Chapter 4

Stefan Problem With Supercooling: Classical Formulation and Analysis

4.1 INTRODUCTION

In Sections 2.2.2 and 2.2.3, supercooling in the melt was taken into account by redefining the equilibrium phase-change temperature with the help of Gibbs–Thomson relation and the kinetic condition. When both these effects are considered together, we shall call the resulting equilibrium temperature relation as *modified Gibbs–Thomson relation*. In this case, the new equilibrium temperature denoted by T_e is given by

$$T_e(x,t) = T_m - (\sigma/[\hat{S}]_E)\bar{K}_c - \alpha\sigma|V_n|/[\hat{S}]_E. \tag{4.1.1}$$

The symbols T_m, σ, $\hat{S}$, $\vec{K}_c$ and V_n have the same meaning as explained in the earlier sections; the parameter α is related to the microscopic relaxation time, $[\hat{S}]_E$ is the difference in the entropies per unit volume of the liquid and the solid at the equilibrium temperature. The last two terms in Eq. (4.1.1) are the correction terms arising due to the curvature and the velocity of the interface, respectively. Eq. (4.2.11) deals with the units associated with σ, $\hat{S}$ and α. Has the solidification of a supercooled liquid been correctly and satisfactorily modelled by the equilibrium temperature in Eq. (4.1.1)? To answer this question we have to go back to the formation of solid from a supercooled liquid in the solidification process. It may be noted that Eq. (4.1.1) was discussed earlier also with the help of some thermodynamical and metallurgical considerations. A rigorous mathematical justification will be provided now.

   The origin of solidification of a supercooled liquid of a pure substance is not in the growth of a sharp interface separating solid and liquid phases but in the finite size effect of the interface lying between stable solid and stable liquid phases as shown in Fig. 4.1.1. In other words, it can be said that the solidification of a supercooled liquid cannot progress without the formation of a mushy region in front of the solidification front. The mushy region contains both solid and liquid phases and solid could be present in it in the form of dendrites of different types. Therefore it is clear that any mathematical modelling of the solidification of a supercooled liquid should take into account solid, liquid and mushy regions, i.e. the finite-size effect of the interface. Does it mean that the classical formulation of the Stefan problem with supercooling

accounted for by the Gibbs–Thomson law is not justified as there is no mushy region in the formulation? The rigorous mathematical justification of the sharp freezing front model (classical formulation) with equilibrium temperature given by Eq. (4.1.1) comes from the fact that the modified Gibbs–Thomson relation can be obtained if appropriate limits of the *phase-field model*, which considers the finite width of the interface, are taken. Some phase-field models are being discussed here with this objective.

What should be the starting point in the modelling of solidification of a supercooled liquid? Research workers have used different approaches giving rise to different models. The differences arose due to the incapability of some models to predict accurately some physical situations or nonacceptability of some models due to the so-called inconsistencies. The existing literature on supercooling is vast. Some selected approaches in the modelling of solidification of a supercooled liquid are being presented here. It is not possible to describe here even these selected models completely. What is presented below is a suitable compromise between length restrictions and understandability of these models.
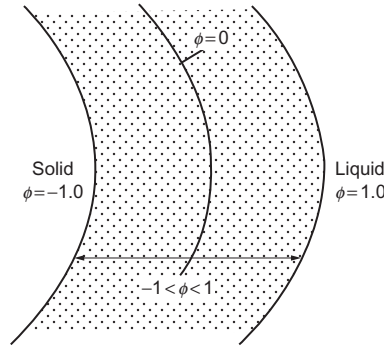

Fig. 4.1.1 Finite size of the interface.

4.2 A PHASE-FIELD MODEL FOR SOLIDIFICATION USING LANDAU–GINZBURG FREE ENERGY FUNCTIONAL

If the interface in the solidification of a supercooled liquid is assumed to be of finite-width, then the modified Gibbs–Thomson relation would imply that there is a sharp interface which is continuously progressing through the finite-width interface. This in turn suggests exploring the enthalpy formulation given below in Eq. (4.2.1) in which a phase function $\phi(x, t)$ has been introduced which is continuously varying through the finite-width interface. Enthalpy $H(T)$ (per unit volume) is defined by

$$
\begin{aligned}
H(T) &= \rho_S C_S T_S + \rho_S \frac{l}{2}\phi, \quad T < 0, \quad \phi = -1 \\
&= [-\rho_S l/2, \rho_L l/2], \quad T = 0, \quad -1 < \phi < 1 \\
&= \rho_L C_L T_L + \rho_L \frac{l}{2}\phi, \quad T > 0, \quad \phi = 1.
\end{aligned} \tag{4.2.1}
$$

Here ϕ is called a *phase function* or an *order parameter* which in the classical formulation has the value -1 in the liquid phase and 1 in the solid phase. Some authors take $\phi = 1$ and $\phi = 0$

in liquid and solid phases, respectively, and take l in the place of $l/2$. The phase function ϕ defines the state of the system. The phase-change temperature has been taken to be zero. $H(T)$ versus T has been plotted in Fig. 4.2.1. Enthalpy is a multivalued function of temperature but the temperature is a continuous function of enthalpy. The equation for energy in terms of enthalpy is given by

$$\frac{\partial H}{\partial t} = \nabla^2(KT), \quad x \in \Omega \subset R^n, \ 0 < t < t_*. \tag{4.2.2}$$

Eq. (4.2.2) is valid only in the distributional sense as at $T = 0$ the derivative of H is not defined (see Section 5.2). K can have different values in different phases. It is clear from Eq. (4.2.1) that a sharp interface cannot be identified by $T = 0$ as done in the classical formulation because at $T = 0$ there exists a region and not a sharp interface. However a sharp interface can be identified by $\phi = 0$ as ϕ is a continuous variable and $\phi = 0$ corresponds to the centre of the mushy region. An equation for $\phi(x, t)$ is needed. If ϕ is considered to be a continuous function of x and t, then it will look as in Fig. 4.2.2. When $\phi = 0$, T is also zero. $T = 0$ does not imply a sharp interface in the enthalpy model but $\phi = 0$ does.

The starting point of a phase-field continuum model to be discussed later for the solid–liquid phase-change process has been taken here as the so-called *Landau–Ginzburg free energy functional F* defined as [80]

$$F\{\phi(x)\} = \int_{\Omega} \left\{ \frac{\xi^2}{2}(\nabla\phi)^2 + \frac{1}{8a}f(\phi(x, t)) - \frac{[\hat{S}]_E}{2}(T - T_m)\phi \right\} d\Omega. \tag{4.2.3}$$

Here ξ is a length scale associated with the 'microscopic interaction strength' (ξ is the length such that two particles at a distance ξ apart will have the probability $1/2$ of being in the same phase or state). a^{-1} is the measure of the depth of the *double-well* and is the indication of the barrier which must be crossed in the transition between the phases, $a^{1/2}\xi$ is the 'correlation length', $[\hat{S}]_E$ is the entropy difference between the phases at the equilibrium temperature per unit volume. All the terms in the integrand of Eq. (4.2.3) are in the units of energy per unit volume. $\Omega \subset R^n$, $n \geq 1$ is a fixed region in space in which the phase-change process is taking place. In the phase transition problems with two distinct phases such as solid and liquid, f is a symmetric double-well function of ϕ with two distinct minima, one for each phase. The last two terms in the integrand in Eq. (4.2.3) can be thought of as the 'local Helmholtz free energy
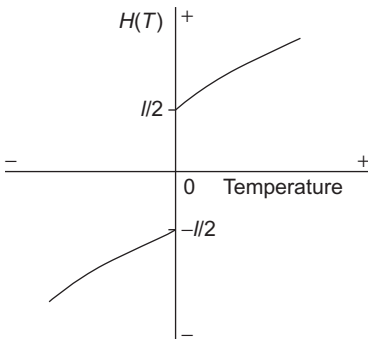

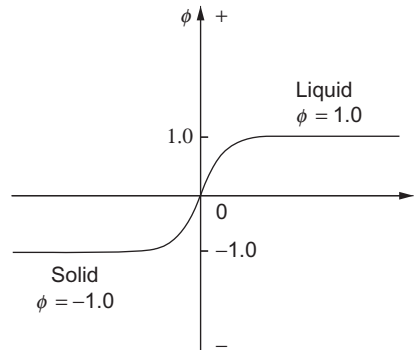**Fig. 4.2.1**   Enthalpy versus temperature.

Fig. 4.2.2   Continuity of the phase function.

density' and $(\nabla\phi)^2$ is the 'basic interaction term' arising due to the interaction of atoms with a mean field created by other atoms [81]. The minimum of $F(\phi)$ is attained at that value of ϕ which satisfies the following *Euler–Lagrange equation* derived under the condition that either ϕ is prescribed or $\nabla\phi \cdot \vec{n} = 0$ on the boundary of Ω:

$$-\frac{\delta F(\phi)}{\delta\phi} = \xi^2 \nabla^2 \phi - \frac{1}{8a} f'(\phi) + \frac{[\hat{S}]_E}{2}(T - T_m) = 0. \tag{4.2.4}$$

Here the dash denotes differentiation with respect to the argument. $\delta F/\delta\phi$ is the 'variational derivative' of ϕ which can be easily calculated (cf. [82]). Eq. (4.2.4) holds for an equilibrium state and ϕ is a function only of x, $x \in \Omega$. Note that F is a function of ϕ and not of $T(x, t)$ and so T in Eq. (4.2.3) is fixed. For a transient or a nonequilibrium process, the free energy will not be minimum but will satisfy the following relation:

$$\hat{\delta}\frac{\partial\phi}{\partial t}(x, t) = -\frac{\delta F}{\delta\phi}\{\phi(x, t)\}, \tag{4.2.5}$$

where $\hat{\delta} > 0$ is the relaxation time [83]. Eq. (4.2.5) is valid for the case when ϕ is not conserved, i.e. the volume integral of $\phi(x, t)$ over Ω is not prescribed. The basis of Eq. (4.2.5) is the standard idea of 'nonequilibrium thermodynamics' which assumes that ϕ returns to equilibrium with a 'force' proportional to the extent to which it was out of equilibrium.

If ϕ is conserved, then

$$\frac{\partial\phi}{\partial t}(x, t) = \text{div}\left[M\text{grad}\left\{\frac{\delta F}{\delta\phi}(\phi(x, t))\right\}\right], \tag{4.2.6}$$

where M is a coefficient related to diffusion or an interdiffusion coefficient which may depend on $\phi(x, t)$ and on the temperature [83, 84]. The second law of thermodynamics requires that along the solution paths, the free energy should necessarily decrease with time, failing which the model will be 'thermodynamically inconsistent'. If F in Eq. (4.2.3) is a function of ϕ alone, then the second law of thermodynamics is satisfied but not when F is a function of the temperature and ϕ. The time derivative of $F\{\phi(x, t)\}$ gives

$$\frac{d}{dt}F\{\phi(x, t)\} = \int_\Omega \frac{\delta F}{\delta\phi}\{\phi(x, t)\}\frac{\partial\phi}{\partial t}d\Omega = -\frac{1}{\hat{\delta}}\int_\Omega\left(\frac{\delta F}{\delta\phi}\right)^2 d\Omega \le 0. \tag{4.2.7}$$

In order to derive Eq. (4.2.7) take F as in Eq. (4.2.3) and proceed with the first principles to obtain the time derivative of F. In calculating dF/dt, at some stage of calculations Green's formula is to be applied to the volume integral of $\nabla\phi \cdot \nabla\partial\phi/\partial t$ and if it is assumed that on the boundary of Ω the normal derivative of ϕ is zero then we get Eq. (4.2.7). The second law of thermodynamics is satisfied even if ϕ is conserved, provided $M\text{grad}\,\delta F/\delta\phi$ is zero on the boundary of Ω.

Sometimes, since the order parameter ϕ alone is not sufficient to describe the local state of the system, additional fields are introduced. One such extra field is temperature. If the heat conduction is very 'fast' then it can be assumed that the material is at a uniform temperature but this assumption is not valid if heat conduction is 'slow'. A second equation for heat transport in the material should be considered along with Eq. (4.2.4) or (4.2.6). An example of this type of modelling is the phase-field model which consists of the following system of equations:

$$\alpha\varepsilon^2\frac{\partial\phi}{\partial t} = \varepsilon^2\nabla^2\phi + \frac{1}{2}(\phi - \phi^3) + \frac{\varepsilon[\hat{S}]_E}{3\sigma}(T - T_m), \tag{4.2.8}$$

$$\frac{\partial T}{\partial t} + \frac{l}{2}\frac{\partial\phi}{\partial t} = k\nabla^2 T. \tag{4.2.9}$$

In Eqs (4.2.8), (4.2.9), ϕ and T are coupled but in deriving Eq. (4.2.8) no coupling between ϕ and T was considered. The double-well symmetric function f with distinct minima at $\phi = \pm 1$ is taken as $f = (\phi^2 - 1)^2$. The parameter ε and α are defined as

$$\varepsilon = \xi a^{1/2}, \quad \alpha = \hat{\delta}/\xi^2. \tag{4.2.10}$$

ε is a measure of the interface thickness and is of the order of 10^{-8} cm, σ is the surface tension, $\hat{S}$ is the entropy per unit volume, k is the thermal diffusivity. The units of σ, $\hat{S}$, α are as follows:

$$\sigma := \text{unit of energy/(length)}^{(n-1)}, \quad \hat{S} := \text{unit of energy/}\{(\text{length})^n \cdot \text{degree}\}$$
$$\alpha := \text{unit of time/(length)}^2, \quad n = \text{spacial dimension of } \Omega. \tag{4.2.11}$$

At a deeper level of physics there are significant differences between the Stefan problem and the phase-field model in that the phase-field model incorporates the microscopic physics in an average sense and also takes into account macroscopic parameters. Stefan problem deals only with macroscopic modelling.

Both Eqs (4.2.8), (4.2.9) hold good throughout Ω and the sharp interface separating solid and liquid phases has been replaced by a finite-width interface. Therefore there are no boundary conditions at the interface. The region corresponding to $T = 0$ is now given by $-1 < \phi < 1$, and $\phi = 0$ is the centre of the interface. Initial and boundary conditions for both ϕ and T are to be prescribed. For example, on the boundary $\partial\Omega$ of Ω, we may have

$$\left.\frac{\partial\phi}{\partial n}\right|_{\partial\Omega} = 0; \quad \left.\frac{\partial T}{\partial n}\right|_{\partial\Omega} = 0, \tag{4.2.12}$$

or

$$\phi|_{\partial\Omega} = \phi(x), \quad x \in \partial\Omega; \quad \left.\frac{\partial T}{\partial n}\right|_{\partial\Omega} = 0, \tag{4.2.13}$$

or any combination of these boundary conditions.

Note that for both $T < 0$ and $T > 0$, Eq. (4.2.9) is well defined and the region $T = 0$ is not defined by the enthalpy but is identified by the phase function ϕ, $-1 < \phi < 1$. The phase-field equations were first formulated in [85] on the basis of the model discussed in [80]. The last term in the integral in Eq. (4.2.3) can be taken in the form of a more general expression such as $-2u\gamma G(\phi)$ (cf. [86]), where u is the dimensionless temperature and

$$u = (T - T_m)/(l/C_P). \tag{4.2.14}$$

Here γ is a microscopic parameter related to a macroscopic parameter and has the dimension of energy per unit volume, $G(\phi)$ is an increasing function related to the entropy distribution across the interface and

$$[\hat{S}]_E = 2\gamma \int_{-1}^{1} G'(\phi)d\phi. \tag{4.2.15}$$

If $G(\phi) = \phi$ and the units of energy and temperature are suitably chosen, then

$$[\hat{S}]_E = 4 \text{ units of energy per unit volume/degree} \tag{4.2.16}$$

and

$$-2u\gamma G(\phi) = -2u\phi. \tag{4.2.17}$$

In Fig. 4.2.3 the last term on the r.h.s. in the equation to determine ϕ has been taken as $2u$. By defining ε and α through Eq. (4.2.10) and σ in units of free energy, the last term on the r.h.s. in Eq. (4.2.8) can be obtained.

The capillary length d_0 is defined as (cf. [87])

$$d_0 = \sigma/\{[\hat{S}]_E l/C_P\} \tag{4.2.18}$$

and it is easy to check that with the help of Eq. (4.2.18), Eq. (4.2.8) becomes

$$\alpha\varepsilon^2\frac{\partial\phi}{\partial t} = \varepsilon^2\nabla^2\phi + \frac{1}{2}(\phi - \phi^3) + \frac{\varepsilon}{3d_0}u. \tag{4.2.19}$$

Eq. (4.2.19) has two length scales, viz., ε and d_0. Note that there is only one length scale in the modified Gibbs–Thomson relation (4.1.1). Using Eq. (4.2.18), Eq. (4.1.1) can be written in terms of u as

$$u = -d_0\bar{K}_c - \alpha d_0|V_n|. \tag{4.2.20}$$

In Eq. (4.2.9), specific heats, thermal conductivity and densities have been taken to be equal in both solid and liquid phases. This is generally done for convenience as the mathematics does not change significantly even if different thermophysical properties are taken in different phases. There are several advantages of phase-field models. A variety of phenomena ranging from motion by mean curvature to stable anisotropic crystal growth and single-needle dendrites are obtained by simply varying the parameters. Phase-field equations are amenable to numerical computations [88]. Computations involving self-interactions of the interface do not pose difficulties in the phase-field model. The phase-field equations are guaranteed to have a smooth solution (ϕ, T) if the initial and boundary data are sufficiently smooth (cf. [81, 89]).

Rigorous mathematical analysis for obtaining Gibbs–Thomson relation by taking appropriate limits of some parameters was first presented in [81]. The 'inner' and 'outer' expansions of the order parameter $\phi(x, t)$ were obtained as $\xi \to 0$ and by matching these expansions, it was proved that under suitable assumptions

$$u(x) = -\sigma_0\bar{K}_c/4 + O(\xi), \quad x \in \partial\Omega_0, \tag{4.2.21}$$

where $\partial\Omega_0$ is the centre of the finite-width interface or where $\phi = 0$; $\bar{K}_c$ is the sum of the principal curvatures of the interface $\phi = 0$ and σ_0 is defined by the equation

$$\sigma_0 = \frac{2}{3}\xi. \tag{4.2.22}$$

It was shown that

$$\sigma = \sigma_0 + O(\xi^2). \tag{4.2.23}$$

Based on the mathematical procedure presented in [81], and by taking appropriate limits, modified Gibbs–Thomson relation was derived in [90] and the Gibbs–Thomson relation in [81].

In Figs 4.2.3 and 4.2.4 (cf. [90, 91]), the appropriate limits of the parameters to be taken, and the corresponding Stefan and Stefan-like problems obtained have been shown. Although the limiting cases obtained in Fig. 4.2.3 are covered in Fig. 4.2.4, the limits are more explicitly defined in Fig. 4.2.3.

The role of microscopic anisotropy in the macroscopic behaviour of the phase boundary was analysed in [92] using Landau–Ginzburg [80] free energy functional. The continuum limit for a lattice spin system with 'anisotropic interactions' J_i and spacing a_i leads to the following equation for the phase function ϕ:

$$\hat{\delta}\frac{\partial \phi}{\partial t} = \sum_{i=1}^{d} \xi_i^2 \frac{\partial^2 \phi}{\partial x_i^2} + \frac{1}{2}(\phi - \phi^3) + 2u, \tag{4.2.24}$$

where d is the spacial dimension of the space, $\hat{\delta}$ is the relaxation time and u is defined by Eq. (4.2.14). The temperature and ϕ are coupled through an equation of the type (4.2.9) and ξ_i is related to J_i and a_i. A modified Gibbs–Thomson law in polar coordinates (r, θ) was derived for the equilibrium temperature which has the form

$$[\hat{S}]_E u(r, \theta) = -[\sigma(\theta) + \sigma''(\theta)]\bar{K}_c - \hat{\delta}|V_n|\sigma(\theta)/\xi_A^2(\theta) + O(\xi^2). \tag{4.2.25}$$

Here $\xi_A(\theta)$ is a measure of the thickness of the interface and $\sigma(\theta)$ is the angle-dependent surface tension. In [93] the basic phase-field model was extended to physical problems in which fluid properties such as velocity, pressure and density variations were incorporated along with heat properties and a unified and consistent derivation of equations was obtained.

Since many phase-field models for solidification have been proposed in the literature, the phase-field model consisting of Eqs (4.2.8), (4.2.9) will be called *standard phase-field model* or SPF model.

4.3   SOME THERMODYNAMICALLY CONSISTENT PHASE-FIELD AND PHASE RELAXATION MODELS OF SOLIDIFICATION

It was assumed in Eq. (4.2.3) that the energy functional F is a function of ϕ alone, and that T is a constant. If a more general energy functional of the form

$$F\{(T(x,t), \phi(x,t)\} = \int_{\Omega} \left\{ f(T, \phi) + \frac{1}{2}B|\nabla\phi(x)|^2 \right\} d\Omega, \tag{4.3.1}$$
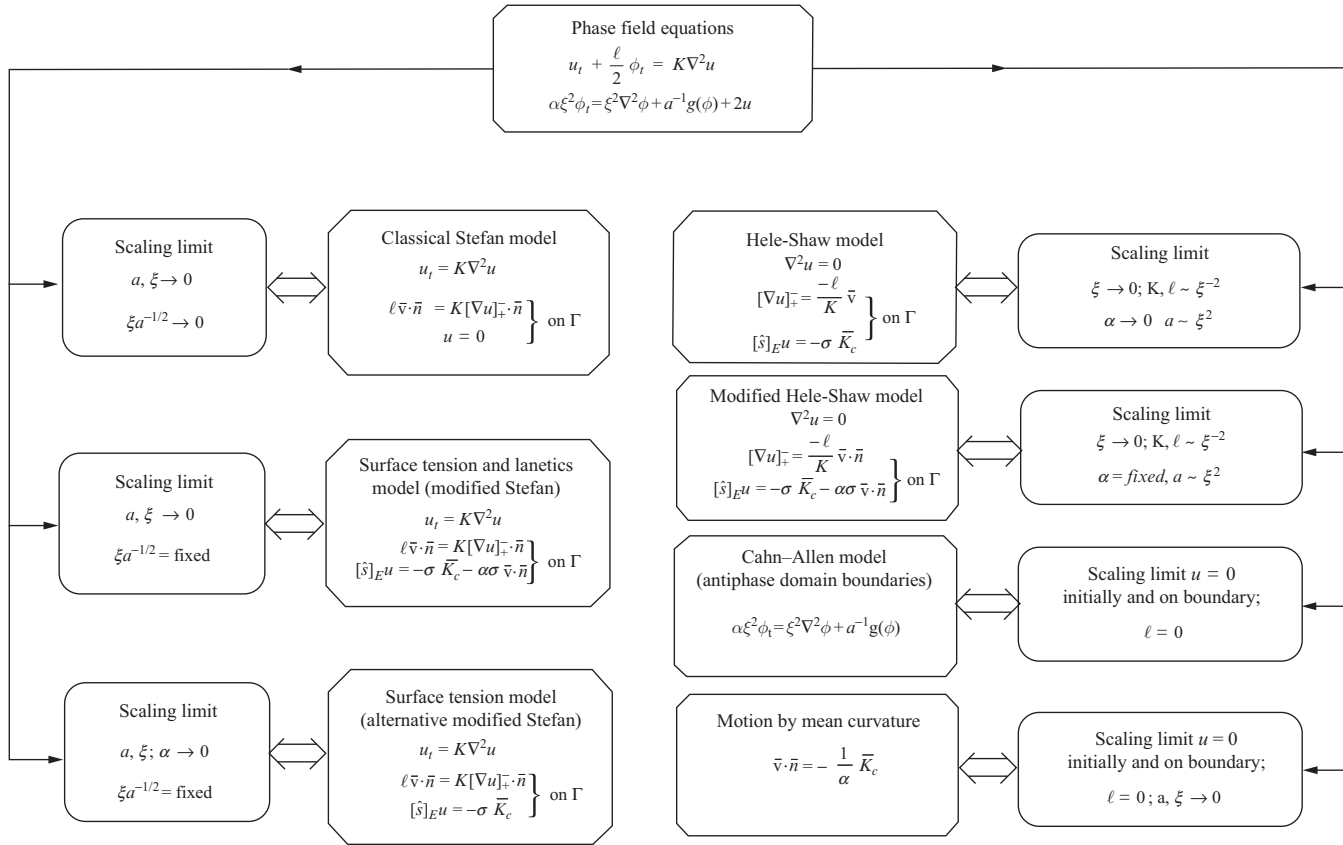
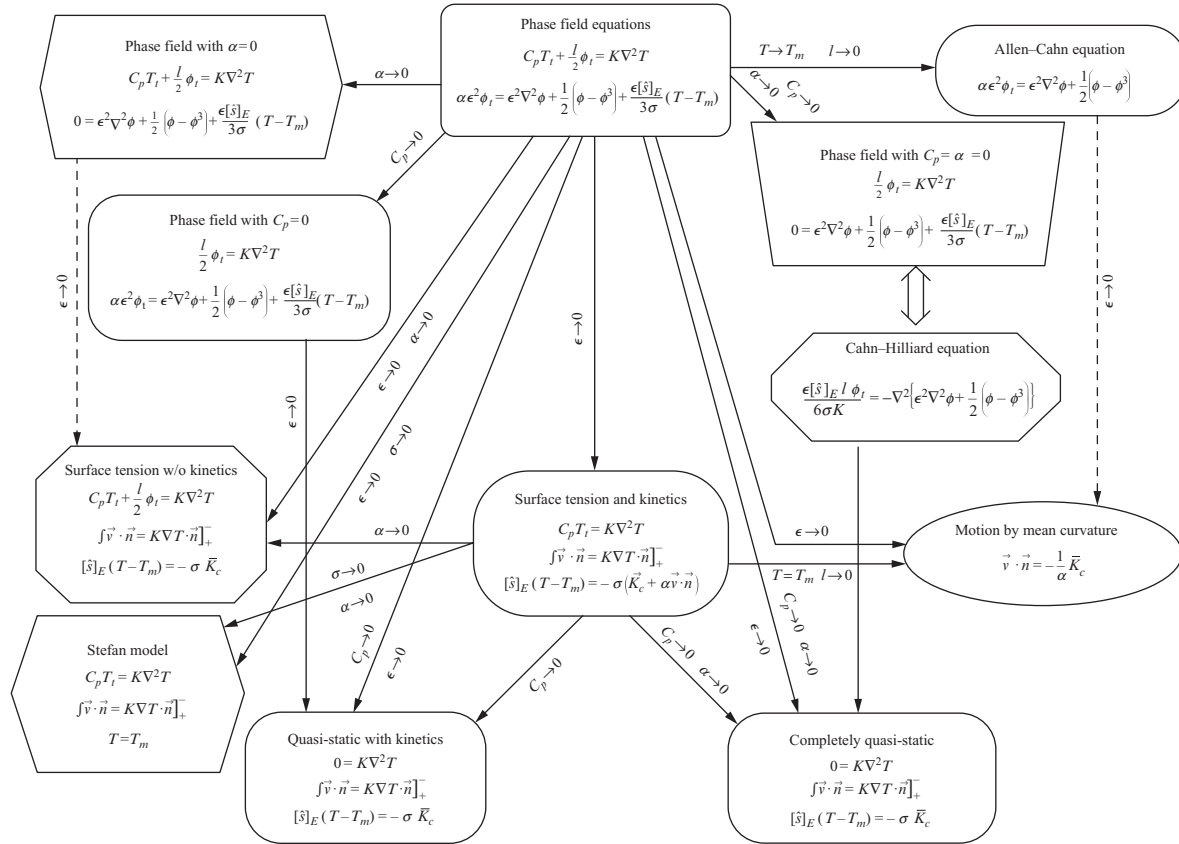**Fig. 4.2.3** Limits of phase-field equations I.

Phase field equations
$$C_p T_t + \frac{l}{2}\phi_t = K\nabla^2 T$$
$$\alpha\epsilon^2\phi_t = \epsilon^2\nabla^2\phi + \frac{1}{2}\left(\phi-\phi^3\right) + \frac{\epsilon[\hat{s}]_E}{3\sigma}(T-T_m)$$

Phase field with $\alpha=0$
$$C_p T_t + \frac{l}{2}\phi_t = K\nabla^2 T$$
$$0 = \epsilon^2\nabla^2\phi + \frac{1}{2}\left(\phi-\phi^3\right) + \frac{\epsilon[\hat{s}]_E}{3\sigma}(T-T_m)$$

Allen–Cahn equation
$$\alpha\epsilon^2\phi_t = \epsilon^2\nabla^2\phi + \frac{1}{2}\left(\phi-\phi^3\right)$$

Phase field with $C_p=\alpha=0$
$$\frac{l}{2}\phi_t = K\nabla^2 T$$
$$0 = \epsilon^2\nabla^2\phi + \frac{1}{2}\left(\phi-\phi^3\right) + \frac{\epsilon[\hat{s}]_E}{3\sigma}(T-T_m)$$

Phase field with $C_p=0$
$$\frac{l}{2}\phi_t = K\nabla^2 T$$
$$\alpha\epsilon^2\phi_t = \epsilon^2\nabla^2\phi + \frac{1}{2}\left(\phi-\phi^3\right) + \frac{\epsilon[\hat{s}]_E}{3\sigma}(T-T_m)$$

Cahn–Hilliard equation
$$\frac{\epsilon[\hat{s}]_E\, l}{6\sigma K}\phi_t = -\nabla^2\left\{\epsilon^2\nabla^2\phi + \frac{1}{2}\left(\phi-\phi^3\right)\right\}$$

Surface tension w/o kinetics
$$C_p T_t + \frac{l}{2}\phi_t = K\nabla^2 T$$
$$\int \vec{v}\cdot\vec{n} = K\nabla T\cdot\vec{n}]_+^-$$
$$[\hat{s}]_E(T-T_m) = -\sigma\,\bar{K}_c$$

Surface tension and kinetics
$$C_p T_t = K\nabla^2 T$$
$$\int \vec{v}\cdot\vec{n} = K\nabla T\cdot\vec{n}]_+^-$$
$$[\hat{s}]_E(T-T_m) = -\sigma\left(\vec{K}_c + \alpha\vec{v}\cdot\vec{n}\right)$$

Motion by mean curvature
$$\vec{v}\cdot\vec{n} = -\frac{1}{\alpha}\bar{K}_c$$

Stefan model
$$C_p T_t = K\nabla^2 T$$
$$\int\vec{v}\cdot\vec{n} = K\nabla T\cdot\vec{n}]_+^-$$
$$T = T_m$$

Quasi-static with kinetics
$$0 = K\nabla^2 T$$
$$\int\vec{v}\cdot\vec{n} = K\nabla T\cdot\vec{n}]_+^-$$
$$[\hat{s}]_E(T-T_m) = -\sigma\,\bar{K}_c$$

Completely quasi-static
$$0 = K\nabla^2 T$$
$$\int\vec{v}\cdot\vec{n} = K\nabla T\cdot\vec{n}]_+^-$$
$$[\hat{s}]_E(T-T_m) = -\sigma\,\bar{K}_c$$

Arrow labels: $\alpha\to0$, $T\to T_m$, $l\to0$, $\alpha\to0$, $C_p\to0$, $C_p\to0$, $\epsilon\to0$, $l\to0$, $\alpha\to0$, $\sigma\to0$, $C_p\to0$, $\epsilon\to0$, $\sigma\to0$, $\alpha\to0$, $\epsilon\to0$, $T=T_m$ $l\to0$, $C_p\to0$, $\alpha\to0$, $\epsilon\to0$, $\alpha\to0$

Fig. 4.2.4 Limits of phase-field equations II.

is taken, in which B is either a positive constant or a function of T but not of ϕ, then F will not always decrease on the solution paths and the thermodynamical consistency condition (4.2.7) will not be satisfied. However either the SPF model can be obtained as a particular case of some thermodynamically consistent models or the modified Gibbs–Thomson relation can be derived independently of the SPF model. Several thermodynamically consistent models have been proposed in the literature (cf. [94–98]). Our interest here is only in briefly indicating the derivation of some thermodynamically consistent models from which the modified Gibbs–Thomson relation can be obtained by a rigorous limiting process.

Entropy Functional

The model proposed in [97] and described below is based on an entropy functional and is on the same lines as the model proposed earlier in [94]. The starting point of the formulation in [97] is to define an entropy functional $\hat{F}\{\phi(x,t), e(x,t)\}$ for a subregion Ω_g of a closed and bounded domain $\Omega \subset R^3$ in which the phase-change is taking place

$$\hat{F} = \int_{\Omega_g} \left\{ \hat{S} - \frac{1}{2}\varepsilon^2(\nabla\phi)^2 \right\} d\Omega_g. \tag{4.3.2}$$

Here $\hat{S}(e, \phi)$ is the entropy per unit volume, ϕ is the phase function as defined in Section 4.2, $e(x, t)$ is the internal energy density and ε is a constant. $e(x, t)$ satisfies the equation

$$\dot{e} + \nabla\vec{q} = 0, \quad \text{in } \Omega_g, \tag{4.3.3}$$

where $\vec{q}$ is the heat flux vector. The time derivative of $\hat{F}$ can be calculated as follows:

$$\frac{d}{dt}(\hat{F}) = \int_{\Omega_g} \left\{ \left(\frac{\partial\hat{S}}{\partial e}\right)_\phi \dot{e} + \left[\left(\frac{\partial\hat{S}}{\partial\phi}\right)_e + \varepsilon^2\nabla^2\phi \right]\dot{\phi} - \varepsilon^2\nabla \cdot (\dot{\phi}\nabla\phi) \right\} d\Omega_g \tag{4.3.4}$$

$$= \int_{\Omega_g} \left\{ \vec{q} \cdot \nabla\left(\frac{\partial\hat{S}}{\partial e}\right)_\phi + \left[\left(\frac{\partial\hat{S}}{\partial\phi}\right)_e + \varepsilon^2\nabla^2\phi \right]\dot{\phi} \right\} d\Omega_g$$

$$- \int_{A_g} \left\{ \left(\frac{\partial\hat{S}}{\partial e}\right)_\phi \vec{q} + \varepsilon^2\dot{\phi}\nabla\phi \right\} \cdot \vec{n}dA_g. \tag{4.3.5}$$

Here A_g is the surface area of Ω_g, dA_g is the elementary surface area and $\vec{n}$ is the outward unit normal to A_g. The derivation of Eq. (4.3.5) from Eq. (4.3.4) requires a simple application of Gauss's theorem. The thermodynamical consistency of this entropy model requires that the local entropy production be nonnegative. If the entropy flux through the surface of Ω_g is subtracted from $d\hat{F}/dt$, then the entropy produced can be obtained. The consistency condition requires that

$$\frac{d\hat{F}}{dt} + \int_{A_g} \left(\frac{\vec{q}}{T} \cdot \vec{n} + \varepsilon^2\dot{\phi}\nabla\phi \cdot \vec{n} \right) dA_g \geq 0, \tag{4.3.6}$$

as the rate at which entropy is produced cannot be negative. $\vec{q}/T$ in the first term in the surface integral in Eq. (4.3.6) is the entropy flux due to heat flow (see Eq. 2.1.2). T is the absolute

temperature. The quantity $\varepsilon^2 \dot{\phi} \nabla \phi$ is the entropy flux related to the changes in the phase function at the boundary of the subregion Ω_g. Both solid and liquid phases have been taken at rest. If $d\hat{F}/dt$ from Eq. (4.3.5) is substituted in Eq. (4.3.6) and the relation

$$\left(\frac{\partial \hat{S}}{\partial e}\right)_\phi = \frac{1}{T} \tag{4.3.7}$$

is used, then we get the following consistency condition:

$$\int_{\Omega_g} \left\{ \vec{q} \cdot \nabla \left(\frac{1}{T}\right) + \left[\left(\frac{\partial \hat{S}}{\partial \phi}\right)_e + \varepsilon^2 \nabla^2 \phi\right] \dot{\phi} \right\} d\Omega_g \geq 0. \tag{4.3.8}$$

The derivation of Eq. (4.3.7) deserves some discussion. In Eq. (2.1.15), the phase function ϕ has not been considered. Therefore, as suggested in [94], it will be assumed that even when the free energy density G and the entropy density $\hat{S}$ depend on the order parameter ϕ and the temperature T, they are concave in T and e, respectively (though not necessarily in ϕ) and they still obey 'Legendre transform relation' and its inversion [99]

$$G(T, \phi) = \inf_e [e(\hat{S}, \phi) - T\hat{S}(e, \phi)] \tag{4.3.9}$$

and

$$\hat{S}(e, \phi) = \inf_T \left(\frac{e(\hat{S}, \phi)}{T} - \frac{G(T, \phi)}{T}\right). \tag{4.3.10}$$

The differentiations of Eq. (4.3.10) with respect to e and ϕ give the following results:

$$\frac{\partial \hat{S}}{\partial e}(e, \phi)\bigg|_\phi = \frac{1}{T(e, \phi)} \tag{4.3.11}$$

and

$$\frac{\partial \hat{S}}{\partial \phi}(e, \phi)\bigg|_e = -\frac{1}{T(e, \phi)} \frac{\partial G}{\partial \phi}(T(e, \phi), \phi)\bigg|_T, \tag{4.3.12}$$

where $T(e, \phi)$ is the value of T at which the infimum in Eq. (4.3.10) occurs. For those values of T where no phase-change occurs, G is differentiable, and

$$\frac{\partial \{G(T, \phi)/T\}}{\partial T} = -e/T^2. \tag{4.3.13}$$

The consistency condition (4.3.8) gets satisfied if $\vec{q}$ and $\dot{\phi}$ are chosen such that

$$\vec{q} = M_T \nabla \left(\frac{1}{T}\right) \tag{4.3.14}$$

and

$$\hat{\delta}\dot{\phi} = \left(\frac{\partial \hat{S}}{\partial \phi}\right)_e + \varepsilon^2 \nabla^2 \phi. \tag{4.3.15}$$

Here $\hat{\delta}$ is the relaxation time and is a positive constant, and M_T could be a positive constant or a function of temperature but not of ϕ. In both [94, 97], the starting point for the derivation of phase-field equations is the same entropy functional (4.3.2) but the consistency condition $d\hat{F}/dt \geq 0$ is satisfied in different ways. We describe very briefly the procedure adopted in [94]. The transient equations for $\phi(x,t)$ and $e(x,t)$ have been obtained from Eq. (4.3.2) using the same arguments which lead to Eqs (4.2.5), (4.2.6). While $e(x,t)$ is conserved, ϕ may or not be conserved. The quantities $\delta\hat{F}/\delta\phi$ and $\delta\hat{F}/\delta e$, which are required in deriving transient equations for ϕ and e can be easily calculated, see [94]. Having obtained the transient equations, the consistency condition can be established as in Eq. (4.2.7). Note that the time derivative of the entropy functional contains both $\delta\hat{F}/\delta\phi$ and $\delta\hat{F}/\delta e$ and it should be nondecreasing.

The quantity $(\partial\hat{S}/\partial\phi)_e$ in Eq. (4.3.15) is not convenient to handle. So it should be expressed in terms of $(\partial G/\partial\phi)_T$ as in Eq. (4.3.12). Integration of Eq. (4.3.13) gives

$$G(T, \phi) = T\left(-\int_{T_m}^{T} \frac{e(\xi, \phi)}{\xi^2} d\xi + f(\phi)\right), \tag{4.3.16}$$

where $f(\phi)$ is an unknown function. A suitable definition of $e(T, \phi)$ agreeing with the classical definition of enthalpy can be developed if we take

$$\left.\begin{aligned} e(T, \phi) &= e_S(T) + p(\phi)\hat{L}(T), \\ &= e_L(T) + [p(\phi) - 1]\hat{L}(T), \end{aligned}\right\} \tag{4.3.17}$$

where $p(\phi)$ is an arbitrary function except that $p(0) = 0$ and $p(1) = 1$. In the present model, we take $\phi = 0$ is the solid phase and $\phi = 1$ is the liquid phase. $\hat{L}(T) = e_L(T) - e_S(T)$. When $T = T_m$, $\hat{L}(T_m) = \tilde{l}_m$, where $\tilde{l}_m$ is the latent heat of fusion per unit volume. Any of the expressions for e given in Eq. (4.3.17) can be used in Eq. (4.3.16). If the second definition in Eq. (4.3.17) is used in Eq. (4.3.16), then we obtain

$$G(T, \phi) = T\left(-\int_{T_m}^{T} \frac{e_L(\xi)}{\xi^2} d\xi - [p(\phi) - 1]Q(T) + f(\phi)\right), \tag{4.3.18}$$

where

$$Q(T) = \int_{T_m}^{T} \frac{\hat{L}(\xi)}{\xi^2} d\xi. \tag{4.3.19}$$

By differentiating Eq. (4.3.18) w.r.t. ϕ, we obtain,

$$\left(\frac{\partial G}{\partial \phi}\right)_T = -TQ(T)p'(\phi) + Tf'(\phi). \tag{4.3.20}$$

Note that e_L and e_S are functions of T and not of ϕ. It is now a simple matter to derive the phase-field model. Substituting e and $\vec{q}$ from Eqs (4.3.17), (4.3.14) in the energy equation (4.3.3), we obtain

$$\dot{e}_L(T) + \dot{p}(\phi)\hat{L}(T) + [p(\phi) - 1]\frac{d\hat{L}}{dt}(T) = -\nabla \cdot \left[M_T\nabla\left(\frac{1}{T}\right)\right]. \tag{4.3.21}$$

If $M_T = KT^2$ and $\phi = 0, 1$ in Eq. (4.3.21), then we get heat conduction equations in solid and liquid phases, respectively. In order to obtain kinetic equation for ϕ, we substitute $\partial\hat{S}/\partial\phi$ from Eq. (4.3.12) in Eq. (4.3.15) and use Eq. (4.3.20). We obtain

$$\hat{\delta}\dot{\phi} = Q(T)p'(\phi) - f'(\phi) + \varepsilon\nabla^2\phi. \tag{4.3.22}$$

Here $f(\phi)$ is a double-well symmetric function with two distinct minima at $\phi = 0$ and $\phi = 1$, and is taken as

$$f(\phi) = \phi^2(1 - \phi)^2. \tag{4.3.23}$$

It is not possible to determine $p(\phi)$ uniquely. Eqs (4.3.21), (4.3.22) can be presented in some more suitable dimensionalized forms (see [97]).

The SPF model was obtained as a particular case of the phase-field model constructed in [95] subject to the conditions that the energy density vary linearly with the order parameter and the entropy be a nonconcave function of the order parameter. Since SPF model can be obtained as a particular case of a thermodynamically consistent model, it can also be regarded as a consistent model. In [97], two phase-field models have been presented. One of them partially resembles the model in [85] and the other the model in [98]. Although SPF model cannot be obtained as a particular case of any of the models constructed in [97], it has been reported that by taking appropriate limits of the dimensionless equations derived in [97] and following the procedure discussed in [81], modified Gibbs–Thomson law can be derived.

Some Thermodynamically Consistent Phase Relaxation Models for Supercooling

The Stefan condition (1.4.11) imposed in the classical Stefan problem formulation does not arise in the phase-field models discussed earlier. Like an enthalpy formulation, phase-field model is also a continuum formulation, and ϕ is defined as

$$\left.\begin{aligned}\phi &= -1, & T &< 0, \\ &= (-1, 1), & T &= 0, \\ &= 1, & T &> 0.\end{aligned}\right\} \tag{4.3.24}$$

The equations of the type (4.3.24) are valid throughout Ω, which is the region under consideration. As mentioned earlier, in an enthalpy formulation, $T = 0$ does not give the middle of the mushy region but in the phase-field model, $\phi = 0$, gives the middle of the finite-size interface. In Eq. (4.3.24), the sharp interface separating solid and liquid regions is given by $\phi = 0$ and not by $T = 0$. It is well known that in the case of supercooling or superheating, a mushy region develops, and the free boundary progresses through the mushy region. Therefore to obtain an equiaxed or columnar growth of the interface or the amount of supercooling or superheating, the phase function ϕ, should be in some ways associated with the structure of the mushy region. It should be pointed out here that $T = T_m$ (or $T = 0$) is not the actual temperature of the mushy region. It is an average value of the temperature. The actual situation is shown in Fig. 4.3.1.

Several mathematical models based on relaxation dynamics have been constructed in the literature in terms of ϕ and T, with which modified Gibbs–Thomson relation, mushy region, dendritic growth, etc. (cf. [100–103]) can be described. Most of these models are based on the weak formulation which is not the emphasis in this volume. We give below a classical formulation concerned with a family of thermodynamically consistent models of phase transitions. Phase diffusion is neglected in this formulation by assuming that no interfacial energy occurs [100]. This means that the term $\xi^2(\nabla\phi)^2/2$ occurring in Eq. (4.2.3) is taken to be zero. Therefore, only a rate-type constitutive law governing the evolution of ϕ accounts for the *phase relaxation*.
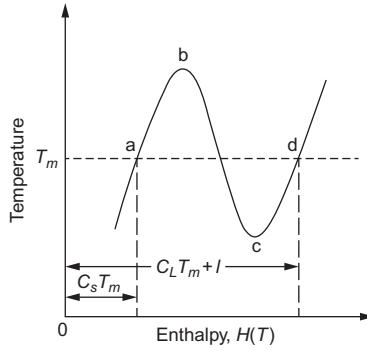
Fig. 4.3.1   ab, metastable state for the solid; cd, metastable state for the liquid.

The internal energy density $e(T,\phi)$ can be taken as

$$e(T,\phi) = f_0(T) + f_1(\phi), \tag{4.3.25}$$

where Eq. (4.3.25) is the generalization of the energy equation considered in the earlier phase transition models. If $C_S = C_L$, then the specific enthalpy (or internal energy) is given by

$$e = C_V T + l\phi, \quad 0 \le \phi \le 1. \tag{4.3.26}$$

As $C_V = (\partial e/\partial T)_V > 0$, we should have $f_0'(T) > 0$ in Eq. (4.3.25). The dash denotes differentiation with respect to the argument. If $\phi = 0$ represents the solid phase and $\phi = 1$ represents the liquid phase, which is a more energetic phase then we should have $f_1'(\phi) \ge 0$. For the sake of convenience, let

$$e(T,\phi) = T^2 F_0'(T) + T_m^c F_1(\phi), \tag{4.3.27}$$

where the functions F_0 and F_1 are assumed to be continuous with $F_1'(\phi) \ge 0$ and T_m^c is the phase-change temperature which could be T_m or be different from T_m. The energy balance equation has the standard form

$$\dot{e}(T,\phi) + \operatorname{div}\vec{q} = \dot{r}; \quad \vec{q} = -\hat{K}(T)\nabla T, \tag{4.3.28}$$

where the dot denotes time derivative, r is the heat source density function and e is given by Eq. (4.3.27). To derive a constitutive equation for ϕ it will be assumed that ϕ is not an explicit

function of the space variables which means that $\nabla\phi = 0$ or that no interfacial diffusion occurs which was present in Eq. (4.2.4). Therefore the constitutive relation for ϕ can be assumed to be of the form

$$\dot{\phi} = \beta(T, \phi), \tag{4.3.29}$$

where β is an unknown continuous function. The functions F_0, F_1 and β are unknown but not completely arbitrary. For example, if the system of Eqs (4.3.28), (4.3.29) is thermodynamically consistent, then the *Clausius–Duhem inequality* should be satisfied, which implies that

$$\dot{G} + \hat{S}\dot{T} + \frac{\vec{q} \cdot \nabla T}{T^2} \le 0. \tag{4.3.30}$$

Here G is the free energy density which is related to entropy $\hat{S}$, e and T by the following relation:

$$G(T, \phi) = \inf_{T}\{e(\hat{S}, \phi) - T\hat{S}(e, \phi)\}. \tag{4.3.31}$$

The time derivative of G gives

$$\dot{G} = \frac{\partial G}{\partial T}\dot{T} + \frac{\partial G}{\partial \phi}\dot{\phi}. \tag{4.3.32}$$

Using Eq. (4.3.32) in Eq. (4.3.30), we obtain

$$\left(\frac{\partial G}{\partial T} + \hat{S}\right)\dot{T} + \frac{\partial G}{\partial \phi}\dot{\phi} - \frac{\hat{K}(T)|\nabla T|^2}{T^2} \le 0. \tag{4.3.33}$$

The inequality (4.3.33) is satisfied if it is assumed that

$$\frac{\partial G}{\partial T} + \hat{S} = 0, \quad \frac{\partial G}{\partial \phi}\beta(T, \phi) \le 0, \quad \hat{K} \ge 0. \tag{4.3.34}$$

Substituting $\hat{S} = -\partial G/\partial T$ in Eq. (4.3.31), and using Eq. (4.3.27), the following equation is obtained:

$$G - T\frac{\partial G}{\partial T} = T^2 F_0'(T) + T_m^c F_1(\phi). \tag{4.3.35}$$

It is easy to check that $G(T, \phi)$ given by

$$G(T, \phi) = -TF_0(T) + TB(\phi) - (T - T_m^c)F_1(\phi), \tag{4.3.36}$$

satisfies Eq. (4.3.35). $B(\phi)$ is an unknown arbitrary function. The second condition in Eq. (4.3.34) is satisfied if $\beta(T, \phi)$ is taken as

$$\beta(T, \phi) = -\frac{1}{g(T, \phi)}\frac{\partial G}{\partial \phi}; \quad g(T, \phi) > 0. \tag{4.3.37}$$

For the sake of simplicity $g(T, \phi)$ is taken as

$$g(T, \phi) = F_2'(\phi)N(T). \tag{4.3.38}$$

If β is continuous, and $g > 0$ and continuous, then $N(T)$ should be continuous and $N(T) > 0$ for $\forall T$. Also F_2 should be a monotonically increasing C^1 function, i.e. $F_2'(\phi) > 0$ for $\forall \phi$. The constitutive equation for ϕ can now be written as

$$\frac{\partial G}{\partial \phi}(T, \phi) + N(T)F_2'(\phi)\dot{\phi} = 0. \tag{4.3.39}$$

With constitutive equations (4.3.28), (4.3.39), a thermodynamically consistent phase relaxation model is complete. By suitable choice of unknown functions F_0, F_1, $F_2(\phi)$ and $N(T)$, several well-known relaxation models can be derived as particular cases of this model (cf. [100]). Our interest here is only in analysing supercooling and superheating effects.

As discussed earlier, when a phase is in a stable equilibrium, its free energy is minimum. Therefore, for stable solid and stable liquid phases, i.e. for $\phi = 0$ and $\phi = 1$ at any fixed temperature, we have

$$\left.\frac{\partial G}{\partial \phi}\right|_{\phi=0} \geq 0 \text{ and } \left.\frac{\partial G}{\partial \phi}\right|_{\phi=1} \leq 0, \tag{4.3.40}$$

as $\phi = 0$ and $\phi = 1$ are the end points of the interval [0,1]. If ϕ_e is any internal equilibrium point, i.e. $\phi_e \in (0, 1)$, then

$$\left.\frac{\partial G}{\partial \phi}\right|_{\phi=\phi_e} = 0. \tag{4.3.41}$$

If the mushy region is at equilibrium temperature T_m, i.e. $T_m^c = T_m$ then for all possible values of $\phi \in [0, 1]$ there is equilibrium. From Eq. (4.3.36), at $T = T_m^c = T_m$, we get

$$G(T, \phi) = -TF_0(T) + TB(\phi). \tag{4.3.42}$$

From Eq. (4.3.41), $\partial B(\phi)/\partial \phi = 0$ for $\phi \in [0, 1]$. Therefore $B(\phi)$ has a constant value in the interval [0,1]. In this case

$$\begin{aligned} B = I(\phi) &= 0, \quad \text{if } \phi \in [0, 1] \\ &= \infty, \quad \text{otherwise.} \end{aligned} \tag{4.3.43}$$

$I(\phi)$ is called a *indicator function* which has no classical derivative in R, but since I is a proper *lower semicontinuous function*, its subdifferential ∂I exists. The subdifferential of the function $I(\phi)$ is defined as

$$\alpha \in \partial I(\phi) \quad \text{if and only if} \quad \alpha(\phi - \xi) \geq I(\phi) - I(\xi), \quad \text{for } \forall \xi \in R, \ \alpha \in R. \tag{4.3.44}$$

With the help of the above definition it is easy to check that $\partial I = H_g^{-1}$ where H_g^{-1} is the inverse of the *Heaviside graph* H_g defined in the following:

$$H_g(x) = 0, \quad x < 0$$
$$= (0, 1), \quad x = 0,$$
$$= 1, \quad x > 0.$$

$$(4.3.45)$$

It is easy to obtain H_g^{-1} or ∂I by using Eq. (4.3.44), and we have

$$\partial I(x) = \emptyset, \quad x \notin [0, 1],$$
$$= \{0\}, \quad x \in (0, 1),$$
$$= R^+, \quad x = 1, \quad R^- \quad \text{if } x = 0.$$

$$(4.3.46)$$

To avoid ϕ taking values outside the interval [0,1], but to preserve strict minima at the ends $\phi = 0$ and $\phi = 1$, a double well function should be added to the indicator function. Therefore $B(\phi)$ should be of the form

$$B(\phi) = I(\phi) + B_1(\phi), \tag{4.3.47}$$

where $B_1(\phi)$ is a smooth 'double-well function' forcing B to have only two strict minima at $\phi = 0$ and $\phi = 1$. Depending on the physical situation, $I(\phi)$ or $B_1(\phi)$ could be zero or nonzero. $B_1(\phi)$ is generally taken in the form

$$B_1(\phi) = v\phi^2(1 - \phi)^2, \quad v > 0. \tag{4.3.48}$$

$F_1(\phi)$ in Eq. (4.3.36) has been assumed to be nondecreasing and it should have strict minima at $\phi = 0$ and $\phi = 1$, as G possesses these two minima. $F_1(\phi)$ satisfies these conditions if it is taken as [100]

$$F_1(\phi) = \frac{\lambda}{3}\phi^3(3 - 2\phi), \quad \lambda > 0. \tag{4.3.49}$$

Superheating and Supercooling Effects

When a solid is superheated, $\phi = 0$ even at those points of the region where $T > T_m$. Note that superheating or supercooling is assessed with respect to T_m and not with respect to T_m^c. Similarly, for a supercooled liquid, $\phi = 1$ even when $T < T_m$. Therefore the free energy G must exhibit minima at $\phi = 0$ and $\phi = 1$ for all temperatures T such that $|T - T_m|/T_m < \varepsilon$ where ε is a sufficiently small positive number. In particular, minima exists at $T = T_m$ also.

We first consider the case $T > T_m^c$. For $T > T_m^c$, the last term in Eq. (4.3.36) is nonpositive if $F_1(\phi)$ is taken as in Eq. (4.3.49). If $B = B_1$ in Eq. (4.3.36), then G has an absolute minimum at $\phi = 1$. Fig. 2.1.1 suggests that the solid is superheated. For $T < T_m^c$, the last term in Eq. (4.3.36) is nonnegative and G (with $B = B_1$) has an absolute minimum at $\phi = 0$. Fig. 2.2.1 suggests that the liquid is supercooled. Let $u(T) = \lambda(T - T_m^c)/(vT)$, $\lambda > v > 0$. If B_1 from Eq. (4.3.48) and F_1 from Eq. (4.3.49) are substituted in Eq. (4.3.36) and G is differentiated, then we get

$$\frac{\partial G}{\partial \phi} = 4vT\phi(\phi - 1)[\phi - (1 - u(T))2]. \tag{4.3.50}$$

If $u(T) \in (-1, 1)$, then G takes two strict minima at $\phi = 0$ and $\phi = 1$ (check $\partial^2 G/\partial\phi^2$ also) and superheating and supercooling can occur when T lies in the interval

$$\left(\frac{\lambda T_m}{\lambda + \nu} < T < \frac{\lambda T_m}{\lambda - \nu}\right). \tag{4.3.51}$$

In Eq. (4.3.51), T_m^c has been replaced by T_m as supercooling and superheating are assessed with respect to T_m. It is clear from Eq. (4.3.51) that if the mushy region exists at $T = T_m$, then supercooling and superheating effects do not occur.

In essence, the mathematical model described above consists of the following coupled differential equations:

$$\frac{\partial}{\partial t}(T^2 F_0'(T) + T_m^c F_1(\phi)) - \mathrm{div}(\hat{K}(T)\mathrm{grad}\, T) = \dot{r} \tag{4.3.52}$$

and

$$\frac{\partial}{\partial t}(F_2(\phi)) + \partial I(\phi) + \frac{T}{N(T)}B_1'(\phi) \ni \frac{T - T_m^c}{N(T)}F_1'(\phi). \tag{4.3.53}$$

Eq. (4.3.52) can be obtained from Eqs (4.3.27), (4.3.28) while Eq. (4.3.53) can be obtained from Eqs (4.3.36), (4.3.39). Due to the presence of the term $\partial I(\phi)$, the l.h.s. in Eq. (4.3.53) is a multivalued function and the relation (4.3.53) cannot be written as an equation. The system consisting of Eqs (4.3.52), (4.3.53) should be supplemented with the boundary and initial conditions. For example, the boundary condition could be

$$\vec{q} \cdot \vec{n} = -\hat{K}(T)\frac{\partial T}{\partial n} = 0, \quad \text{on } \Sigma = \partial\Omega \times (0, t_*), \tag{4.3.54}$$

where $\partial\Omega$ is the boundary of the region Ω under consideration and the initial conditions could be

$$\{T^2 F_0'(T) + T_m^c F_1(\phi)\}_{t=0} = e_0, \quad (F_2(\phi))|_{t=0} = \phi_0, \tag{4.3.55}$$

where e_0 and ϕ_0 are known quantities. In Fourier's heat conduction law, $\hat{K}(T) = K(T) > 0$, where K is the thermal conductivity. In irreversible thermodynamics, $\vec{q} = \hat{K}(T)\nabla(1/T)$. $N(T)$ is a prescribed quantity. For example, in [95], $N(T)$ has been taken to be T. If $I(\phi) = 0$, then Eq. (4.3.53) is a classical equation.

If $\hat{K}(T) = K$, a constant, and if suitable assumptions are made about various functions then the existence and uniqueness of systems (4.3.52), (4.3.53) has been proved in [100].

4.4 SOLIDIFICATION OF SUPERCOOLED LIQUID WITHOUT CURVATURE EFFECT AND KINETIC UNDERCOOLING: ANALYSIS OF THE SOLUTION

In Sections 4.2 and 4.3 some phase-field models were considered. With their help supercooling/superheating effects can be discussed if appropriate limits of parameters are taken. These models provided rigorous justification of the incorporation of the modified Gibbs–Thomson relation in the classical formulation when curvature effect and kinetic undercooling

are included. Many physical situations can be modelled by suitable choices of arbitrary functions occurring in phase-field models and phase-relaxation models. In this section we want to discuss the issues like: (i) existence, uniqueness and well-posedness of solutions and (ii) blow-up and regularization of Stefan problems with supercooling. It may be made clear that by 'Stefan problem with supercooling' we mean classical formulations of either solidification of a supercooled liquid or one- or two-phase solidification problems with modified Gibbs–Thomson relation.

4.4.1 One-Dimensional One-Phase Solidification of Supercooled Liquid (SSP)

The mathematical model of this problem has already been discussed in Eqs (3.1.8)–(3.1.12). Because of its simplicity this problem has been extensively studied. It should be remembered that neither the curvature effect nor the kinetic condition has been incorporated in this model. It was mentioned in Section 3.1.2 that oxygen-diffusion problem (ODP) (Eqs 3.3.34–3.3.38) can be transformed to supercooled Stefan problem (SSP) and vice versa and $c(x, t)$ and $T(x, t)$ are related through Eq. (3.3.39). We shall now consider a more general ODP and take

$$c(x, 0) = c_0(x), \quad 0 \le x \le 1, \tag{4.4.1}$$

where $c_0(x)$ could be different from $0.5(1 - x)^2$. From Eq. (3.3.39), we have

$$c_0(x) = \int_1^x d\xi \int_1^\xi (T_0(\eta) + 1) d\eta; \quad c_0''(x) = T_0(x) + 1, \tag{4.4.2}$$

and $c_x(0, t)$ is given by (cf. [104])

$$c_x(0, t) = c_0'(0) + \int_0^t g(\tau) d\tau. \tag{4.4.3}$$

Here $g(t)$ is the same as in Eq. (3.1.10). The second equation in Eq. (4.4.2) suggests that $c_0(x)$ should be sufficiently regular. For the existence and uniqueness of solutions some compatibility conditions should also be satisfied by the initial temperature and the boundary conditions. If the boundary condition (3.1.10) is replaced by the boundary condition $T(0, t) = F(t)$, then we obtain [104]

$$c(0, t) = c_0(0) + \int_0^t F(\tau) d\tau. \tag{4.4.4}$$

The essential difference between the classical Stefan problems concerning solidification of a liquid and the solidification of a supercooled liquid is in the sign requirements of the temperature difference $(T - T_m)$. The temperature of a supercooled liquid is less than T_m, whereas in the classical Stefan problem without supercooling, the temperature of the liquid is greater than or equal to T_m. As mentioned earlier, whenever the classical solution of a Stefan problem is discussed here, it is implied that the solution satisfies some conditions of the form (i)–(iv) given in Section 3.1.1. Depending on the problem under consideration appropriate changes have to be made in these conditions. A global-in-time classical solution is known to exist for the one-dimensional Stefan problem under suitable data assumptions (cf. [57, 75]). If

the liquid is supercooled or if the solid is superheated, a solution may still exist for a short-time but a *finite-time blow-up* (explained later) may occur, which prevents continuation of the solution.

Assuming that a solution of a Stefan problem with superheating/supercooling exists, some important questions to be investigated further are:

(A) Can a classical solution of the problem exist for an arbitrarily long time?

(B) Does there exist a constant $t_b > 0$ such that $\lim_{t \to t_b-} S(t) = 0$? Here $S(t)$ is progressing towards $x = 0$.

(C) Does there exist a constant $t_c > 0$ such that $S(t) > 0$ for $t \in (0, t_c]$ and $\lim_{t \to t_c} \dot{S}(t) = -\infty$?

Question (B) pertains to *finite-time extinction* and (C) pertains to the blow-up of a solution defined as follows.

Finite-time blow-up: If $S(t)$ is the free boundary in a free boundary problem, and if at some time $t = t_* < \infty$, $S(t_*) > 0$ and $\liminf_{t \to t_*-} \dot{S}(t) = -\infty$, then it is said that a finite-time blow-up has occurred.

Essential blow-up: If the solution of the free boundary problem cannot be continued beyond the blow-up time, then the blow-up is called essential. It may be pointed out that blow-up is not a physically realistic phenomenon and it indicates defects in the mathematical model of the problem.

Nonessential blow-up: It may be possible to continue the solution of the free boundary problem beyond the blow-up time $t = t_*$ with $S(t_*)$ and $\lim_{t \to t_*-} T(x, t) = \hat{T}_0(x)$ as the initial data. In this case we have a nonessential blow-up.

Many studies are available on the analysis of SSP. Each study contains several results. Only a few of these can be presented here. In [59, 104, 105] the boundary condition (3.1.10) in SSP has been replaced with the following:

$$T_x(0, t) = 0, \quad 0 < t < t_*. \tag{4.4.5}$$

Let Q be a constant defined as

$$Q = \int_0^1 (T_0(x) + 1)dx. \tag{4.4.6}$$

The quantity $(1 + T_0(x))$ in which the latent heat has been suitably scaled and taken as unity represents the sum of the latent heat and the sensible heat. Q can be interpreted as the global energy of the supercooled liquid at $t = 0$ and should be greater than or equal to zero. Q plays an important role in analysing questions (A), (B) and (C) mentioned previously.

Let $T_0(x)$ be nonpositive and continuous in [0,1]. If $T_0(1) = 0$ and $T_0(x)$ is Hölder-continuous at $x = 1$, then the supercooled problem possesses one solution valid for sufficiently small time $t < t_0$. The uniqueness and well-posedness of the solution can also be proved. If $T_0(x)$ is constant not exceeding -1, then SSP has no solution [75].

Some of the results reported in [75, 104, 105] are summarized below in the form of Propositions 4.4.1–4.4.5. It should be remembered that in the discussion pertaining to these propositions, the term SSP means the mathematical formulations (3.1.8)–(3.1.12) in which

Eq. (3.1.10) has been replaced by Eq. (4.4.5). Similarly ODP would mean the problem obtained by transforming the new SSP with the help of the transformation (3.3.39).

Proposition 4.4.1. *If the closure of the set $\{T_0(x) < -1\}$ is either void or if it is compact and contains the origin, then in the solution of SSP the conditions $Q > 0$, $Q = 0$ and $Q < 0$ are necessary and sufficient for global existence, finite-time extinction and blow-up, respectively. Blow-up always occurs when $Q < 0$ while $Q = 0$ is necessary for a finite-time extinction.*

If the constraint $c \geq 0$ is not added in ODP with initial concentration given by Eq. (4.4.1), then the free boundary in both SSP and unconstrained ODP (UODP) coincides and both will have a finite-time blow-up at a time at which the negativity set of $c(x, t)$ reaches $x = S(t)$. For $t \in (0, t_*)$, define

$$N(t) = \{x : 0 \leq x < S(t), c(x, t) < 0\}. \tag{4.4.7}$$

In [104, 105], several results concerning blow-up in SSP and UODP have been reported. Some of them are given as follows.

Proposition 4.4.2. *If $N(t) \neq \emptyset$, then*

(i) *for any $t_2 \in (t_1, t_*)$, $N(t_1) \subset\subset N(t_2)$, i.e. the negativity set expands,*

(ii) *if for some $\hat{t} > t_1$, the boundary $\partial N(\hat{t})$ touches the free boundary then $\dot{S}(t)$ is singular as $t \to \hat{t}$,*

(iii) *the case above actually occurs.*

Proposition 4.4.3. *A necessary and sufficient condition for an essential blow-up at the point $(S(\hat{t}), \hat{t})$ is that the point belongs to $\partial N(\hat{t})$.*

Proposition 4.4.4. *A necessary and sufficient condition for having $\dot{S}(t)$ singular at a point $(S(\hat{t}), \hat{t})$ is that the set $\{(x, t) : T(x, t) = -1\}$ reaches the free boundary at such a point.*

Proposition 4.4.5. *There are initial data such that ODP corresponding to SSP with Eq. (4.4.5) admits global solutions with $\lim_{t \to t_0} \dot{S}(t) = -\infty$ for some $t_0 > 0$.*

The last proposition is a case of a nonessential blow-up and in [104] this case has been demonstrated with the help of an example.

4.4.2 Regularization of a Blow-Up in SSP by Looking at CODP

The question which will be discussed now is, 'how to stop blow-up in SSP'? This is called regularization. Note that there are methods other than the one discussed below for *regularization*. Let us first examine which physical quantity is responsible for the blow-up. The integral

$$E(x, t) = \int_x^{S(t)} (T(\xi, t) + 1) d\xi = -c_x, \tag{4.4.8}$$

represents the thermal energy in the layer $(x, S(t))$ (cf. Eq. 3.3.39). $E(0, t) = E(0, 0) = Q$ (cf. Eq. 4.4.6). Here $c(x, t)$ is the concentration in ODP.

If the mean energy $\bar{E}$ in the supercooled layer is defined as

$$\bar{E}(x,t) = (S(t) - x)^{-1} \int_x^{S(t)} d\xi \int_\xi^{S(t)} (T(\eta,t) + 1)d\eta \tag{4.4.9}$$

$$= (S(t) - x)^{-1} c(x,t), \tag{4.4.10}$$

then blow-up occurs if and only if $\bar{E}(x,t)$ is negative at some point (x,t). This implies that at the blow-up point $c(x,t) < 0$. Thus any regularization of SSP or UODP has to prevent $\bar{E}(x,t)$ from taking negative values by shifting UODP to constrained ODP (CODP). It seems reasonable to conjecture that this argument holds for multidimensional problems also (cf. [105]). The absolute minimum of $\bar{E}(x,t)$ is $E(0,t)$ or Q. Blow-up occurs if and only if $Q < 0$. If $Q < 0$, then it implies that the system does not have enough energy in the form of latent heat to cancel out the 'cold' of the supercooled liquid. Another way to look at the blow-up points is to look at the roots of the equation $T(x,t) + 1 = 0$. Either the set of points (x,t) for which $T(x,t) + 1 = 0$ is empty or it has a positive distance from the free boundary. In the latter case, if this set reaches the free boundary at $t = t_0$ then $\lim_{t \to t_0} \dot{S}(t) = -\infty$ (cf. [75]). For $t < t_0$, $\dot{S}(t)$ is bounded. This implies that there is too much 'cold' too near the free boundary, and blow-up occurs because the energy cannot reach the point of blow-up by diffusion.

To stop finite-time blow-up in SSP some mathematical techniques have been suggested in [104] which consist of modifying UODP to CODP provided CODP is formulated classically, with a new free boundary appearing each time $c(x,t)$ becomes zero. We can call it 'nucleation' of new free boundaries. In this case we have always a finite-time extinction. This 'nucleation' of new free boundaries can be achieved in SSP also. Let $Q = 0$, $c_0 \geq 0$. This implies that $c_x(0,t) = 0$. There is no change in the energy of the system in this 'nucleation' but the creation of the new phase boundaries rearranges the energy fluxes in such a way that the blow-up that would occur due to the deficit of energy near $x = S(t)$ is prevented by a counter-balancing surplus near $x = 0$.

There are techniques such as incorporation of curvature effects and kinetic undercooling for the regularization of blow-up during solidification of a supercooled liquid. Curvature effects cannot be included in SSP as it is a one-dimensional slab problem. If the kinetic condition is also excluded in the formulation, then we have to resort to other techniques for regularization such as nucleation described previously.

Some of the results obtained in [105] have been extended to a two-phase problem considered in [106]. Let us assume that there is some solid region (finite or infinite) to the right of $x = S(t)$ in SSP whose temperature is $T_1(x,t) < 0$ for $t > 0$. The boundary and initial conditions are such that $T(x,t) < 0$, $t > 0$ is guaranteed till the solution exists. The following proposition, which is false for the one-phase SSP problem, is true for the two-phase problem.

Proposition 4.4.6. If $Q = 0$, an essential blow-up will occur, while, for finite-time extinction $Q > 0$ is necessary.

The above result has been proved by obtaining an integral equation for $S(t)$.

4.4.3   Analysis of Problems With Some Changes in the Initial and Boundary Conditions in SSP

Let us consider the formulations (3.1.8)–(3.1.12) with the boundary condition

$$T(0,t) = f(t), \quad 0 < t < t_*. \tag{4.4.11}$$

By using the transformation (3.3.39) and using Eq. (4.4.4), a formulation in terms of $c(x, t)$ can be obtained. Let us assume that in the transformed problem

$$c(x, 0) = c_0(x), \quad 0 \le x \le 1. \tag{4.4.12}$$

The following results have been proved in [107].

Proposition 4.4.7. *Assume that for some $x_0 > 0$ the following condition is satisfied:*

$$c_0(x) \le 0, \quad \text{for } x \in (1 - x_0, 1). \tag{4.4.13}$$

Then the solution of SSP with Eq. (3.1.10) replaced by Eq. (4.4.11) does not exist.

Proposition 4.4.8. *Assume that there exists $x_0 > 0$ such that the initial temperature $T_0(x) \ge -1$, $T_0(x) \not\equiv -1$ in $(1 - x_0, 1)$. Then SSP with Eq. (4.4.11) has at most one solution in the local sense.*

Proposition 4.4.9. *Assume that there exists $x_0 > 0$ such that $T_0(x) > -1$ for x in $(1 - x_0, 1)$. Then SSP with Eq. (4.4.11) possesses a unique local-in-time classical solution. Existence can also be proved in a special case in which $\lim_{x \to 1-} \inf T_0(x) > -1$.*

The convexity of the free boundary in SSP has been proved in [108] with no flux boundary condition imposed at $x = 0$, i.e. in Eq. (3.1.10), $g(t) = 0$. In [109] also, the convexity of the free boundary has been established but under special assumptions on $T_0(x)$. The initial data considered in [108] is of the form

$$T_0(x) \le 0, \ x \in [0, 1]; \quad T_0(1) = 0; \quad T_0(x) \in C^2[0, 1]. \tag{4.4.14}$$

The main tool used in [109] in proving the results was the introduction of the function

$$v(x, t) = T_{xx}/T_x \tag{4.4.15}$$

and the study of its level curves and this was done in [108] also. SSP can be formulated in terms of $v(x, t)$ which will not be discussed here. Let

$$M = \{x : x \in [0, 1], T_0'(x) \ne 0\}. \tag{4.4.16}$$

If $T_0(x) \not\equiv 0$, then M is not void. Set

$$P(x) = T_0''(x)/T_0'(x), \quad x \in M. \tag{4.4.17}$$

Out of the several results reported in [108], we present only one here.

Proposition 4.4.10. *Assume that Eq. (4.4.14) is satisfied, and $P(x)$ is nonnegative and nonincreasing in M. If $P(1) > T_0'(1)$, then $\ddot{S}(t) > 0$ for any $t \in (0, t_*)$ and SSP with $g(t) = 0$ in Eq. (3.1.10) is solvable for any arbitrary $t_* > 0$.*

Some results can be obtained for ODP also by following the approach adopted for SSP. In particular it can be proved that the free boundary in ODP with $c_0(x) = 0.5(1 - x)^2$ is concave. See [108] for further details.

In [110], SSP with Eq. (3.1.10) replaced by the prescribed temperature condition $T(0, t) = f(t)$ has been considered. The questions (A), (B) and (C) raised earlier in this section have been analysed. Several results have been obtained in terms of a quantity $R(t)$ defined as

$$R(t) = \frac{1}{2} + \int_0^1 xT_0(x)dx + \int_0^t f(\tau)d\tau. \tag{4.4.18}$$

The motivation for considering $R(t)$ comes from the equation

$$\frac{(S(t))^2 - 1}{2} = \int_0^1 xT_0(x)dx + \int_0^t f(\tau)d\tau - \int_0^{S(t)} xT(x,t)dx. \tag{4.4.19}$$

When $S(t) = 0$, we have $R(t) = 0$. Eq. (4.4.19) and several other equations of this kind can be derived by using the following Green's identity (cf. [57]):

$$\int_{D_t} (vP(T) - TP^*(v))dxd\tau = \int_{\partial D_t} \left[(T_xv - Tv_x)d\tau + k^{-1}Tvdx \right], \tag{4.4.20}$$

where P is the heat operator $k^{-1}T_{xx} - T_t$ and P^* is its adjoint operator, $D_t = \{(x,t) : 0 < x < S(t), 0 < t < t_*\}$. By choosing v and v_x suitably, several relations of the type (4.4.19) can be developed.

Proposition 4.4.11. *Assume that the solution of SSP (with temperature prescribed in the place of Eq. 3.1.10) exists, and $T_0(x)$ and $f(t)$ satisfy the following hypotheses:*

(i) $T_0(x) \leq 0$ *is an increasing function in [0,1],*

(ii) $f(t) \leq 0$ *is a decreasing function of t, $t \geq 0$.*

If case (C) (Section 4.4.1) occurs, then it implies $R(t_c) \leq 0$ (t_c is the same as defined in (C)).

The following convective boundary condition at $x = 0$ in SSP was considered in [111] in the place of Eq. (3.1.10):

$$K\frac{\partial T}{\partial x}(0,t) = \bar{h}(T(0,t) - g(t)), \quad g(t) \leq 0, \quad 0 < t \leq t_*. \tag{4.4.21}$$

The questions (A), (B) and (C) (Section 4.4.1) were investigated and in answering these questions, the key role is played by the quantity $Q_1(t)$ defined as

$$Q_1(t) = 1 + \frac{\beta}{2} + \int_0^1 (1 + \beta x)T_0(x)dx + \int_0^t \beta G(\tau)d\tau, \tag{4.4.22}$$

where $\beta = \bar{h}/Kb$ is a dimensionless parameter, b has the dimension of length with which the space coordinate can be dimensionalized to obtain the supercooled region as $0 \leq x \leq 1$ and

$$G(t) = \frac{C}{l}g\left(\frac{b^2\rho Ct}{K}\right). \tag{4.4.23}$$

We present here one of the results reported in [111].

Proposition 4.4.12. *If the solution of this changed SSP with Eq. (4.4.21) exists and the initial and boundary data satisfy the following conditions:*

$$
\left.
\begin{aligned}
&\text{(i) } T_0(x) \geq M(x-1) \quad and \quad T_0'(x) \geq 0, \quad 0 \leq x \leq 1, \quad 0 < M < 1, \\
&\text{(ii) } G(t) \geq -M, \quad t > 0, \\
&\text{(iii) } T_0'(0) = \beta(T(0) - g(0)),
\end{aligned}
\right\}
\tag{4.4.24}
$$

and there exists a time t_b such that $Q_1(t_b) = 0$, then $t = t_b$ is the time in the case (B).

The solidification of a supercooled liquid has been studied in geometries other than a slab. In a one-dimensional radially symmetric spherical geometry or in a one-dimensional radially symmetric cylindrical geometry, in principle, curvature effects can be included. The curvature effect and the kinetic condition have in general a regularizing effect. If curvature effect is not included in cylindrical and spherical geometries, then the questions (A), (B) and (C) become more meaningful and should be investigated. This has been done in the next two problems. These problems can be easily formulated on the same lines as the formulation given in Eqs (3.1.8)–(3.1.12).

One-dimensional radially symmetric solidification of a supercooled liquid in the spherical region $r_0 \leq r \leq 1$, $r_0 > 0$ was considered in [112]. The quantity $Q_2(t)$ given below plays a key role in the study of questions (A), (B) and (C)

$$
Q_2(t) = 1 + 3 \int_{r_0}^{1} r^2 T_0(r) dr - 3r_0^2 \int_0^{\tau} g(\tau) d\tau.
\tag{4.4.25}
$$

Here $T_0(r)$ is the initial temperature and $g(t)$ is the prescribed flux at $r = r_0$ in the spherical geometry. A result concerning finite-time extinction is as follows.

Proposition 4.4.13. *If $T_0(r) \leq 0$, $r_0 < r < 1$, and continuous and $T_0(r) \geq -h_1(1-r)$, $h_1 \leq 1$, $0 < g(t) \leq h_1$ for $t > 0$, then case (B) occurs and $Q_2(t_b) = r_0^3$.*

Solidification of supercooled liquid in a one-dimensional radially symmetric cylindrical region $r_0 \leq r \leq b$ was considered in [113] with temperature prescribed at $r = r_0$. A flux prescribed case can also be discussed in a similar way. One existence and uniqueness result is given below.

Proposition 4.4.14. *Let the initial temperature $T_0(r)$, $r_0 \leq r \leq b$ be such that*

$$
T_0(r) > -1, \quad b - d_0 < r < b
\tag{4.4.26}
$$

for some $d_0 \in (0, b - r_0]$. Then the solution of the cylindrical problem exists in the interval $0 < t < t_*$ for some $t_* > 0$. The case $T_0(b) = -1$ is allowed as long as conditions in Eq. (4.4.26) are fulfilled. Uniqueness of the solution can be proved as in [107].

The SSP considered in [114] is ODP transformed into SSP. The initial concentration in ODP is $0.5(1-x)^2$ but at $x = 0$ nonzero flux is prescribed which is a monotonically increasing function of time with $c_x(0, 0) = -1$. This ODP can be transformed to SSP with the initial temperature zero and the flux at $x = 0$ given by $T_x(0, t) = g(t)$, $0 < t < t_*$. It is assumed that $g(t)$ is a nonnegative piecewise continuous function in $(0, \infty)$, bounded in every interval $(0, t)$, $t > 0$. The questions (A), (B) and (C) have been analysed for the transformed SSP. By using an appropriate Green's identity, the relation given below can be obtained

$$
S(t) = 1 - \int_0^t g(\tau) d\tau - \int_0^{S(t)} T(x, t) dx, \quad 0 < t < t_*.
\tag{4.4.27}
$$

A unique solution of the transformed SSP exists if and only if

$$\int_0^t g(\tau)d\tau < 1 \quad \text{for any } t > 0. \tag{4.4.28}$$

For other results, see [114].

4.5 ANALYSIS OF SSPs WITH THE MODIFIED GIBBS–THOMSON RELATION

4.5.1 Introduction

A supercooled liquid is in a metastable state, and, if left to itself, will remain in that state for a long time. In the absence of curvature effect or kinetic undercooling in the equilibrium temperature, supercooled liquid has a destabilizing effect on the planar phase-change boundary. Imagine a small solid protrusion into the supercooled liquid at the planar interface. Suppose that the temperature of the supercooled liquid is decreasing as we move away from the planar front. Let the equilibrium temperature be T_m which is the ideal phase-change temperature. This solid protrusion will have a large temperature gradient. According to Stefan condition (1.4.22), its growth velocity will be greater than that of its neighbours on the planar front, and so this protrusion will grow and not dye. This indicates instability.

The effect of surface tension is to stabilize the phase-change boundary. Since the surface tension decreases the equilibrium temperature, any protrusion at the planar free boundary gets liquified. Without surface tension, supercooling could lead to a totally unstable system. In real physical systems when supercooling is present, and which is generally the case, local instabilities such as dendrites will be present. These are counter balanced by the nonlinear stabilizing effects of surface tension. In some sense, these arguments also hold for kinetic undercooling as well [86] that kinetic undercooling has a stabilizing effect in the sense that in the perturbation of the planar boundary an unstable mode remains unstable but with smaller amplitude. Large surface tension is incompatible with large curvature as large surface tension in supercooling implies that the deviation of the new equilibrium temperature from T_m is negative and large. This means that protrusions will be dissolved. This also means that the interface is nearly planar and the curvature is small. Therefore if the initial and boundary conditions are suitably chosen, then supercooling can be restricted. Surface tension is an equilibrium phenomenon, as it arises in equilibrium thermodynamics, but kinetic undercooling is a nonequilibrium phenomenon. It may be noted that in the Stefan problem, phase-change boundary is moving but it is assumed that there is an instantaneous equilibrium so that laws of equilibrium thermodynamics can be applied.

4.5.2 One-Dimensional One-Phase SSPs With the Modified Gibbs–Thomson Relation

Consider the formulation given in Eqs (3.1.8)–(3.1.12) with $g(t) = 0$ in Eqs (3.1.10), (3.1.11) taken as

$$T(S(t), t) = \varepsilon \dot{S}(t), \quad \varepsilon > 0, \ \dot{S}(t) < 0. \tag{4.5.1}$$

Eqs (3.1.8), (3.1.9), (3.1.10), (3.1.12), (4.5.1) constitute our new SSP. In Eq. (4.5.1) kinetic undercooling has been incorporated. Note that since $S(t)$ is moving towards $x = 0$, $\dot{S}(t)$ is negative. In the problem considered in is [115], $S(0) = 0$ and $\dot{S}(t) > 0$ which are different from our formulation. This change in essence does not affect the results of [115]. It has been established in [115] that if the initial temperature $T_0(x)$ is such that $T_0'(x)$ is continuous in $0 \leq x \leq 1$ and $T_0'(0) = 0$ then the kinetic undercooling will have a regularizing effect and blow-up will be prevented. In physical terms, the kinetic undercooling term allows more energy to enter the liquid at the moving boundary than would be the case if this energy is supplied by the latent heat alone (as in SSP without kinetic undercooling). The rate of change of energy is given by (cf. Eq. 4.4.8 for $E(x,t)$)

$$\frac{dE}{dt} = \frac{d}{dt} \int_0^{S(t)} \{T(x,t) + 1\}dx = \varepsilon \dot{S}^2. \tag{4.5.2}$$

As $\varepsilon > 0$, there is an additional energy $\varepsilon \dot{S}^2$ available which compensates any energy deficit in $T_0(x)$. The kinetic undercooling term in Eq. (4.5.1) imposes a limit on the speed of the interface. For some results concerning a one-dimensional two-phase problem and a semiinfinite problem, see [115].

A one-dimensional supercooled problem in a semiinfinite region $0 \leq x < \infty$ has been considered in [116]. The region under consideration is $S(t) \leq x < \infty$, $t > 0$ and $S(0) = 0$. Let $T_0(x) \leq 0$, $0 \leq x < \infty$, $T_0(x) \in C^1[0,\infty)$ be the initial temperature of the supercooled liquid and

$$T_0(x) \to -1 - \tilde{\delta} \quad \text{as } x \to \infty, \tag{4.5.3}$$

where $\tilde{\delta}$ is a constant. If kinetic undercooling is considered, then

$$T(S(t),t) = -\varepsilon \dot{S}(t), \quad \varepsilon \geq 0, \ \dot{S}(t) > 0, \ t > 0. \tag{4.5.4}$$

No fixed boundary condition at $x = 0$ is required as the region $x < 0$ is ice at time $t = 0$. Several cases for $\tilde{\delta} > 0, = 0, < 0$ have been analysed when $\varepsilon > 0$ and $\varepsilon = 0$. When $\varepsilon = 0$, and $\tilde{\delta} > 0$, a finite-time blow-up occurs. When $\varepsilon > 0$ and $\tilde{\delta} < 0$, similarity solutions exist and $S(t) = \beta \sqrt{t}$ (for β see [116]). When $\varepsilon > 0$ and $\tilde{\delta} > 0$, travelling wave solutions exist with $S(t) = \tilde{\delta}t/\varepsilon$. If $\varepsilon > 0$ and $\tilde{\delta} = 0$; $S(t) \sim dt^\alpha$, $\frac{1}{2} < \alpha < 1$, where d is a constant depending on several parameters including ε.

A radially symmetric spherical problem in the region $S(0) \leq r < \infty$, $S(0) \neq 0$ was also considered in [116]. Both surface tension and kinetic condition have been considered so that

$$T(S(t),t) = -\varepsilon \dot{S} - 2\sigma/S, \quad \dot{S} > 0, \ t > 0. \tag{4.5.5}$$

Note that in this case the curvature $\bar{K}_c = 1/r$ and the free boundary is $r = S(t)$. Initial temperature is of the same type as in Eq. (4.5.3). If $\varepsilon = 0$ and $\tilde{\delta} > 0$, then even with surface tension a finite-time blow-up occurs. However if $\varepsilon > 0$, and $\tilde{\delta} > 0, = 0$ or < 0, finite-time blow-up does not occur. For other results see [116].

In [117], the effect of both kinetic undercooling and latent heat on the solution has been analysed. Consider SSP described by Eqs (3.1.8)–(3.1.12) in which instead of Eq. (3.1.10), the boundary condition $T(0,t) = f(t)$ is prescribed. The interface conditions are

$$T(S(t), t) = \varepsilon \dot{S}, \quad \varepsilon > 0, \quad \dot{S} < 0 \quad \text{and} \quad T_x(S(t), t) = -l\dot{S}. \tag{4.5.6}$$

$T_0(x)$ and $f(t)$ are continuous nonpositive functions such that $T_0(0) = f(0)$. When $\varepsilon = 0$ and $l < 0$ (l is the latent heat) we have a one-phase Stefan problem concerning solidification. When $\varepsilon = 0$ and $l > 0$ we have a SSP. In the latter case, if $\varepsilon > 0$, then it will be a supercooled problem with a kinetic condition. Several cases have been considered for different signs of ε and l but our interest at present is in the case $\varepsilon > 0$ and $l > 0$ for which the following result has been proved in [117].

Proposition 4.5.1. *If $T_0(x)$ and $f(t)$ satisfy the assumptions stated above, then the supercooled problem with Eq. (4.5.6) in which $\varepsilon > 0$, and $l > 0$ admits a unique solution and the free boundary $S(t)$ is a smooth function in $(0, t_*)$ where t_* is such that $S(t_*) = 0$ and $S(t) > 0$ for $t < t_*$.*

4.5.3   One-Dimensional Two-Phase Stefan Problems With the Modified Gibbs–Thomson Relation

Although a two-phase Stefan problem with the modified Gibbs–Thomson relation can be easily formulated, for the sake of better understanding of the results, we present here the formulation of a two-phase Stefan problem with a kinetic condition

$$\frac{\partial T_S}{\partial t} = k_S \frac{\partial^2 T_S}{\partial x^2}, \quad \text{in } Q_1 = \{(x, t) : 0 < x < S(t), 0 < t < t_*\}, \tag{4.5.7}$$

$$\frac{\partial T_L}{\partial t} = k_L \frac{\partial^2 T_L}{\partial x^2}, \quad \text{in } Q_2 = \{(x, t) : S(t) < x < 1, 0 < t < t_*\}, \tag{4.5.8}$$

$$T_S(S(t) - 0, t) = T_L(S(t) + 0, t) = T(S(t), t), \quad 0 \le t < t_*, \tag{4.5.9}$$

$$\dot{S}(t) = g(T(S(t), t), \tag{4.5.10}$$

$$S(0) = S_0, \quad 0 < S_0 < 1, \tag{4.5.11}$$

$$\left\{ K_S \frac{\partial T_S}{\partial x} - K_L \frac{\partial T_L}{\partial x} \right\}_{x = S(t)} = l\dot{S}(t), \quad l > 0, \quad 0 \le \dot{S}(t) \le \text{constant}, \tag{4.5.12}$$

$$T(x, 0) = T_0(x), \quad 0 \le x \le 1, \tag{4.5.13}$$

$$T_L(1, t) = h_L(t), \quad T_S(0, t) = h_S(t). \tag{4.5.14}$$

This solidification problem has been considered in [118]. The main interest in [118] is to establish the existence and uniqueness of the classical solution of the problem if $g(T)$ is of the form

$$g(T) \in C^1(R) \quad \text{and} \quad g(T) = T^m, \quad m \in N. \tag{4.5.15}$$

The condition (4.5.12) is satisfied at $x = S_0$ also. $h_i(t) \in C^{\alpha_1}[0, t_*]$, $i = S, L$, $\frac{1}{2} < \alpha_1 < 1$, $T_0(x) \in C^{\alpha_2}[0, S_0] \cap C^{\alpha_2}[S_0, 1]$, $2 < \alpha_2 < 3$, $T_0(0) = h_S(0)$, $T_0(1) = h_L(0)$ and S_0 satisfies a constraint (cf. [118]) which involves the L^∞-norms of the initial and boundary

temperatures. No sign constraints have been prescribed on the initial and boundary data. It has been proved that there exists a t_* such that $\lim_{t \to t_*} S(t) = 1$. Travelling wave solutions of the problem have also been obtained. A similar problem with $g(T) \in C^1(R)$ and $|g(T)| \leq a(|T|^m + 1)$, where a and $m \geq 1$ are positive constants, was considered in [119] and local existence of the classical solution was proved under some assumptions some of which are the same as in [118].

A two-phase problem in $-\infty < x < \infty$ with kinetic undercooling condition (4.5.10) has been considered in [120]. It was proved in [120] that if $|g(T)| \leq Me^{\gamma|T|}$ for some $M > 0$ and $\gamma \in (0, 1/4)$, then a global solution to the problem (4.5.7)–(4.5.14) exists under suitable assumptions. If $g(T) \geq ae^{\gamma_1|T|}$ for some constant a and large γ_1, then blow-up in finite time may occur. A critical value of the exponent γ was obtained in [121] as $\gamma = \sqrt{2\pi e}$ such that for $\gamma \in (0, \sqrt{2\pi e})$, a global-in-time solution exists and blow-up in finite time occurs if $g(T) \geq ae^{\gamma|T|}$.

In [122], the problem (4.5.7)–(4.5.14) was considered and a single function $\psi(x, t)$ represents both initial and boundary conditions

$$T(x, t) = \psi(x, t), \quad (x, t) \in \partial^b Q_{t_*}, \tag{4.5.16}$$

where

$$\partial^b Q_{t_*} = \{(x, 0) : x \in (0, 1)\} \cup \{(0, t) : t \in (0, t_*)\} \cup \{(1, t) : t \in (0, t_*)\}.$$

It was proved that if $g(T) \in C^\beta(R)$, $0 < \beta < 1$, $\psi \in W_q^{2,1}(Q_{t_*})$, $q > 3$ and the following conditions are satisfied (any one out of Eqs 4.5.17, 4.5.18):

$$g(T) \leq 0, \quad T \leq m_1, \quad g(T) \geq 0, \quad T \geq m_2 \quad \text{for some } m_1, m_2 \in R, \tag{4.5.17}$$

$$|g(T)| \leq a_1|T| + a_2, \quad a_1 \text{ and } a_2 \text{ are constants,} \tag{4.5.18}$$

$$g(\psi|_{x=0}) = g(\psi|_{x=1}) = 0, \tag{4.5.19}$$

then a global classical solution exists such that $S(t) \in C^{1+\lambda/2}[0, t_*]$, $\lambda \in (0, 1)$. $W_q^{2,1}(Q_{t_*})$, $q \geq 1$ is the Sobolev space of functions $u(x, t)$ in the domain $Q_{t_*}(\bar{Q}_1 \cup \bar{Q}_2 \times (0, t_*))$ with bounded norm

$$\|u\|_{W_q^{2,1}(Q_{t_*})} = \left(\int_{Q_{t_*}} (|u|^q + |u_x|^q + |u_{xx}|^q + |u_t|^q) dxdt \right)^{1/q}. \tag{4.5.20}$$

Replace the condition (4.5.10) in problem (4.5.7)–(4.5.14) by the following kinetic condition:

$$T^\varepsilon(S^\varepsilon(t), t) = -\varepsilon \dot{S}(t), \quad \varepsilon > 0, \quad 0 < t < t_*, \tag{4.5.21}$$

where T^ε and S^ε are written in place of T and S to signify that both T and S now depend on ε. This problem has been considered in [123], and the results given in Proposition 4.5.2 have been established.

Proposition 4.5.2. *Let $T_0(x)$, h_S and h_L satisfy the following smoothness assumptions:*

$$T_0(x) \in C^1[0, S_0] \cap C^1[S_0, 1] \cap C[0, 1] \quad \text{and} \quad h_L(h_S) \in C^1(R) \cap L_\infty(R). \tag{4.5.22}$$

The consistency conditions at $x = 0$ and $x = 1$ for the initial temperature and boundary conditions are satisfied and the functions h_S and h_L do not change sign for $t > 0$. Under the above assumptions a unique classical solution $(T^\varepsilon, S^\varepsilon)$ (in the sense of Section 1.4.6) of Eqs (4.5.7)–(4.5.14) with Eq. (4.5.21) taken in the place of Eq. (4.5.10) exists for every $\varepsilon > 0$ and for some $t_*^\varepsilon > 0$. Either $t_*^\varepsilon = +\infty$ or $\min\{1 - S^\varepsilon(t_*^\varepsilon), S^\varepsilon(t_*^\varepsilon)\} = 0$.

Depending on the boundary conditions, $\dot{S}$ could be greater or less than zero. By considering a sequence of problems $\{T^{\varepsilon_n}, S^{\varepsilon_n}\}$, $\varepsilon_n > 0$, $n = 1, 2 \ldots$ and taking the limit $\varepsilon_n \to 0$, the existence of a weak solution has been established in [123] and it has been shown that $T(S(t), t) \to 0$ for a.a. $t \in (0, t_*)$.

Suppose the initial data is such that for some $S_1 \in [S_0, 1]$

$$T_0(x)(x - S_1) > 0, \quad x \in [0, 1], \ x \ne S_1, \ S_0. \tag{4.5.23}$$

If Eq. (4.5.23) is satisfied, then a supercooled liquid phase exists between stable solid and stable liquid phases. It has been proved in [123] that the simply connected supercooled liquid region disappears in finite time, after which the solution becomes a classical one. In Eq. (4.5.23), the degree of supercooling is not prescribed. It was pointed out earlier for a one-phase supercooled problem (cf. Proposition 4.4.1) that the negativity set $\{T_0(x) < -1\}$ is responsible for a blow-up (roughly speaking). The initial data given below gives rise to a discontinuity in the free boundary.

Let S_1^+ and $S_1^- \in (S_0, 1)$ be such that

$$T_0(x) < -l, \quad x \in (S_1^-, S_1^+), \tag{4.5.24}$$

$$T_0(x) > -l, \quad x \in (S_0, S_1^-) \cup (S_1^+, 1), \tag{4.5.25}$$

where l is the latent heat, and $l > 0$. Under suitable assumptions, it has been shown in [123] that the free boundary is smooth everywhere except at a point $t = \hat{t} < t_*$. At this point $S(t)$ may have a jump. $S(\hat{t} + 0) - S(\hat{t} - 0) > 0$ will be exactly equal to the length of the interval in which $T(x, \hat{t} - 0) \le -l$.

In the Neumann solution (1.3.11)–(1.3.16), the velocity of the interface (cf. Eq. 1.3.13) is infinite at $t = 0$ which seems to be inconsistent with the assumption of local thermodynamic equilibrium at a constant freezing temperature. If the kinetic condition (4.5.26) is incorporated in Eq. (1.3.5), $\rho_S = \rho_L$ and in the place of $\hat{l} = \{l + (C_L - C_S)T_m\}$, l is taken, then we get a problem considered in [123]. Let

$$T_S(S(t), t) = T_L(S(t), t) = -\varepsilon \dot{S}(t), \quad \varepsilon > 0, \ \dot{S} > 0. \tag{4.5.26}$$

Under suitable assumptions, the existence and uniqueness of the Neumann solution with the condition (4.5.26) and other changes have been proved. It has been shown that $T(x, t) \in C^\infty(Q_1) \cap C^\infty(Q_2)$ and $S(t) \in C^\infty(0, t_*)$, where $Q_1(Q_2) = \{x > 0, x - S(t) > 0(< 0), 0 < t < t_*\}$. $S(t) \ge \gamma t$ for $t \in (0, t_*)$, where γ is a positive constant. An analytic solution has been obtained which is validated by a numerical solution obtained by a finite-difference scheme [123]. An equation for the phase-change temperature has been obtained in [124]

by considering the entropy production in the interface, pressure-induced undercooling and viscosity-induced variations in the freezing temperature. A fairly general expression for the latent heat depending on the thermal expansion coefficient, temperature, pressure, etc., has also been obtained. In deriving phase-change temperature and latent heat expressions, nonequilibrium thermodynamical considerations have been used.

Dissolution of a spherical ice ball in supercooled water has been discussed in [125]. This one-dimensional radially symmetric spherical problem is closely related to a Stefan problem with modified Gibbs–Thomson relation. In [125], a weak solution has also been discussed. We give below only the classical formulation of the problem of dissolution of a solid ice ball of radius $S(t)$ in a supercooled liquid. Consider the following equations:

$$\frac{1}{r}\frac{\partial^2}{\partial r^2}(rT_i) = \frac{\partial T_i}{\partial t}, \quad i = S, L; \text{ in } Q_{t_*}^i, \tag{4.5.27}$$

$$T(r,0) = T_0(r) \leq 0, \quad 0 \leq r \leq r_0, \quad T_0'(0) = 0; \quad T_L(r_0,t) = T_1(t), \quad t > 0, \tag{4.5.28}$$

$$T_S(S(t),t) = T_L(S(t),t) = -\frac{1}{S(t)} + \beta\frac{dS}{dt}, \quad r = S(t), \ t > 0; \ S(0) = 1, \tag{4.5.29}$$

$$\frac{\partial T_S}{\partial r} - \frac{\partial T_L}{\partial r} = -l\frac{dS}{dt}, \quad \text{on } r = S(t), \ t > 0. \tag{4.5.30}$$

Here $\beta > 0$ is the relaxation parameter arising in the kinetic condition, the surface tension in Eq. (4.5.29) is taken unity and

$$Q_{t_*}^S = \{(r,t) : 0 < r < S(t); 0 < t < t_*, S(0) = 1\},$$
$$Q_{t_*}^L = \{(r,t) : S(t) < r < r_0; 0 < t < t_*, r_0 > 1\}.$$

It will be assumed that Eqs (4.5.27)–(4.5.30) have been suitably dimensionalized. In Eq. (4.5.29) both curvature effect and kinetic undercooling have been incorporated. Except β and l, all other parameters have been taken to be unity.

To discuss melting of ice in a supercooled liquid, the transformation

$$\hat{T} = rT(r,t) + 1 \tag{4.5.31}$$

is made which changes the problem (4.5.27)–(4.5.30) to the following problem:

$$\frac{\partial \hat{T}_i}{\partial t} = \frac{\partial^2 \hat{T}_i}{\partial r^2}, \quad r \in Q_{t_*}^i, \ i = S, L, \ t > 0, \tag{4.5.32}$$

$$\hat{T}(r,0) = \hat{T}_0(r), \quad r \in Q_{t_*}^L \cup Q_{t_*}^S \cup S(t); \quad \hat{T}_S(0,t) = 1, \ t > 0; \quad \hat{T}_L(r_0,t) = \hat{T}_1(t), \tag{4.5.33}$$

$$\hat{T}_i(S(t),t) = -\beta S(t)\dot{S}(t), \quad i = S, L, \tag{4.5.34}$$

$$\left[\frac{\partial \hat{T}}{\partial r}\right]_{S(t)+0}^{S(t)-0} = -lS(t)\dot{S}(t). \tag{4.5.35}$$

If $\beta = 0$ in Eq. (4.5.29), then we have only curvature effect in $T(S(t), t)$. Eq. (4.5.35) suggests that we have a Stefan problem with latent heat $-lS(t)$. Now consider the initial and boundary data such that we have a one-phase melting problem for $\hat{T}$. We consider the following formulation:

$$\hat{T}_S(0, t) = 1, \quad t > 0; \quad \hat{T}_S(S(t), t) = 0, \quad t > 0; \quad \hat{T}_S \geq 0, \quad r \in [0, 1], \quad t > 0, \tag{4.5.36}$$

$$\hat{T}_L(r_0, t) = 0, \quad \hat{T}_L \equiv 0, \quad \text{in } r \in (1, r_0), \quad t > 0. \tag{4.5.37}$$

In terms of $T_L(r, t)$, the initial temperature of the liquid is

$$T_L(r, 0) = -1/r, \quad 1 \leq r \leq r_0. \tag{4.5.38}$$

Note that the surface tension which was taken as unity in Eq. (4.5.29) is still present. As the initial temperature of the solid is greater than or equal to $T_L(r, 0)$, the ice ball with centre at $r = 0$ may dissolve partially in the supercooled water at least for a short time. To preserve the classical one-phase Stefan problem structure, we have $\hat{T}(S(t), t) = 0$ which requires that $\beta \to 0$. The key idea in the existence proof for Eqs (4.5.36)–(4.5.38) in which $\beta = 0$ is to consider a sequence of problems for $\beta_n > 0$, $n = 1, 2 \ldots$ and take the limit as $\beta_n \to 0$. This method of proof is generally employed to develop the proof for the case $\beta \to 0$. Under suitable assumptions about the data, a unique classical solution $(\hat{T}_S^\beta, S^\beta)$ exists with the monotonically decreasing free boundary S^β. Some interesting results of [125] are the following:

1. The classical solution of Eqs (4.5.27)–(4.5.30) exists and is unique for $\beta > 0$ and all time $t > 0$.

2. If $\beta = 0$ in Eq. (4.5.29), then the classical solution exists and is unique only locally in time.

3. There exists at least one weak solution for $\beta = 0$ with a monotone free boundary $r = S(t)$ for all time $t > 0$.

4. Nonexistence of the classical solution for the problem with $\beta = 0$ for all time $t > 0$ for certain types of initial data is possible in this one-phase problem. There exists at least one point $t = \hat{t}$ of the discontinuity of $S(t)$ such that

$$0 \leq S(\hat{t} - 0) < S(\hat{t} + 0)$$

or the continuous function $S(t)$ on a small time interval $(0, t_*)$ cannot be absolutely continuous on $(\hat{t}, t_*)$ and it maps some zero-measure set of $(\hat{t}, t_*)$ onto some set of $Q_{t_*}^S \cup Q_{t_*}^L$ with a strictly positive measure.

It turns out that the results for $\beta > 0$ are not the same as for $\beta = 0$. The kinetic condition acts as a regularizing factor in the dissolution of ice ball in the supercooled water whereas surface tension alone does not have the same effect.

The formulation given in Eqs (4.5.27)–(4.5.30) was considered in [126] also but with some minor changes in the region under consideration and some change in the boundary condition. We shall continue with the notations used in Eqs (4.5.27)–(4.5.35) with the change that $S(0) = S_0 < 1$ and $r_0 = 1$. The boundary condition at $r = 1$ could be any of the type given in Eqs (4.5.39), (4.5.40)

$$\hat{T}(1,t) = \Theta(t), \quad t > 0, \tag{4.5.39}$$

$$\hat{C}\hat{T}(1,t) = -\frac{\partial \hat{T}}{\partial r}(1,t) + \hat{T}(1,t) - 1, \quad t > 0. \tag{4.5.40}$$

Both Eqs (4.5.39), (4.5.40) are in nondimensional form. Eq. (4.5.40) is a boundary condition of the fifth kind (cf. Eq. 1.4.44). $\Theta(t)$ is the temperature of the thermostat and $\hat{C}$ is the specific heat of the thermostat. We shall call this changed problem, Problem (GP). Eq. (4.5.40) models the heat exchange between the thermostat and the body. Assume that

$$\hat{T}_0(r) \in C^1[0, S_0] \cap C^1[S_0, 1] \cap C[0, 1] \tag{4.5.41}$$

and the consistency conditions

$$\hat{T}_0(0) = 1, \quad \hat{T}(S_0) = 0, \quad \hat{T}_0(1) = \Theta(0) \tag{4.5.42}$$

are satisfied. The result stated in Proposition 4.5.2 can also be established for Problem (GP) (cf. [126]).

Asymptotic stability of stationary solutions of Problem (GP) was also studied in [126] and it was shown that under suitable assumptions the problem has one or two or three stationary solutions. One of them corresponds to the case in which the solid phase has melted completely. This solution is always asymptotically stable as $t \to +\infty$. The other two stationary solutions have nonempty solid regions. The solution with the largest radius for the solid is stable, the other is unstable.

A two-phase one-dimensional Stefan problem in the region $0 \le x \le 1$ with a kinetic condition of the form

$$T^- = T^+ = \varepsilon \dot{S}(t), \quad \text{at } x = S(t) \tag{4.5.43}$$

was considered in [127]. In Eq. (4.5.43), ε is a constant without sign restrictions. Similarly $\dot{S}(t)$ has no sign restrictions. T^+ is the temperature of the region to the right of $S(t)$ and T^- is the temperature of the region on the left of $S(t)$. There are no sign restrictions on T^+ and T^- and so superheating or supercooling may exist. $S(0) = S_0, 0 < S_0 < 1$. There are no sign restrictions on the initial and boundary data. The main result of this study is that introducing a kinetic term at the interface can prevent finite-time blow-up even if supercooling (superheating) exists. Under suitable assumptions on the initial and boundary data, the existence of a global-in-time solution has been proved using Schauder's fixed point theorem. Here *global-in-time solution* means that either $t_* = \infty$ and $0 < S(t) < 1, t < \infty, 0 < t \le t_*$ or $t_* < +\infty$ and $\lim_{t \to t_* -} S(t) = 0$ or 1. Uniqueness of the solution has also been proved. The solution of the classical Stefan problem can be retrieved by taking the limit $\varepsilon \to 0$ if correct sign restrictions are imposed on the initial and boundary data and the free boundary is assumed to be nondecreasing.

4.5.4 Multidimensional SSPs and Problems With the Modified Gibbs–Thomson Relation

The one-phase SSP in two and three dimensions without regularization by the Gibbs–Thomson condition has been studied in [128] with particular interest in the mechanism of cusp formation for interfaces that are initially smooth. The problem considered is as follows:

$$T_t = \nabla^2 T, \quad x \in \Omega(t) \subset R^N, \quad t > 0, \tag{4.5.44}$$

$$T(x, 0) = T_0(x) \leq 0, \quad \text{for } x \in \Omega(0), \tag{4.5.45}$$

$$T(x, t) = 0, \quad \text{for } x \in \partial\Omega(t), \quad t \geq 0, \tag{4.5.46}$$

$$\vec{V} \cdot \vec{n} = -\nabla T \cdot \vec{n}, \quad x \in \partial\Omega(t), \quad t \geq 0. \tag{4.5.47}$$

Here $N = 2, 3$, $\partial\Omega(t)$ is the boundary of $\Omega(t)$ which is a free boundary and $\vec{n}$ is the outward unit normal on this boundary. As discussed earlier in the one-dimensional case, the equation

$$c_t = \nabla^2 c - \chi_{\Omega(t)}, \quad x \in R^N, \quad t > 0, \tag{4.5.48}$$

where c stands for the concentration, is more suitable to handle a supercooled problem. $\chi_{\Omega(t)}$ is the *characteristic function* of $\Omega(t)$ which for each t takes the value unity if $x \in \Omega(t)$ and zero elsewhere. With the help of Baiocchi transformation [129], $c(x, t)$ can be defined as

$$c(x, t) = -\int_t^{S(x)} T(x, \xi) d\xi, \tag{4.5.49}$$

where the free boundary has been written as $t = S(x)$, $t > 0$, $S(x) = 0$ for $t = 0$ and $T(x, t)$ satisfies Eqs (4.5.44)–(4.5.47). We have

$$\nabla \cdot (\nabla c) = \int_{S(x)}^t \nabla \cdot (\nabla T) d\xi - \nabla(S(x)) \cdot \nabla T(x, S(x)) = \int_{S(x)}^t \frac{\partial T}{\partial t} d\xi + 1$$
$$= T(x, t) + 1 = c_t + 1. \tag{4.5.50}$$

In obtaining Eq. (4.5.50), the relation (4.5.51) has been used which can be derived as follows. Let $\Phi(x, t) = t - S(x) = 0$. On using Eqs (1.4.15), (1.4.25) in Eq. (4.5.47), we obtain

$$\nabla(S(x)) \cdot \nabla T(x, S(x)) = -1. \tag{4.5.51}$$

By differentiating Eq. (4.5.49), we get $c_t = T(x, t)$. In the one-dimensional Stefan problems, to prove the existence and uniqueness of solutions, fixed point arguments combined with classical 'parabolic regularity theory' can be used. In the multidimensional Stefan problems, there is lack of regularity in space at the free boundary which does not allow the fixed point arguments to be used. Suppose the free boundary $\partial\Omega(t) \in C^{m,\alpha}$ for each $t \geq 0$, m(integer) ≥ 0, $0 < \alpha < 1$ then $T(x, t)$ would be at most $C^{m,\alpha}$ in space by the classical regularity theory and then

$$\frac{\partial T}{\partial n} \in C^{m-1,\alpha} \tag{4.5.52}$$

in space. Solving Eq. (4.5.47) by 'characteristics' one would obtain at most $\partial\Omega(t) \in C^{m-1,\alpha}$ in a hypothetical fixed point argument. One way to overcome this difficulty is to regularize the supercooled problem by introducing curvature effects at the free boundary and write

$$T(x,t) = \varepsilon \mathcal{P}(\partial \Omega(t)),\tag{4.5.53}$$

where $\mathcal{P}$ is a regular second-order operator. By taking the limit $\varepsilon \to 0$, Eqs (4.5.44)–(4.5.47) can be obtained provided enough 'a priori' estimates can be proved.

A constructive approach has been adopted in [128] and a method has been described to obtain a short-time solution of the problem transformed in terms of $c(x,t)$. The manner in which cusps develop is described. By using perturbation analysis and matched asymptotic expansions, a mechanism of cusp formation is presented for interfaces that are initially smooth. Even small amount of undercooling can give rise to singularities.

A one-phase two-dimensional Stefan problem with kinetic condition has been considered in [130] in the region $\Omega_t \subset R^2 \times R^+$ where $\Omega_t = \{(x,y) : 0 < y < g(x,t), x \in R, 0 < t < t_*\}$, $y = g(x,t)$ is the equation of the free boundary, $g(x,0) = g_0(x) > 0, x \in R$. The free boundary conditions are

$$\nabla T \cdot \vec{n} = T \quad \text{and} \quad T = \vec{V} \cdot \vec{n} = g_t / (1 + g_x^2)^{1/2}.\tag{4.5.54}$$

The remaining part of the problem formulation consists of the heat equation and initial and boundary conditions are given as follows:

$$T_t = \nabla^2 T, \quad (x,y,t) \in \Omega_t,\tag{4.5.55}$$

$$T(x,y,0) = T_0(x,y); \quad T(x,0,t) = b(x,t).\tag{4.5.56}$$

Under suitable assumptions on the compatibility of initial and boundary conditions at $y = 0$, and at the initial position of the free boundary and some regularity conditions, the local-in-time existence and uniqueness of the classical solution have been proved using *Schauder's fixed point theorem*. It was observed that the introduction of curvature term in the temperature at the free boundary provides more regularity to the temperature than the kinetic condition alone.

A classical two-phase Stefan problem with the modified Gibbs–Thomson relation has been studied in [131] in a region $G \subset R^n, n \geq 2$. Let $G(t) = G \times \{t\}$ for $\forall t \in [0, t_*], G(t) = G_1(t) \cup G_2(t) \cup S(t)$, where $G_1(t)$ is the solid region, $G_2(t)$ is the liquid region and $S(t)$ is the phase-change interface separating solid and liquid regions. Let $G^{t_*} = \cup_{0 \leq t \leq t_*} G(t), i = 1, 2$, and $G_i^{t_*} = \cup_{0 \leq t \leq t_*} G_i(t)$ and $G^{t_*} = G_1^{t_*} \cup G_2^{t_*} \cup \Gamma$ where $\Gamma = \cup_{0 \leq t \leq t_*} S(t)$. On Γ and the parabolic boundary, we have

$$T = -\sigma \bar{K}_c - \beta \vec{V} \cdot \vec{n}, \quad \sigma > 0, \quad \beta > 0, \quad \text{on } \Gamma,\tag{4.5.57}$$

$$T(x,t) = g(x,t), \quad \text{on } \{G \times \{t = 0\}\} \cup \{\partial G \times [0, t_*]\},\tag{4.5.58}$$

$$S(0) = \Gamma_0.\tag{4.5.59}$$

Here $\vec{n}$ is the unit normal vector pointing from $G_1(t)$ to $G_2(t)$. Eqs (4.5.57)–(4.5.59) together with heat equations in the solid and the liquid regions and the Stefan condition at the interface completes the formulation of the problem. Thermal conductivities of the solid and the liquid phase are taken unequal. The main result of [131] is given by the following proposition.

Proposition 4.5.3. *Let*

$$g \in C^0 \left(\bar{G} \times [0, t_*] \right) \cap C^{2+\alpha} \left(\bar{G}_1(0) \times [0, t_*] \right) \cap C^{2+\alpha} \left(\bar{G}_2(0) \times [0, t_*] \right), \tag{4.5.60}$$

for some fixed $\alpha > 0$, $G(0) = G_1(0) \cup G_2(0) \cup \Gamma_0$. *Here* Γ_0 *is the boundary of an open set with*

$$\text{dist}(\Gamma_0, \partial G) > 0 \quad \text{and} \quad \Gamma_0 \in C^{3+\alpha}. \tag{4.5.61}$$

Assume that g and Γ_0 satisfy the compatibility conditions

$$g_t(x, 0) - K_i \nabla^2 g(x, 0) = 0, \quad x \in \partial G \cap \partial G_i(0), \quad i = 1, 2 \tag{4.5.62}$$

and

$$g(x, 0) = -\sigma \bar{K}_c(x) - \beta l \left[K_1 \frac{\partial g_1}{\partial n} - K_2 \frac{\partial g_2}{\partial n} \right] (x, 0), \quad x \in \Gamma_0, \tag{4.5.63}$$

where $g = g_i$ in $G_i(0)$, $i = 1, 2$, $\bar{K}_c(x)$ is the sum of the principal curvatures of Γ_0. If the above conditions are satisfied, then there exists a time $t_0 > 0$ (depending on Γ, σ and β) such that the Stefan problem with condition (4.5.57) admits a unique solution (T, Γ) for $t \in [0, t_0]$ and

$$T \in C^{2+\alpha, (2+\alpha)/2}(\bar{G}_1^{t_0}) \cap C^{2+\alpha, (2+\alpha)/2}(\bar{G}_2^{t_0}) \tag{4.5.64}$$

and

$$\Gamma \in C^{3+\alpha, (3+\alpha)/2}. \tag{4.5.65}$$

The key idea in proving the existence and uniqueness of the solution is that when translated to local coordinates, Eq. (4.5.57) is a quasi-linear parabolic equation on a manifold without boundary. For a given $T(x, t)$ solve Eq. (4.5.57) to obtain the velocity of the interface. This provides us with the interface Γ which can be used to solve the parabolic problem in the bulk with the Stefan condition on Γ. A new temperature function $\hat{T} = \mathcal{P}(T)$ is obtained. Using the regularizing character of the operator $\mathcal{P}$, it can be proved that $\mathcal{P}$ is a contraction on a small time interval. Neumann condition or mixed conditions can also be prescribed on the fixed boundary $\partial G \times [0, t_0]$.

The local-in-time existence of the solution of a more general two-phase Stefan problem with the modified Gibbs–Thomson relation has been proved in [132]. The parabolic operator in the heat equation is of the form

$$\mathcal{P}_j T_j = \left(\frac{\partial}{\partial t} - \nabla_x (A_J(x, t) \nabla_x) \right) T_j = f_j, \quad \text{in } G_J(t) \quad \text{for } \forall t \in [0, t_0], \ J = 1, 2, \tag{4.5.66}$$

and $0 \leq t \leq t_0$ is the time interval in which the solution exists. The domain $G_1(t) \in G \subset R^n$, $n \geq 2$ and $\partial G_1(t) = \Gamma(t) \subset G, \forall t \in [0, t_0]$ is the free surface. $G_2(t) = G \backslash \bar{G}_1(t), 0 \leq t \leq t_0 \cdot G_1$ and G_2 are solid and liquid regions, respectively

$$T_J = -\sigma(x, t) \bar{K}_c(x, t) - \alpha(x, t) \sigma(x, t) \vec{V} \cdot \vec{n}, \quad \text{on } \Gamma(t), \ J = 1, 2, \tag{4.5.67}$$

where $\alpha \geq 0$, and the unit normal $\vec{n}$ is pointing into the liquid. The problem formulation can be completed by adding Stefan condition and initial and boundary conditions to Eqs (4.5.66), (4.5.67). To prove the existence of the solution, the problem in time varying domains $G_J(t)$, $J = 1, 2$ is first converted into a problem in fixed domain $\Omega_J(0)$, $J = 1, 2$ by using *Hanzawa transformation* [133]. Then a local coordinate system is introduced in a neighbourhood of $\Gamma(0)$. Under suitable consistency conditions (see [132]) and the regularity of parameters and coefficients, an initial approximation of the solution of an auxiliary problem makes it possible to construct a classical solution of the given Stefan problem on $\Gamma(0)$. To apply Newton's method of successive approximations it is necessary to obtain conditions for the invertibility of the 'Frechet derivative' [22] on the initial approximation. Once a regularizer of the Frechet derivative is constructed, the existence of the solution in a very small time interval can be proved with the help of Newton's method.

Multidimensional one-phase and two-phase Stefan problems with Gibbs–Thomson relation have been discussed in [134] under the assumption that the surface tension ε is small. Although classical solutions have not been discussed, some of the observations made in [134] are interesting. Under the assumption that the classical Stefan problem with $\varepsilon = 0$ has a smooth free boundary and that its classical temperature solution $\hat{T}$ exists, an approximate solution of the Stefan problem with $\varepsilon \neq 0$ is taken as $\hat{T} + \varepsilon u$ (one-phase problem). The existence and uniqueness of the weak solution of the problem formulated for u has been proved. The free boundary of $\hat{T} + \varepsilon u$ has also been analysed. In the two-phase problem the perturbations are of the form $(\hat{T}_1 + \varepsilon u_1, \hat{T}_2 + \varepsilon u_2)$ where $\hat{T}_1 + \varepsilon u_1$ is the temperature of water region and $\hat{T}_2 + \varepsilon u_2$ is the temperature of ice surrounding the water region. Assuming that Gibbs–Thomson relation lowers the equilibrium temperature, the following conclusions have been drawn. In the one-phase problem, small surface tension decreases the water region for all small times and the small surface tension increases the water region for all large times provided the data are radial or close to radial. The results have been extended to general shapes. This observation is radically different in the two-phase problem in which the small surface tension decreases the water region for all times provided the data are radial or close to radial.

On the basis of physical arguments, it was mentioned earlier in Section 4.5.1 that surface tension has stabilizing effect on the growth of planar phase-change boundary. Investigation of stability or instability of perturbations of the planar phase-change boundaries is a vast subject (cf. [135, 136]) and requires rigorous mathematical treatment. We present here some simple results obtained in [137] on the morphological instability of the *similarity solution* of a one-dimensional Stefan problem in an infinite region. Consider the following two-dimensional one-phase problem of the solidification of a supercooled liquid:

$$T_t = \nabla^2 T, \quad S(x, y, t) \neq 0, \quad t > t_0, \quad (x, y) \in R^2. \tag{4.5.68}$$

On the free boundary $S(x, y, t) = 0$, we have

$$T = -\sigma \bar{K}_c \quad \text{and} \quad (\nabla T \cdot \nabla S) = S_t, \quad t > t_0, \tag{4.5.69}$$

$$\bar{K}_c = \left(|\nabla S|^2 \nabla^2 S - \frac{1}{2} \nabla(|\nabla S|^2) \cdot \nabla S \right) \Big/ (2|\nabla S|^3), \tag{4.5.70}$$

$$T(x, y, t_0) = T_0(x, y); \quad S(x, y, t_0) = S_0(x, y), \tag{4.5.71}$$

$$T_0(x) \to T_\infty \in (-1, 0) \quad \text{as } x \to \infty; \quad T_0(x) \to 0 \quad \text{as } x \to -\infty. \tag{4.5.72}$$

Consider a one-dimensional one-phase problem in the region $-\infty < x < \infty$ in which the region $x < 0$ is ice at the phase-change temperature $T \equiv 0$ and the region $x > 0$ is occupied by the supercooled water at $T = T_\infty$. A similarity solution of this one-dimensional problem can be easily obtained by following the procedure used to obtain the Neumann solution (cf. Eqs 1.3.11–1.3.13). Let this solution for $\sigma = 0$ be denoted by (T_1, S_1), where

$$
\left.
\begin{aligned}
T_1 &= T_\infty + 2\alpha \exp(\alpha^2)(1 - \text{erf}(x/(2\sqrt{t}))), \quad \text{for } x > 2\alpha\sqrt{t}, \\
&= 0, \quad x < 2\alpha\sqrt{t},
\end{aligned}
\right\}
\tag{4.5.73}
$$

$$
S_1(x, t) = (x - 2\alpha\sqrt{t}) = 0.
\tag{4.5.74}
$$

Here α is the root of the transcendental equation

$$
2\alpha \exp(\alpha^2) \int_\alpha^\infty \exp(-y^2)dy = -T_\infty.
\tag{4.5.75}
$$

This similarity solution is perturbed so that

$$
T_\varepsilon(x, y, t) = T_1 + \varepsilon u(x, y, t) + \text{O}(\varepsilon^2),
\tag{4.5.76}
$$

$$
S_\varepsilon(x, y, t) = S_1(x, t) + \varepsilon R(x, y, t) + \text{O}(\varepsilon^2).
\tag{4.5.77}
$$

As the phase-change boundary is no more planar after perturbation, we shall have a two-dimensional problem with the effect of surface tension included in the temperature at the free boundary as in Eq. (4.5.69). For linear stability analysis, T_ε and S_ε are substituted in Eqs (4.5.68)–(4.5.71) and the problem is reformulated in terms of u and R. The Fourier transform with respect to y of the equations yields one-dimensional time-dependent initial-value problems for different values of the transform parameter whose solutions are analysed for the stability analysis (cf. [137]). The linear stability analysis showed that if the surface tension is nonzero, then each perturbation mode with a nonzero wave number will be stable. However, the solution is unstable with respect to perturbations with a zero wave number limit point in their Fourier spectrum.

Concluding Remarks

The discussion in Sections 4.1–4.5 is focussed on some modelling and analysis aspects of supercooling. The phenomena of nucleation, conditions at the contact line of manifolds belonging to the fixed boundary of the domain and the free boundary, and the modelling of surface tension and kinetic condition are quite complicated. For further information references given in [54] are suggested. Surface tension can be taken into account by incorporating surface energy in the energy functional without introducing a sharp phase-change interface [138]. In [139], ideas and methods of the theory of minimal surfaces have been introduced as well as new estimates for time derivatives of noninteger order. Ideas and methods of the geometry of manifolds have been used in [140]. Landau–Ginzburg theory, which is the basis of SPF models, relies on general thermodynamic considerations. In the limit, Stefan problem with modified Gibbs–Thomson law is obtained. Assuming that the solution of phase-field equations exists, an asymptotic solution of the phase-field equations has been constructed in [141] and the existence of its smooth solution has been proved.

4.5.5 Weak Formulation With Supercooling and Superheating Effects

The enthalpy equation (4.2.2) can be written as

$$C_P \frac{\partial T}{\partial t} + l \frac{\partial \chi}{\partial t} = \nabla \cdot (K(T)\nabla T), \quad \text{in } \Omega_* = \Omega \times (0, t_*), \ \Omega \subset R^3, \tag{4.5.78}$$

$$\chi \in H_g(T - T_m). \tag{4.5.79}$$

Here $K(T) = K_S T$, $T < T_m$ and $K(T) = K_L T$, $T > T_m$ and H_g is the Heaviside graph defined in Eq. (4.3.45). χ is the liquid fraction present in any phase. In the classical Stefan problem $\chi = 1$ in the liquid phase and $\chi = 0$ in the solid phase. If the mushy region is present, then $\chi \in [0, 1]$. Eq. (4.5.78) holds in the distributional sense. We shall now include supercooling and superheating effects in the weak formulation given by Eqs (4.5.78), (4.5.79). If the interface is not at the equilibrium temperature T_m, then the condition $T = T_m$ at the interface in the absence of curvature effects is replaced by the kinetic condition

$$\dot{S}(t) = \beta(T(S(t), t)), \tag{4.5.80}$$

where $\beta : R \to R$ is continuous and increasing and $\beta(0) = 0$. This represents supercooling or superheating effects due to the phase-change velocity (kinetic condition). The standard Stefan problem is then obtained in the limit as $\beta'(0) \to +\infty$ (expand β in powers of T). For small departures from the equilibrium temperature, the melting or solidification rate is proportional to the departure [42]. When a mushy region is present, i.e. when $\chi \in [0, 1]$ and χ is considered a function of x and t, Eq. (4.5.79) should be replaced by a relaxation law for χ of the form [101]

$$\alpha \frac{\partial \chi}{\partial t} + H_g^{-1}(\chi) \ni \beta(T - T_m), \quad \text{in } \Omega_*, \tag{4.5.81}$$

where α is a positive constant, $\chi = \chi(x, t)$, $(x, t) \in \Omega_{t_*}$ and the term on the r.h.s. of Eq. (4.5.81) is an approximation of the term on the r.h.s. of Eq. (4.5.80). In Eq. (4.5.81), there is no diffusion of χ. It has been assumed that the phase transition is much faster than the heat diffusion. In the classical Stefan problem the phase-change is driven by the release or absorption of latent heat at the interface. In the relaxation model (4.5.81), the latent heat released or absorbed is diffused into the system. The relation (4.5.81) accounts for the movement of the interface through the mushy region in the weak sense.

As mentioned earlier, in the metallurgical literature concerning solidification of a pure metal, there are two basic modes of solidification, viz., *directional solidification* and *equiaxed solidification*. In the directional solidification, which is also called columnar growth, the kinetic law (4.5.80) is considered at the phase-change boundary and the classical formulation is used. In the equiaxed solidification or phase relaxation model, a weak formulation is considered using Eqs (4.5.78), (4.5.79). In casting, 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 [142] and a large number of references reported there).

In [101], the existence and uniqueness of weak solutions of several Stefan problems with supercooling/superheating effects have been discussed using the theory of nonlinear

semigroups of contractions. These weak formulations correspond to: (i) problems of phase relaxation in homogeneous systems (generalized to heterogeneous systems) in which energy equation is written using nonequilibrium thermodynamics, (ii) Stefan problems with phase relaxation and (iii) wave propagation for heat. In [101, 102] only kinetic condition has been considered.

Weak formulation of the Stefan problem with surface tension has been considered in [143]. By coupling the heat equation with the Euler's equation of a nonconvex functional (which represents the Gibbs free energy), two weak formulations are given and existence of the solution is proved for each one.