta^\varepsilon(\chi_\varepsilon) = F_\theta(\chi)$.*

See Modica [168, 169] and also Luckhaus and Modica [155] for related results.

MACRO-, MESO-, MICRO-SCOPIC LENGTH-SCALES. – Solid–liquid systems can be described at three length-scales.

(i) At a *macroscopic* scale the free energy functional is convex, cf. (1.4). The evolution is described by the weak formulation of the Stefan problem; this can represent either a sharp or a diffuse interface, depending on the occurrence of a mushy region.

(ii) At a *mesoscopic* scale the free energy is nonconvex, cf. (1.2), and the interface is sharp.

(iii) At a *microscopic* scale the free energy is nonconvex, cf. (3.1), and the interface is diffuse. The evolution can be described by the phase-field model.

The mushy region is represented by $|\chi| < 1$ at a macroscopic length-scale. At a mesoscopic scale, one distinguishes solid from liquid parts, hence $|\chi| = 1$. At a microscopic scale, interfaces are replaced by thin transition layers where $|\chi| < 1$,

across which χ varies smoothly. The process of *zooming out* from the microscopic to the mesoscopic scale is represented by the Γ-limit as $\varepsilon \to 0$, and that from the mesoscopic to the macroscopic scale by the Γ-limit as $\sigma \to 0$.

IV. – Nucleation and growth.

The nonconvexity of the free energy fuctional accounts for metastable (e.g., undercooled) states. At a fine length-scale, nucleation is discontinuous and growth occurs by mean curvature flow.

IV.1. *Metastability.*

CASE OF RADIAL SYMMETRY. – Let us consider a homogeneous liquid that occupies a ball Ω of radius $\tilde{R}$ at a uniform temperature $\theta < 0$. Here we investigate whether $\chi = 1$ is an (either relative or absolute) minimizer of the free energy functional F_θ; whenever this property fails, we assume that (isothermal) nucleation occurs, that is, a new solid phase is formed. Here we just deal with *homogeneous* nucleation, corresponding to a new solid phase not in contact with the boundary Γ of Ω.

In our simplified analysis the newborn phase is regarded as isotropic. This assumption is acceptable for liquid nucleation in a vapour, but not for crystallization in a liquid; however here we only want to outline the basic features of the phenomenon, and this simplification is consistent with the classical theory of nucleation. By the isoperimetric property of the sphere, if A is a ball then the corresponding characteristic function minimizes the potential F_θ among subsets of Ω of prescribed volume. Hence we can confine ourselves to varying the phase in balls. The position of the center is immaterial, as we assumed the temperature $\theta(<0)$ to be uniform.

The variation of the free energy functional due to formation of a solid ball of radius R ($\leq \tilde{R}$, say) can be regarded as a function of R, $\delta F_\theta(R)$. (III.1.2) yields

$$\delta F_\theta(R) = 4\pi\sigma R^2 + \frac{4\pi L\theta}{3\tau_E} R^3, \qquad \forall R \in [0, \tilde{R}], \tag{1.1}$$

whence $\delta F'_\theta(R_c) = 0$ for $R_c := -2\sigma\tau_E/L\theta(>0)$. The *critical radius* R_c coincides with the value prescribed by the Gibbs-Thomson law (II.1.2). We assume that $\tilde{R}$ is not too small, so that $\delta F_\theta(\tilde{R}) < 0$. Therefore $R = \tilde{R}$, $R = R_c$, and $R = 0$ are an absolute minimizer, a relative maximizer, and a relative minimizer of δF_θ in $[0, \tilde{R}]$, respectively; cf. Fig. IV.1.

STABILITY AND METASTABILITY. – Since at constant temperature the system tends to reduce its free energy, if $R < R_c$ ($R > R_c$, respect.) the solid ball contracts (grows, respect.). So $R = R_c$ is a point of *unstable equilibrium.*

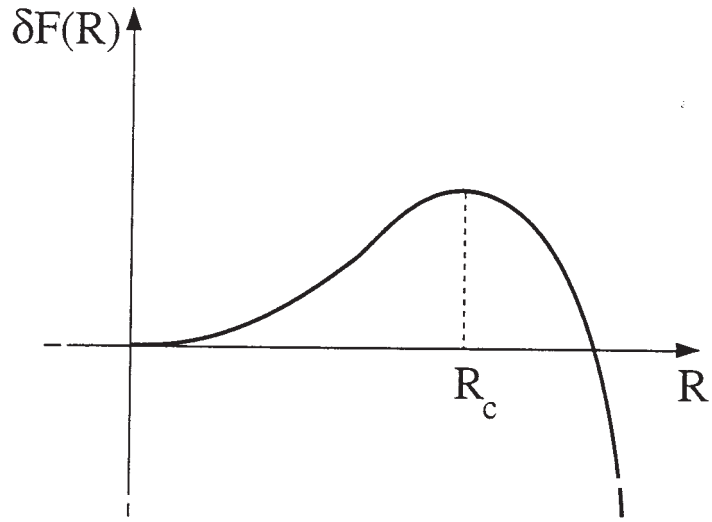

Figure IV.1. – Graph of the function $\delta F_\theta(R) := 4\pi\sigma R^2 + (4\pi L\theta/3\tau_E)R^3$. $R = 0$ sits in a *potential well.*

At any negative temperature, for $R = 0$ the system sits in a *potential well*; so the «all liquid» configuration corresponds to a state of *metastable equilibrium.* A solid ball can nucleate only if a suitable fluctuation lets $\delta F_\theta(R)$ overcome the *potential barrier* $\delta F_\theta(R_c) = 16\pi\sigma^3 T_E^2/3L^2\theta^2$. If we assume that initially nucleation is a *Poisson process,* the probability for it to occur in a small time interval δt is proportional to $\delta t \exp[(-\delta F_\theta(R_c) - F_a)/kT]$; here k is the Boltzmann constant, and $F_a(>0)$ is an *activation energy,* which must be contributed to move molecules from the liquid to the growing crystal surface. In glassy and polymeric materials, viscosity is high and this energy is large; nucleation is then slowed down to a very long time-scale.

These conclusions can easily be extended to any set Ω such that for any $x \in \Omega$, there exists $y \in \Omega$ such that $x \in B_{R^*}(y) \subset \Omega$, where $R^* := 3\sigma\tau_E/L|\theta|$.

NUCLEATION TEMPERATURE. – Let us consider the process of slowly and continuously cooling a liquid metal which is maintained at a uniform temperature $\theta(t) < 0$. Although nucleation is a stochastic phenomenon, according to the classical Volmer-Becker-Döring theory (see e.g. Chalmers [53; Chap. 3], Christian [56; Chap. 10], Flemings [106; Chap. 9], Kurz and Fisher [149; Chap. 2], Woodruff [240; Chap. 2], the rate of *homogeneous* nucleation (namely, the number of nuclei formed in a unit time in a unit volume) varies from almost zero to a large value in a small range of temperatures. For several materials (e.g., metals) this range is so small, that it can be identified with a single critical temperature $\theta_c(<0)$, which is characteristic of the material, of the impurities it might include, and of the time-scale.

Once nuclei have appeared at the mesoscopic scale, they grow to macroscopic size, until either their growth is stopped by impingement on other nuclei, or undercooling is depleted by release of latent heat.

IV.2. *Mean curvature flow.*

GRADIENT FLOW FOR THE FREE ENERGY. – Let us express the free energy variation δF_θ as a function of $A := 4\pi R^2$ (the area of the sphere of radius R): $\delta F_\theta(R) = \sigma A + L\theta A^{3/2}/6\tau_E\sqrt{\pi} =: \delta\widehat{F}_\theta(A)$. The gradient flow for $\delta\widehat{F}_\theta(A)$ reads $cA'(t) = -\delta\widehat{F}'_\theta(A(t)) = -\sigma - L\theta\sqrt{A}/4\tau_E\sqrt{\pi}$, where c is a positive constant, and is equivalent to

$$8\pi cR'(t) = -\frac{\sigma}{R(t)} - \frac{L\theta}{2\tau_E}\,, \qquad \forall R(t) > 0\,. \tag{2.1}$$

(The gradient flow $\tilde{c}R'(t) = -\delta F'_\theta(R(t))$ would yield the same equation for $\tilde{c} = \tilde{c}(R) = 64\pi^2 R^2 c$).

The *Lyapunov function* of this dynamics is $\mathcal{L}(R) = \sigma\log R + L\theta R/2\tau_E$ for any $R > 0$; that is, $\mathcal{L}'(R) \leqslant 0$ along the flow lines, if $R > 0$. Notice that $\mathcal{L}$ has a singularity in the origin, and equation (2.1) cannot represent continuous increase of R from the value 0.

For a space- and time-dependent temperature, we can consider the more general law of mean curvature flow with forcing term:

$$cv_S = \sigma\kappa + \frac{L\theta}{2\tau_E} \qquad \text{on } S\,. \tag{2.2}$$

Here v_S is the normal component of the velocity of the moving solid-liquid interface, which is assumed positive when the liquid advances through the solid; e.g., $v_S = -R'(t)$ for a solid ball. This seems to be adequate to represent the evolution of an isotropic interface. Phase transition causes exchange of latent heat, hence (2.2) must be coupled with the energy balance equation, cf. (I.2.3).

BIBLIOGRAPHICAL NOTE. – Studies on mean curvature flow have flourished in the last ten years, after the pioneering contributions of Brakke [29], Gage [118], Grayson [121], Huisken [139], Barles [15], Sethian [205], Osher and Sethian [118], Evans and Spruck [93], Chen, Giga and Goto [55], and others. For instance, see the reviews of Evans, Soner and Souganidis in [92], Ilmanen [140], and the proceeding volumes [34, 73].

In most of the works that deal with this topic, the evolving surface is represented either as a level set of a function of space and time, or via a time dependent *approximate characteristic function* (or *phase-field*). The latter is a continuous function that is equal to ± 1, with the exception of a *thin* transition zone which is interpreted as a neighbourhood of the evolving surface. The concept of *viscosity solution* has been used. An alternative approach using (exact) *charac-*

teristic functions has been studied by Almgren, Taylor and Wang [5], Almgren and Wang [6], Luckhaus and Sturzenhecker [156], Visintin [234, 236]. Phase transition coupled with mean curvature flow has been studied in the radial case by Visintin [224]. A discussion about gradient flow for interface free energies and various generalizations of the mean curvature flow can be found in Cahn and Taylor [46, 217].

IV.3. *Nonlinear mean curvature flow.*

The mean curvature flow equation (2.2) accounts neither for phase nucleation nor for other singularities in the evolution of the interface. Therefore we consider the following *nonlinear mean curvature flow* equation with forcing term

$$\alpha(v_s) \ni \sigma\kappa + \frac{L\theta}{2\tau_E} \quad \text{on } \mathcal{S}\,, \tag{3.1}$$

where v_s is defined as above and $\alpha: \boldsymbol{R} \to \boldsymbol{R}$ is a nonconstant, bounded, maximal monotone graph. For instance,

$$\alpha(\xi) := \begin{cases} -M & \text{if } \xi < -\dfrac{M}{c}\,, \\ c\xi & \text{if } -\dfrac{M}{c} \leqslant \xi \leqslant \dfrac{M}{c}\,, \\ M & \text{if } \xi > \dfrac{M}{c}\,, \end{cases} \qquad \forall \xi \in \boldsymbol{R}\,, \tag{3.2}$$

where M and c are positive constants. The boundedness of α has a regularizing effect in space, since by (3.1) the mean curvature is uniformly bounded whenever the same holds for θ. On the other hand, this implies a loss of regularity for the front velocity v_s, and in fact evolution can be discontinuous. In particular by (3.1) nucleation can only occur by instantaneous formation of a solid phase in a set of strictly positive volume, like a ball of radius larger than the critical value.

EVOLUTION MODES. – The equation (3.1) accounts for the following modes of phase transition:

(i) *Mean curvature flow of the interface.* This corresponds to $\sigma\kappa + L\theta/2\tau_E = cv_s \in [-M, M]$, is regular in time and occurs at almost any instant.

(ii) *Singular evolution.* For instance, (homogeneous) nucleation occurs in the bulk of an either undercooled or superheated phase. *Formally,* this corresponds to $|v_s| = +\infty$.

Singularities in evolution may appear in several forms: two connected components may merge, or conversely a connected component may split into two com-

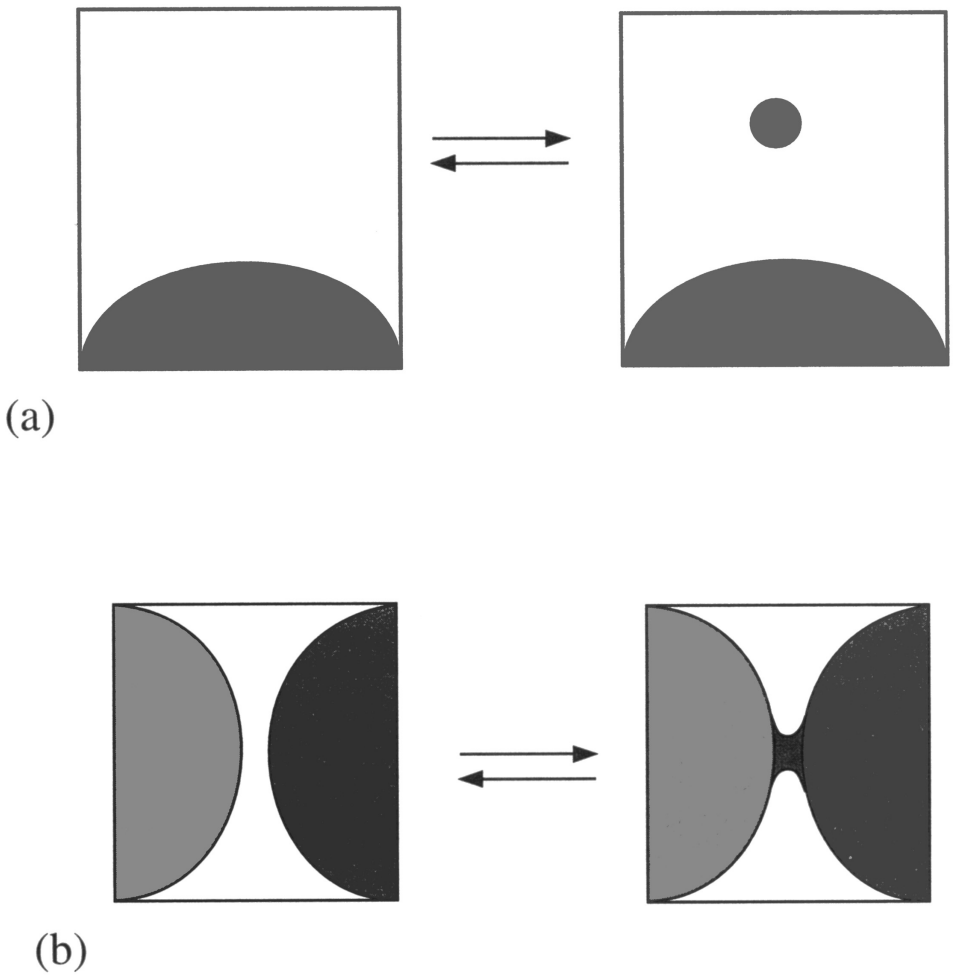

Figure IV.2. – Examples of singular evolution. (*a*) represents nucleation (from left to right) and the opposite phenomenon of annihilation (from right to left). In (*b*) a bridge is either formed (from left to right) or broken (from right to left) between two colliding (or separating) domains. In any of these cases phase transition occurs instantaneously in a set of *positive* (mesoscopic) volume.

ponents; a new phase may appear (nucleation), or conversely a phase may vanish (*annihilation*), and so on.

More generally, we conjecture that (3.1) implies that the phase volume is discontinuous as any change occurs in the phase topology. Notice that here we are dealing with the mesoscopic length scale, because of the size of the surface tension coefficient σ. On the macroscopic scale usually phase nucleation occurs without any volume change.

IV.4. *Nucleation.*

NUCLEATION AND HYSTERESIS. – For a moment let us neglect the dependence on x, and set $\chi_{\pm}(t) := \chi(t \pm 0)$ for any t. The undercooling and superheating prior to nucleation are schematically outlined in Fig. IV.3, where a is a positive parameter (for the sake of simplicity, here we assume that the two thresholds are symmetric). This setting can be represented by the inclusion $\chi_+ \in \operatorname{sign}(\theta + a\chi_-)$ coupled with the constraint $|\chi| = 1$, for any t. Setting $\psi(v) := 0$ if $|v| = 1$ and $\psi(v) := +\infty$ otherwise, this is equivalent to the variational inequality

$$\psi(\chi_+) - \psi(v) \leqslant (\theta + a\chi_-)(\chi_+ - v), \qquad \forall v \in \boldsymbol{R}, \ \forall t\,. \tag{4.1}$$

Now we insert the x-dependence and the surface tension term, define P as in (III.1.1), assume that $\theta(\cdot, t) \in L^\infty(\Omega)$ for any t, and represent nucleation by the variational inequality

$$\sigma P(\chi_+) - \sigma P(v) + \frac{\sigma_L - \sigma_S}{2} \int_\Gamma (\chi_+ - v)\, d\Gamma \leqslant \frac{L}{2\tau_E} \int_\Omega (\theta + a\chi_-)(\chi_+ - v)\, dx\,, \tag{4.2}$$

$$\forall v \in L^\infty(\Omega), \ \text{ in } [0, T];$$

that is, cf. (III.1.2),

$$F_\theta(\chi_+) - F_\theta(v) \leqslant \frac{aL}{2\tau_E} \int_\Omega \chi_-(\chi_+ - v)\, dx\,, \qquad \forall v \in L^\infty(\Omega), \ \text{ in } [0, T]. \tag{4.3}$$

On account of the constitutive relation $u = C_V\theta + L\chi/2$, the values $a = 0$ and $a = L/2C_V$ respectively correspond to isothermal and adiabatic nucleation (namely, occurring either at constant temperature or at constant internal energy).

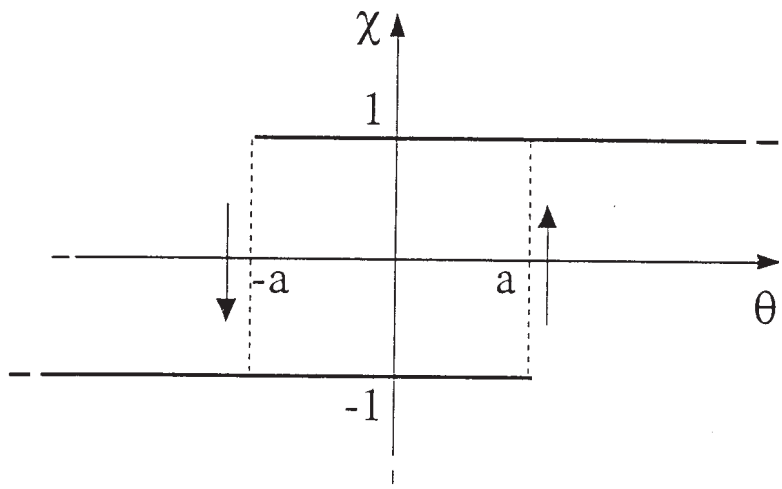

Figure IV.3. – Schematic description of undercooling and superheating prior to nucleation.

ADIABATIC AND NONADIABATIC NUCLEATION. – In the framework developed so far, nucleation is regarded as instantaneous whereas heat diffusion is not; hence nucleation can occur in a set of nonvanishing volume only adiabatically, that is, without exchange of latent heat. This corresponds to a limit undercooling $\theta_c = -L/2C_V$, which is much larger than usually observed; for instance for water at atmospheric pressure this corresponds to $\theta_c = -40$ °C.

We then have two alternatives: (i) either the dynamics of nucleation should be accounted for, by dealing with a very short time scale; (ii) or diffusion of (part of the) latent heat should be regarded as instantaneous. The latter approach is studied in Visintin [231-233] dealing with the Gibbs-Thomson law (II.1.2), and in Visintin [235] including mean curvature flow.

Existence of a solution of the Stefan problem with the Gibbs-Thomson law and adiabatic nucleation has been proved by Luckhaus [153]; see also Chen and Reitich [54], Plotnikov and Starovoitov [182], Radkevitch [187], and others.

IV.5. *Conclusions.*

PHASE TRANSITION MODES. – The above discussion yields the following picture of phase nucleation and growth.

Systems consisting of materials capable of attaining two phases can be in metastable equilibrium; an undercooled liquid is a typical example. At prescribed temperature, those states correspond to relative minimizers of the free energy, which can be represented as a functional of the phase variable χ. The occurrence of such states is due to the nonconvexity of that functional, and the compactness provided by the perimeter term. Without the latter, minimizing sequences would not necessarily preserve the nonconvex constraint «$|\chi| = 1$ a.e. in Ω» in the limit. Indeed passing to the Γ-limit as $\sigma \to 0$ one retrieves the convex macroscopic free energy functional, and relative minimizers disappear.

An accurate analysis of nucleation and growth should involve statistical mechanics and stochastic differential equations. A wide class of processes governed by descent along a nonconvex potential may be expected to exhibit continuous deterministic evolution via a gradient flow. This evolution might be stopped by *steep* potential wells; the exit from these wells might be represented by discontinuous stochastic evolution via a Poisson process. These two modes of evolution should be extreme cases of a more general law (presumably a nonlinear stochastic P.D.E.), which should also express their *competition* in an intermediate range.

V. – Final remarks.

An impressive amount of research has been devoted to the Stefan problem in the last decades. Indeed this model is simple to be stated, combines analytical and geometrical aspects, has a suggestive physical substrate, is relevant for sev-

eral applications, and is the prototype of the large class of evolutive free boundary problems. However it is a simplified model, and is far from accounting for the richness of the physics of phase transitions. Therefore many open questions are left to modelling and analysis, especially concerning microstructures and their evolution. Actually the last years have seen an increasing collaboration among material scientists and mathematicians, and new analytical tools have also been developed.

Here we only point out two possible directions of research. One is the combined use of analytic and stochastic methods in phase transitions. For instance, we have seen the need of such an approach in Sect. IV.3, while dealing with nucleation.

Another topic concerns the study of the regularity of the solution, which, so far has only been investigated in rather simplified formulations, as it is justified by the deepness of these questions. Might that sort of *fine grain* analysis also provide a better understanding of the physical adequacy of more refined models?

BIBLIOGRAPHICAL NOTE. – A large mathematical literature has been devoted to the analysis of the Stefan problem and of its generalizations. In particular information can be found in the monographs Alexiades and Solomon [2], Brokate and Sprekels [33], Gurtin [128], Meirmanov [166], Romano [195], Rubinstein [196], Visintin [233], and in the surveys Primicerio [184, 185], Danilyuk [74], Niezgódka [172], Magenes [159], Fasano [94], Tarzia [213], Rodrigues [192], Oleĭnik, Primicerio and Radkevich [177]. Phase transitions are also considered by other books dealing with free boundary problems: Crank [63], Elliott and Ockendon [89], Friedman [114], Kinderlehrer and Stampacchia [147].

Large collections of references are provided by Wilson, Solomon and Trent [239], Cannon [47], Tarzia [215], and by the proceedings of the conferences on free boundary problems which have regularly been held in the last twenty years: Bossavit, Damlamian and Frémond [27], Chadam and Rasmussen [50-52], Diaz, Herrero, Liñán and Vázquez [75], Fasano and Primicerio [97], Hoffmann and Sprekels [136, 137], Magenes [158], Niezgódka [172], Ockendon and Hodgkins [175], Wilson, Solomon and Boggs [238].

Physical and engineering aspects of phase transitions have also been dealt by a huge literature. Here we just quote some monographs: Abraham [1], Brice [32], Chalmers [53], Christian [56], Doremus [83], Flemings [106], Kurz and Fisher [149], Pamplin [179], Skripov [208], Turnbull [218], Ubbelohde [219], Woodruff [240].

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