

## Chapter 2

# Thermodynamical and Metallurgical Aspects of Stefan Problems

## 2.1 THERMODYNAMICAL ASPECTS

Several generalizations and extensions of the two-phase problem (1.4.4)–(1.4.8) are possible but before dealing with them, we give some definitions. Many terms like equilibrium temperature, thermal conductivity, latent heat, enthalpy, etc., have been used earlier without defining or explaining them for the reason that greater concern was shown for the mathematical formulation. Some thermodynamical aspects of Stefan problems will be discussed in this section.

### 2.1.1 Microscopic and Macroscopic Models

A system is called *microscopic* if it is of ‘small dimensions’, roughly of the size of an atom or a molecule, i.e. of the size of  $10^{-10}$  m. In a *microscopic model*, thermal, mechanical or chemical phenomenon is studied at an atomic or molecular level. In a *macroscopic model*, the system is ‘large enough’ of the order of  $1\text{ }\mu\text{m}$ , be visible with a microscope using ordinary light. A macroscopic system consists of large numbers of atoms or molecules. There is an important difference between a microscopic model and a macroscopic model. In the microscopic model, the description of an individual particle motion/action, even if available would not disclose the gross behaviour/properties of the system. For example, it is a striking fact, and one which is difficult to understand in microscopic detail that simple atoms forming a gas can condense abruptly to form a liquid with very different properties.

It is well known that a transport phenomenon whether it is electrical, heat or mass transfer, occurs due to changes in the energy levels of atoms or molecules. Imagine applying Newtonian laws of motion to  $10^{20}$  molecules and obtaining information for each molecule in a transport phenomenon such as heat transfer. It is an awesome task. All the mathematical formulations discussed earlier are based on macroscopic modelling. Does it mean that microscopic modelling is not required? However complicated, microscopic models cannot be totally discarded. Kinetic theory of matter (cf. [35, 36]) applies the laws of mechanics to individual molecules of a system and enables one to calculate, for example, the numerical values of heat capacities, heats of transformation and viscosity. These parameters can be

explicitly defined in a macroscopic model, but their numerical values can be obtained only on the basis of a molecular model. As stated earlier some of the equations of mathematical physics, for example, the heat equation can be easily derived on the basis of a microscopic model.

The advantage of the macroscopic model or a continuum hypothesis, and in which we are interested is that the gross behaviour of the system can be studied and laws of Newtonian mechanics can be applied to the bulk matter. An approach more general than macroscopic modelling is of statistical thermodynamics which, ignores the detailed consideration of molecules as individuals, and applies statistical methods to find the distribution of very large number of molecules that make up a macroscopic piece of matter over energy states of the matter. The equations of conservation of mass, momentum and energy arising in continuum mechanics can be obtained as particular cases of the Boltzmann equation [36].

Both kinetic theory and statistical thermodynamics were first developed on the assumption that the laws of mechanics deduced from the behaviour of matter in bulk, could be applied without change to particles like molecules and electrons. As science progressed, it became evident that at least in some respects this assumption was not correct, that the conclusions drawn from it by logical methods did not agree with experimental facts. For example, experiments suggest that the specific heat of many solids at constant volume approach the Dulong–Petit [35] value of  $3R$  ( $R$  is universal gas constant) at high temperatures, but decreases to zero at very low temperatures. This behaviour of solids can be explained with the help of a quantum mechanics approach. The failure of small-scale systems to obey the same laws as large-scale systems led to the development of quantum theory and quantum mechanics. Statistical thermodynamics is best treated today from the view point of quantum mechanics. On a microscopic scale classical mechanics does not apply and must be replaced by quantum mechanics. For further details of quantum theory, the reader is referred to [35–37].

### 2.1.2 Laws of Classical Thermodynamics

We shall be dealing here mostly with equilibrium thermodynamics. Thermodynamics is the study of energy and its transformation. There are many different types of energy but most studies of thermodynamics are primarily concerned with two forms of energy: heat and work. Thermodynamics deals with the macroscopic properties of matter and is an empirical science. It is developed on a small number of principles which are generalizations made from experience.

*Thermodynamic equilibrium:* When a system is in thermal, mechanical and chemical equilibrium, it is said to be in *thermodynamic equilibrium*. In thermal equilibrium, the temperature will be the same at all points of the system. In mechanical equilibrium, all motions, expansions or contractions of the system are absent. Note that atoms are still in motion. When all the chemical reactions stop then the system is in chemical equilibrium.

*Reversible and quasi-static process:* A process is called reversible if the initial state of the system can be restored with no observable effects in the system and its surroundings. If a process is not reversible, it is called irreversible. If a process is carried out in such a way that at any time the system departs only infinitesimally from the equilibrium state it is called a quasi-static process.

### First Law of Thermodynamics

*Internal energy* (internal heat energy) of a system is the sum of all the individual kinetic energies of motion and energies of interaction (potential energies) of the particles in the system. Internal energy can be transformed to do work and produce heat. One form of the first law of equilibrium thermodynamics is

$$dU = d'Q - d'W. \quad (2.1.1)$$

Here  $dU$  is the change in the internal energy of the system from equilibrium state  $a$  to another equilibrium state  $b$ ,  $d'Q$  is the heat flow into the system during the change of state and  $d'W$  is the work done by the system when the system changes its equilibrium state from  $a$  to  $b$ . The dash indicates that the quantities are not exact differentials. Internal energy is a state property, i.e. internal energy in state  $b$  does not depend on the process by which the system has been brought from state  $a$  to state  $b$ .  $dU$  is an exact differential but not  $d'Q$  and  $d'W$ . It can be easily shown that work is path dependent and so is heat flow [35]. Eq. (2.1.1) holds for both reversible and irreversible processes.

### Second Law of Thermodynamics: Entropy

Some changes in a system can take place only in one direction. Consider an isolated system in which a body at temperature  $T_1$  is in contact with a heat reservoir at temperature  $T_2 > T_1$ . Heat will flow from the reservoir to the body and raise its temperature to  $T_2$ . Is it possible for the body to cool down to temperature  $T_1$  by releasing heat to the reservoir? The change in this direction is not possible. It may be noted that the total energy of the system consisting of the body and the reservoir is conserved even if a reverse change takes place. Therefore if we are looking for some property of the system whose change can tell us the direction in which the reverse change is possible, then it cannot be energy. This property of the system is called *entropy*, denoted by  $\hat{S}$  and defined as

$$d\hat{S} = \hat{S}_2 - \hat{S}_1 = \int_1^2 \frac{d'Q}{T} \quad (\text{reversible changes}). \quad (2.1.2)$$

Here 1 and 2 are the two equilibrium states of a system. Entropy is defined only for reversible processes. The *second law of thermodynamics* states that processes in which the entropy of an isolated system (i.e.  $dQ = 0$ ) would decrease do not exist. Specific entropy (entropy per unit mass) will be denoted by  $\hat{s}$ .

If hot water is mixed with cold water, then the entropy of the cold water will increase more than the decrease in the entropy of the hot water which can be checked from Eq. (2.1.2). So there will be an increase in the entropy of the system consisting of both cold and hot water. This tells us that heat cannot flow from cold water to hot water as decrease in the entropy of an isolated system is not possible. Unlike energy or momentum, entropy is not conserved. The first law of thermodynamics states that energy can neither be created nor destroyed and the second law states that entropy cannot be destroyed but it can be created. The process is called *isentropic* if the entropy of the system does not change during the process.

### 2.1.3 Some Thermodynamic Variables and Thermal Parameters

*Specific heat capacity or specific heat:* If no phase-change takes place in a process, then the heat capacity  $\hat{C}$  at any temperature is defined by the equation

$$d'Q = \hat{C}dT, \quad (2.1.3)$$

where  $d'Q$  is the quantity of heat added to the system which changes its temperature by  $dT$ . The process could be reversible or irreversible. If the volume of the system does not change in the process, then  $\hat{C}$  is denoted by  $\hat{C}_V$  and is called heat capacity at constant volume. At constant volume,  $dV = 0$ . From Eq. (2.1.1), we obtain

$$d'Q = dU + PdV = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]dV = \left(\frac{\partial U}{\partial T}\right)_V dT, \quad (2.1.4)$$

where the only work done is by the pressure  $P$  in changing the volume. From Eq. (2.1.3), we get

$$\hat{C}_V = \left(\frac{\partial U}{\partial T}\right)_V. \quad (2.1.5)$$

It may be noted that  $Q$  is not a function of temperature. Therefore  $\hat{C}$  is not the derivative of  $Q$  with respect to  $T$  but is only the ratio of  $d'Q$  and  $dT$  or the ratio of very small amount of heat supplied and the change in the temperature.

A *specific value* of an *extensive property* (a property such as energy which depends on the mass) is its value per unit mass. *Specific heat* is defined as the heat capacity per unit mass and will be denoted by  $C$ .

*Enthalpy:* If the pressure  $P$  does not change in the process, then from Eq. (2.1.1), we get

$$dU = d'Q - PdV. \quad (2.1.6)$$

Also

$$dU + PdV = dU + PdV + VdP = dU + d(PV) = d(U + PV). \quad (2.1.7)$$

Let  $H = U + PV$ , where  $P$  is constant.  $H$  is called *enthalpy* and *specific enthalpy* will be denoted by  $h$ .  $H$  is a function of state, or a *thermodynamical property*. In this volume,  $H$  has also been used for enthalpy per unit volume. If a thermodynamic quantity depends only on the state of the system and not on the process by which it has been brought to that state, then it is called a thermodynamical property. Temperature and pressure are examples of thermodynamical properties. From Eqs (2.1.6), (2.1.7), we have

$$dH = dQ = \hat{C}_P dT \quad (2.1.8)$$

or

$$\hat{C}_P = \left(\frac{\partial H}{\partial T}\right)_P. \quad (2.1.9)$$

Here  $\hat{C}_P$  is the heat capacity at constant pressure.

From the relation  $dH = dQ$  (at constant pressure), it is clear that enthalpy can be regarded as the heat content of the system. A positive  $\Delta H$  (change in  $H$ ) means that heat is absorbed while a negative  $\Delta H$  means that heat is released.

*Gibbs free energy and Helmholtz free energy:* We now ask ‘Is it possible to describe the thermal equilibrium of a system in terms of some property of the system itself even if it is in contact with surroundings’? A system and its surroundings together is called a ‘universe’. Universe is considered to be isolated and closed. For an isolated system,  $d'Q = 0$  and so  $d\hat{S} = 0$ . Let  $d\hat{S}$  and  $d\hat{S}_*$  be the changes in the entropies of the system and its surroundings, respectively, then from the second law of thermodynamics

$$(d\hat{S} + d\hat{S}_*) \geq 0. \quad (2.1.10)$$

Let the system absorb some heat  $d'Q$  from its surroundings so that the internal energy of the system changes from  $U$  to  $U + dU$  and the system does some work  $d'W = PdV$  in a ‘PVT system’. If  $T$  is the temperature of the system and its surroundings, then

$$d\hat{S}_* = -d'Q/T \quad \text{and} \quad (d\hat{S} - d'Q/T) \geq 0. \quad (2.1.11)$$

Substituting  $d'Q$  from Eq. (2.1.1) in Eq. (2.1.11), we get

$$dU + PdV - Td\hat{S} \leq 0. \quad (2.1.12)$$

All the quantities in Eq. (2.1.12) belong to the system. In any reversible process between two equilibrium states,  $d\hat{S} + d\hat{S}_* = 0$  and so

$$dU + PdV - Td\hat{S} = 0. \quad (2.1.13)$$

If  $P$  and  $T$  are constant, then

$$d(U + PV - T\hat{S}) = dU + PdV - Td\hat{S} = 0. \quad (2.1.14)$$

Therefore, the quantity  $U + PV - T\hat{S}$  is a function of the state of the system. It is called *Gibbs free energy* denoted by  $G$  and

$$G = U + PV - T\hat{S} = H - T\hat{S}, \quad H = U + PV. \quad (2.1.15)$$

Note that  $G$  is the free energy of the system and not the free energy per unit volume. Interestingly in deriving Eq. (2.1.15) we had assumed that the process is reversible. But  $G$  is a function of the state as all the quantities on the r.h.s. of Eq. (2.1.15) are functions of state. It does not matter whether the state of the system is changed by a reversible process or by an irreversible process.

Eq. (2.1.15) is very general and applies to a system of any nature. The process may be a change of state, or a change of phase, or a chemical reaction. Suppose the temperature of the system rises by an amount  $dT$  under constant pressure. When the system changes from one equilibrium state to another then from Eq. (2.1.15), we get

$$dG = dH - Td\hat{S} - \hat{S}dT. \quad (2.1.16)$$

From Eq. (2.1.3),  $dQ = \hat{C}_p dT$  (under constant pressure  $d'Q = dQ$ ) and therefore from Eq. (2.1.2)

$$d\hat{S} = \hat{C}_p dT/T. \quad (2.1.17)$$

Since  $dH = dQ = \hat{C}_p dT$ , we have

$$dG = -\hat{S}dT. \quad (2.1.18)$$

The free energy decreases with the rise in temperature at constant pressure. The Gibbs free energy is the most useful of all thermodynamical properties and provides a practical criterion for a system to be in thermodynamical equilibrium. If a system is in thermodynamical equilibrium, then  $dT = 0$  and

$$dG = 0. \quad (2.1.19)$$

Out of the infinitely many states in which a system can exist, the equilibrium state is the one whose free energy does not change in any process which is carried out under constant pressure and constant temperature.  $dG = 0$  also implies that in an equilibrium state, free energy would be minimum.

Let us now consider a system at constant temperature and constant volume. It is easy to see that

$$d(U - T\hat{S}) = dU - Td\hat{S} = 0. \quad (2.1.20)$$

The quantity  $F = U - T\hat{S}$  is called *Helmholtz free energy*.  $F$  is also a function of state and plays the same role at constant temperature and constant volume as Gibbs free energy plays at constant temperature and pressure.  $dF$  can be expressed as

$$dF = -\hat{S}dT - PdV. \quad (2.1.21)$$

*Latent heat:* When a solid metal piece is heated, the temperature rises and reaches an equilibrium temperature  $T_m$  (see Section 2.2.1). When more heat is supplied, the heat is first absorbed without raising the temperature of the piece. The heat so absorbed is called latent heat of melting. It is measured in terms of per unit mass and is the ratio of the heat absorbed and the mass  $m$  undergoing the change of phase. Why is heat absorbed? In solid metals, the free atoms are closely packed. Atomic arrangement is disordered in liquids in comparison to that in solids. So the latent heat of fusion (or melting) is the energy required to pull the atoms apart to the more openly packed structure of the liquid [38]. In general when a phase changes isothermally from solid to liquid or liquid to vapour or solid to vapour, the system absorbs heat. The heat absorbed in these three transformations is called latent heat of fusion, latent heat of vaporization and latent heat of sublimation, respectively. When a liquid solidifies latent heat is released. Latent heat released per unit mass is taken as positive, and is denoted by  $l$ . Latent heat of solidification is the negative of the latent heat of fusion.

*Thermal conductivity:* Thermal conductivity is a transport property and is not a function of state. Transport of heat energy takes place by molecular motion/vibration and is called heat conduction. Heat conduction in equilibrium thermodynamics takes place according to an empirical law called the law of Fourier's heat conduction. For isotropic bodies this law is given by Eq. (1.3.8) and for anisotropic bodies by Eq. (1.4.9).

### 2.1.4 Equilibrium Temperature: Clapeyron's Equation

*Melting or freezing temperature:* The free energy curves versus temperature (pressure constant) for solid and liquid phases of a metal are given in Fig. 2.1.1. Since free energies of the two phases are the same at the temperature  $T_m$ , the two phases can stay in equilibrium at  $T_m$  as no exchange of free energy can take place.  $T_m$  is called equilibrium temperature.  $T_m$  is also called melting or freezing temperature. It can be called an *ideal equilibrium temperature* as the phase-change takes place at  $T_m$  under ideal conditions which ensure that the phase-change boundary is planar. In alloys phase-change takes place over a temperature range. If the temperature of the liquid is less than  $T_m$ , the liquid is called *supercooled*. It is clear from Fig. 2.1.1 that for  $T < T_m$ , the free energy of the solid is less than the free energy of the liquid. Therefore solid phase is a stable phase for  $T < T_m$  and supercooled liquid is not a stable phase.

For a solid, the specific enthalpy  $h$  is given by

$$h = C_S T, \quad T < T_m. \quad (2.1.22)$$

For a liquid

$$h = C_L T + l, \quad l > 0; \quad T > T_m. \quad (2.1.23)$$

At  $T = T_m$ ,

$$h \in [C_S T_m, C_L T_m + l]. \quad (2.1.24)$$

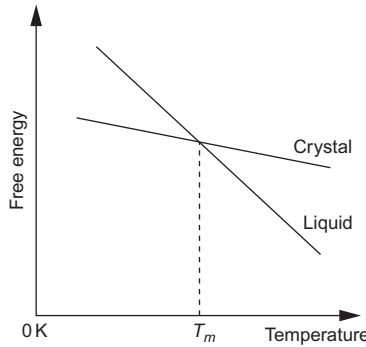


Fig. 2.1.1 Free energy versus temperature.

From Eq. (2.1.15),  $\Delta H = T_m \Delta \hat{S}$  as  $\Delta G = 0$  at  $T = T_m$ , where  $\Delta H$  and  $\Delta G$  stand for the difference between their values in the two phases at  $T = T_m$ . Therefore

$$\Delta \hat{S} = \frac{l + (C_L - C_S)T_m}{T_m} = \frac{\hat{l}}{T_m}, \quad (2.1.25)$$

where  $\Delta \hat{S}$  is the specific entropy of the liquid minus the specific entropy of the solid at  $T = T_m$ .

*Clapeyron's equation:* When two phases have different specific volumes their temperature of mutual equilibrium depends on the pressure as the phase-change causes work  $PdV$  to be done. Let  $G_1(T, P)$  and  $G_2(T, P)$  be the Gibbs free energies of the solid and liquid phases, respectively. Since the phases are in equilibrium

$$G_1(T, P) - G_2(T, P) = 0 \quad (2.1.26)$$

or

$$\left( \frac{\partial G_1}{\partial T} - \frac{\partial G_2}{\partial T} \right) dT + \left( \frac{\partial G_1}{\partial P} - \frac{\partial G_2}{\partial P} \right) dP = 0.$$

On using the definitions of  $G_1$  and  $G_2$  and Eq. (2.1.25), we obtain

$$\frac{dP}{dT} = \frac{l + (C_L - C_S)T_m}{(V_L - V_S)T_m}, \quad (2.1.27)$$

where  $V$  stands for the volume and subscripts  $L$  and  $S$  for liquid and solid, respectively.

## 2.2 SOME METALLURGICAL ASPECTS OF STEFAN PROBLEMS

### 2.2.1 Nucleation and Supercooling

It is a common experience that when most liquids are cooled sufficiently, they become solid in course of time. A liquid metal normally solidifies by crystallization. In addition to the solid state, metals also exist in a glassy or an amorphous solid state, a state which is hard but not crystalline. The first step in the growth of a crystal is *nucleation*. A small nucleus appears in the liquid phase which then grows by the addition of more material from the liquid phase. The formation of a rain drop in a cloud is a familiar example.

The theory of 'nucleation' is important not only in crystal growth but also in understanding supercooling/superheating and supersaturation effects. Some authors use the term *undercooling* in the place of supercooling. A nucleus may form at the surface of the mould or inside the melt. When the probability of forming a nucleus is the same anywhere in the melt, then the system is in a state suitable for *homogeneous nucleation*. If some sites are more suitable for nucleation than others, then the system is in a state suitable for *heterogeneous nucleation*. In nature most nucleations occur heterogeneously. For heterogeneous nucleation we refer the reader to [39].

How does nucleation occur? A phase transformation involves rearrangement of atoms and requires some irreversible departure from equilibrium. Phase transitions are driven by thermal fluctuations and in liquid metals, random fluctuations may create minute crystalline regions called 'clusters' or 'embryos' even at temperatures higher than  $T_m$ . On this already existing new phase which has grown randomly some more material of the new phase should grow for a crystal formation. Some sites such as rough surfaces of the mould, foreign bodies in the melt and seeds of the new phase added to the melt help the process of nucleation. Further details of heterogeneous nucleation or even homogeneous nucleation are too complicated to be presented here.



For a nucleus to grow, some work has to be done by the system which results in a change in the free energy  $\Delta G$  (per unit volume) which is the difference between the total free energy of the new phase (solid) and the total free energy of the old phase (liquid). Total free energy is the sum of the bulk energy and the surface energy, and is given by

$$\Delta G = r^3 \Delta G_V + \alpha r^2 \sigma, \quad (2.2.1)$$

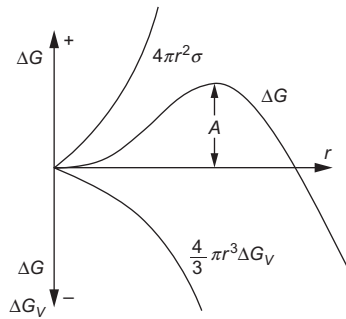
where  $r$  is the linear dimension of the nucleus and  $r^3$  its volume,  $\Delta G_V$  is the change in the bulk free energy of the volume,  $\alpha r^2$  is the surface area of the nucleus and  $\sigma$  is the surface energy per unit area.  $\sigma$  is generally positive.  $\Delta G_V$  is negative as the enthalpy of the liquid is greater than that of the solid. When the radius of the nucleus is very small, the second term on the r.h.s. of Eq. (2.2.1) dominates the first ( $\sigma$  is large when the nucleus is very small) term making  $\Delta G$  positive.  $\Delta G$  reaches its maximum when at  $r = r_0$  (see Fig. 2.2.1) and

$$\left. \frac{d(\Delta G)}{dr} \right|_{r=r_0} = 0. \quad (2.2.2)$$

Using Eq. (2.2.1) in Eq. (2.2.2), we obtain

$$r = r_0 = -2\alpha\sigma/(3\Delta G_V) \quad \text{and} \quad A = \Delta G|_{r=r_0} = \frac{4\alpha^3\sigma^3}{27(\Delta G_V)^2}. \quad (2.2.3)$$

Since at equilibrium  $\Delta G_V = 0$ ,  $\Delta G$  becomes very large near  $r = r_0$ . The nucleus cannot grow beyond  $r = r_0$  until this large energy barrier is crossed, for example, by artificial seeding with the fragments of the new phase. Once this barrier of energy is crossed,  $\Delta G$  starts decreasing and nuclei are formed when  $\Delta G$  is negative. The critical size  $r = r_0$  of the nucleus corresponds to an unstable equilibrium between the nucleus and its parent phase;  $\Delta G$  makes larger one grow and smaller one shrink.



**Fig. 2.2.1**  $\Delta G$ ,  $\Delta G_V$  and surface energy versus  $r$ .

*Supercooled state:* A state in which the temperature of a liquid is below the ideal equilibrium temperature  $T_m$  is called a supercooled state and the liquid is said to be supercooled. If the temperature of the solid is greater than  $T_m$ , the solid is said to be *superheated*. It may

be mentioned that the term supercooling defined here is different from the *constitutional supercooling* which arises in alloy solidification and in which the freezing temperature may decrease with the rise in concentration.

### Degree of Supercooling

For simplicity the formation of a single nucleus in homogeneous nucleation will be considered. Let  $T$  be the nucleation temperature. From Eqs (2.1.18), (2.1.25), we have

$$\frac{d(\Delta G_V)}{dT} = -\Delta \hat{S} = -\frac{\Delta H}{T} = \frac{l_m}{V_m T_m}. \quad (2.2.4)$$

Here  $G_V$  is the free energy per unit volume. It has been assumed in Eq. (2.2.4) that  $C_S = C_L$ , a small change in the entropy due to a temperature change can be neglected and  $T_m$  can be used in the place of  $T$ .  $l_m$  is the latent heat per mole and  $V_m$  is the molar volume. The ‘mole’ or the ‘mole number’ of a substance is defined as the ratio of its mass and the molecular weight and the ‘molar volume’ is the ratio of volume and the mole number. Using Taylor’s series expansion for  $\Delta G_V$ , we obtain

$$\begin{aligned} (\Delta G_V)|_T &= (\Delta G_V)|_{T_m} + (T - T_m) \left. \frac{d(\Delta G_V)}{dT} \right|_{T_m} + \cdots = -(T_m - T) \left. \frac{d(\Delta G_V)}{dT} \right|_{T_m} \\ &= -\frac{(T_m - T)l_m}{V_m T_m}. \end{aligned} \quad (2.2.5)$$

In deriving Eq. (2.2.5) we take  $(\Delta G_V)|_{T_m} = 0$  as at  $T = T_m$  the bulk free energies of solid and liquid phases are the same and higher order terms have been neglected. If  $T < T_m$  in Eq. (2.2.5), then  $(\Delta G_V)_T$  is negative. For large radius of the nucleus,  $\Delta G$  can be taken to be equal to  $\Delta G_V$  as the second term in Eq. (2.2.1) is very small. If the phase-change from liquid to solid takes place at a temperature lower than  $T_m$ , then the liquid is supercooled and  $(T_m - T)$  gives the degree of supercooling. Note that  $\Delta G$  is negative, which it should be for a crystal growth. If a system exists in a state of its lowest free energy, then the system is in a stable state and it can remain in this state for a long time. However, systems often exist for long times in states not of lowest free energy, for example, a mixture of oxygen and hydrogen gases can stay unchanged at room temperature even though the stable state is water. Such systems are said to be *metastable*. Supercooled liquid and superheated solids are in metastable states and if they get some extra energy to rearrange a group of atoms into a next and more stable phase, the phase-change to a stable phase will take place. The stable state for a supercooled liquid is solid and for a superheated solid, it is liquid. The extra energy can be provided to the supercooled liquid, for example, by artificial seeding. During solidification, latent heat is released by the liquid which warms up the growing crystal and the solid–liquid interface attains the temperature  $T_m$  (see Fig. 2.3.7).

Supercooling is generally small but can be as large as  $0.2T_m$ . For typical metals  $T_m \sim 1000\text{--}2000$  K. It may be noted that  $T_m$  is actually an ideal freezing temperature as the phase-change from liquid to solid generally takes place at a temperature lower than  $T_m$ . This is because of the effect of interface curvature and the kinetic undercooling which are discussed in Section 2.2.2.

## 2.2.2 The Effect of Interface Curvature

In the crystallization of a pure metal, at the interface between nucleated crystal and its melt, there is considerable activity amongst the atoms. This is because of the small amount of *activation energy* required to change the phase. In simple words, activation energy can be described as the least amount of energy required to change a metastable phase to a new and more stable phase. Some atoms break away from the crystal at the surface to join the liquid and some atoms in the liquid crystallize on the surface and become part of the crystal. If the rates of these two opposing processes are equal, then the surface is at the crystal-liquid equilibrium temperature. This equilibrium temperature need not be the ideal equilibrium temperature  $T_m$ . If the surface of the crystal is curved, and the centre of curvature lies inside the crystal, then on an average the atoms at the surface are less surrounded by neighbouring atoms of the crystal than otherwise and their escape tendency into the liquid increases. Less energy is required for a phase-change and phase-change takes place at a lower temperature. The equilibrium temperature is lower than the ideal value  $T_m$ , refer [40]. Conversely, if the centre of curvature lies outside the crystal, then the equilibrium temperature will be higher than  $T_m$ . These effects are small unless radius of curvature is small. The deviation  $\Delta T$  from the ideal equilibrium temperature  $T_m$  (which is the temperature of a planar phase-change interface) is given by

$$\Delta T = T_m^c - T_m = \bar{K}_c \Gamma_0 = \frac{\sigma \bar{K}_c T_m V_m}{l_m}, \quad (2.2.6)$$

where  $T_m^c$  is the new equilibrium temperature due to the curvature effect,  $\bar{K}_c$  is the sum of the principal curvatures of the curved surface,  $\sigma$  is the surface energy per unit area and  $l_m$  is the latent heat per mole. Note that the curvature  $\bar{K}_c$  and the constant  $\Gamma_0$  are defined in such a way that a positive undercooling, i.e. a decrease in the equilibrium temperature is associated with a portion of solid-liquid interface which is convex towards the liquid phase (see Figs 2.4.2 and 2.4.3).  $\bar{K}_c$  is negative in this case. Eq. (2.2.6) is called *Gibbs–Thomson relation*. The relation (2.2.6) can be obtained as follows.

Consider a small solid particle (crystal) in the melt. The sum of the principle curvatures of the curved surface of this particle is denoted by  $\bar{K}_c$ . Let  $\Delta G_r$  be the difference between the total free energies (per unit volume) of the new phase (very small crystal) and the old phase (liquid) when the curvature effects are included in the phase-change temperature  $T_m$ . Note that the total free energy in any phase is the sum of the free energy of the bulk and the surface energy.

If the volume of the liquid is much large than the volume of the crystal, and if  $|T_m^c - T_m|$  is not very large, then it can be reasonably assumed that in solidification the free energy of the liquid does not change due to the curvature effect. In this case as discussed in the following  $\Delta G_r$  can be regarded as the difference between the total free energies of a very small crystal (with curvature) forming at temperature  $T_m^c$  and a very small crystal forming at  $T_m$  without curvature:

$$\Delta G_r = \text{total free energy of crystal at } T_m^c - \text{total free energy of liquid at } T_m^c \quad (2.2.7)$$

$$= \text{total free energy of crystal at } T_m^c - \text{total free energy of liquid at } T_m$$

$$= \text{total free energy of crystal at } T_m^c - \text{total free energy of crystal at } T_m. \quad (2.2.8)$$

Since free energies of solid and liquid at  $T_m$  with no curvature are equal, we get Eq. (2.2.8).  $|\Delta G_r|$  can also be calculated with the help of Eqs (2.1.15), (2.2.8) and we get

$$|\Delta G_r| = |\Delta H - T_m^c \Delta \hat{S}| = |\Delta \hat{S}|(T_m - T_m^c). \quad (2.2.9)$$

Here modulus of different quantities has been taken for convenience.  $\Delta \hat{S}$  is the difference between the entropies (per unit volume) of solid and liquid at the temperature  $T_m$ . It can be shown [40] that if  $C_S = C_L$  then

$$(\Delta H)_{T=T_m^c} = (\Delta H)_{T=T_m}. \quad (2.2.10)$$

The change in the free energy of the crystal due to curvature or the change in the free enthalpy of the crystal (per unit volume) due to curvature is due to the change in the internal pressure [40] and so

$$|\Delta G_r| = |\Delta P|. \quad (2.2.11)$$

The internal pressure  $\Delta P$  is given by the relation [40]

$$|\Delta P| = \sigma |\bar{K}_c|. \quad (2.2.12)$$

When Gibbs–Thomson law is written as

$$T_m^c = T_m + \frac{\sigma \bar{K}_c T_m V_m}{l_m}, \quad (2.2.13)$$

then by convention  $\bar{K}_c$  is taken as negative if the phase-change interface is convex towards the liquid, i.e.  $T_m^c < T_m$  as  $\sigma$ ,  $T_m$  and  $l_m$  are taken as positive. If  $T_m > T_m^c$ , then from Eqs (2.2.4), (2.2.9), (2.2.11), (2.2.12) (modulus sign can be removed as we are dealing with positive quantities on both sides), we get

$$T_m - T_m^c = \sigma \bar{K}_c T_m V_m / l_m, \quad \bar{K}_c > 0, \quad (2.2.14)$$

which is the relation (2.2.6).

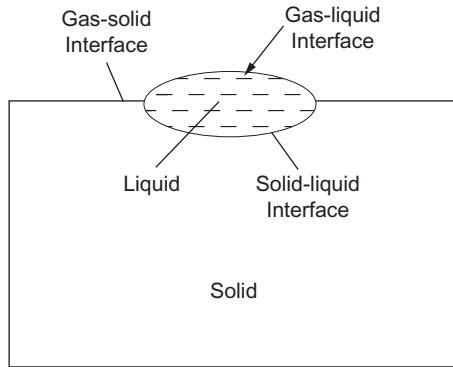
## 2.2.3 Nucleation of Melting, Effect of Interface Kinetics and Glassy Solids

*Nucleation of melting:* Melting of solid can begin without significant superheating in the solid. When nucleation of melting occurs over a solid surface, the nucleus consisting of the liquid phase will be enveloped basically by two different surfaces. On one side is a solid–liquid interface (see Fig. 2.2.2) and on the other side is a gas–liquid interface. The surface energy of the gas–solid interface is generally greater than the combined gas–liquid and solid–liquid surface energies. This implies that the formation of the liquid film on the solid surface will not be opposed by the solid surface and the liquid film spreads over the solid surface without significant superheating. The equilibrium of surface energies is attained at the equilibrium temperature.

*Effect of interface kinetics:* It was suggested in [41] that the interface movement lowers the temperature of the solid–liquid interface below the equilibrium temperature  $T_m$ . The form of the growing phase adapts itself to satisfy the growth velocity–temperature requirement. The movement of the interface is dependent on a driving force which was called the viscous effect or the *interface kinetic effect*. The supercooling as a function of interface velocity can be expressed as

$$T(\vec{V}) = T_m - \vec{\phi} \cdot \vec{V}, \quad (2.2.15)$$

where  $T(\vec{V})$  is the new melting temperature,  $\vec{V}$  is the velocity of the interface and  $\vec{\phi}$  is the viscous correction term. For small departures of  $T(\vec{V})$  from  $T_m$  the rate at which solidification occurs is approximately proportional to the departure [42]. In high-transition rates these effects appear on a macroscopic scale also. Kinetic undercooling is likely to be important only when  $\vec{V} \cdot \vec{n}$  (normal velocity) is large, such as  $\vec{V} \cdot \vec{n} \sim 10$  m/s. The applicability of kinetic effect to a moving interface has been opposed by some authors [43] as the concept devolves from the thermodynamics of equilibrium systems which has been applied in Eq. (2.2.15) to transforming systems. The interfacial free energy of the solid–liquid interface is a thermodynamic quantity only in the limited context of stationary interfaces which are at equilibrium. See [42, 44] for further information.



**Fig. 2.2.2** Nucleation of melting.

*Glassy (amorphous) solids:* At very high-cooling rates, such as those encountered in rapid solidification of liquid metals, there may be insufficient time for the formation of nucleus and a *glassy solid* is formed. While still noncrystalline, it becomes a solid in its mechanical behaviour as its viscosity becomes very high. There is no phase-change boundary associated with glassy materials.

## 2.3 MORPHOLOGICAL INSTABILITY OF THE SOLID–LIQUID INTERFACE

A crucial assumption in the classical formulation of Stefan problems is that there exists a smooth surface which is the phase-change boundary such that on one side of this surface is a stable solid (liquid) region and the other side a stable liquid (solid) region. The solid region

is identified only by its temperature which should be less than or equal to the equilibrium temperature  $T_m$ . Similarly liquid is identified only by its temperature which should be greater than or equal to  $T_m$ . The existence of such a planar solid–liquid interface is an ideal situation and is possible only in special cases such as *columnar solidification* of pure metals or *directional solidification* of alloys in ‘Bridgman type furnace’ [40] under a sufficiently high-temperature gradient.

In unidirectional solidification, in its classical formulation, it has been established mathematically in several references such as in [45] that under certain conditions, such as, in the absence of volumetric heat sources, or a mushy region nonexistent initially, a planar interface remains planar (mushy region does not develop) till the solidification is complete. In multidimensional problems, the existence of a sharp interface has been proved rigorously only for a short-time under suitable assumptions (see Chapter 10). Invariably, a sharp interface separating a stable solid region from a stable liquid region degenerates after a short time into a mushy region. The mushy region contains both solid and liquid phases and separates the stable solid region from the stable liquid region. The solid in the mushy region is present initially in the form of dendrites (Figs 2.3.1 and 2.3.2). Further growth of dendrites leads to a polycrystalline structure with one crystal from each nucleus (Fig. 2.3.3). The diameter of a grain could be as small as  $10^{-5}$  m and as large as  $10^{-2}$  m. Mushy region may also develop during solidification if the liquid is supercooled or during melting if the solid is superheated. This degeneration of sharp interface into a mushy region is attributed to the *morphological instability* of the solid–liquid interface.

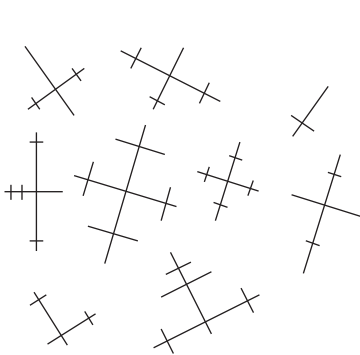


Fig. 2.3.1 Formation of dendrites.

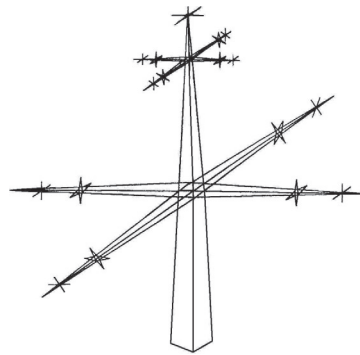
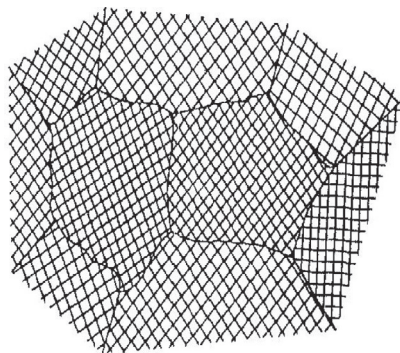
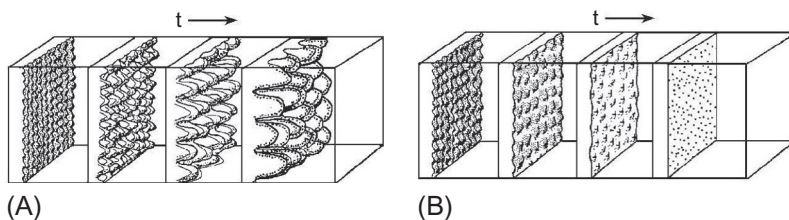


Fig. 2.3.2 Dendrite growth.

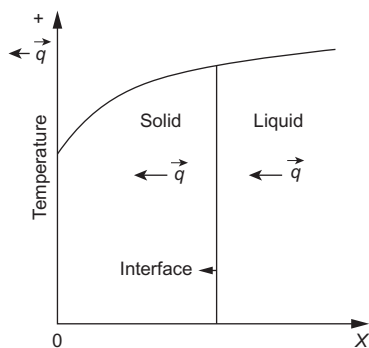
Classical thermodynamic definitions of stability are inapplicable to the determination of the morphology of a growing interface, and current extensions of equilibrium thermodynamics have not yet furnished a fully acceptable alternative [46]. On the basis of a heuristics-based stability criterion, the interface is said to be morphologically unstable/stable if a small perturbation given to the interface grows/dies with time (see Fig. 2.3.4). In Fig. 2.3.4A, the perturbations are growing, making the planar interface unstable. Mushy region will develop in front of the interface. In Fig. 2.3.4B, the perturbations are dying and the planar interface remains planar. Figs 2.3.5–2.3.7 show solid–liquid interface morphology and the temperature distributions in the solid and liquid regions. In Fig. 2.3.5, freezing temperature is equilibrium temperature  $T_m$ . The interface is planar and perpendicular to the direction of heat flow. The hottest part of the system is the liquid region. In Fig. 2.3.6, the growth of freezing front is columnar. The hottest part of the system is liquid. This growth is more common in alloys.



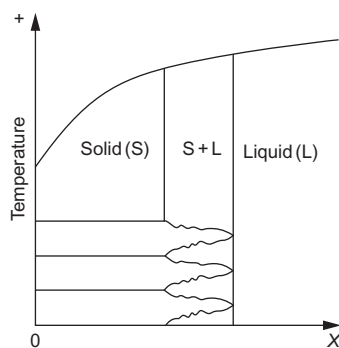
**Fig. 2.3.3** Formation of polycrystalline structure.



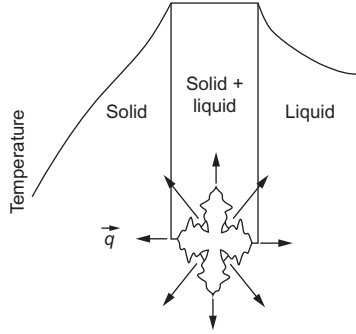
**Fig. 2.3.4** (A) Small perturbations at the interface are growing. (B) Perturbations are dying.



**Fig. 2.3.5** Solid-liquid interface morphology and the temperature distribution. Planar growth.



**Fig. 2.3.6** Solid-liquid interface morphology and the temperature distribution. Columnar growth.



**Fig. 2.3.7** Equiaxed dendrite growth.

In Fig. 2.3.7, the grains are equiaxed and have similar dimensions along all axes. The hottest part of the system is the crystal as the liquid is supercooled. The interface is stable in Fig. 2.3.5 and unstable in Figs 2.3.6 and 2.3.7.

## 2.4 NONMATERIAL SINGULAR SURFACE: GENERALIZED STEFAN CONDITION

A *singular surface* is a surface which does not have any inner structure so as to give rise to discontinuities in the bulk quantities. Solid–liquid interface and shock waves are examples of singular surfaces. The motion of a singular surface could be independent of the motion of the bulk phases.

A *material surface* is a surface which consists of the same material particles all the time. Fluid films and coatings are examples of a material surface. A surface which is not a material surface is called a ‘nonmaterial surface’.

It is well known that surfaces of bodies, and interfaces between pairs of bodies, exhibit properties quite different from those associated with their interiors. There have been several attempts (cf. [46–50]) at formulating the equations of conservation of mass, motion and energy in a moving singular surface embedded in a three-dimensional continuum and dividing the continuum into two regions for which the singular surface is a common boundary. Some thermodynamic fields may have discontinuities across this singular surface. In the classical Stefan condition (1.4.8), the jump in the normal component of the heat flux vector across the phase-change boundary is given in terms of the amount of latent heat released or absorbed at the phase-change boundary. It is assumed that no mechanical work is done. The modern theory of surface thermodynamics and mechanics also takes into account other aspects such as the surface stress, in particular surface tension, and conduction of heat tangential to the surface while balancing energy along the singular surface. The Stefan condition derived later takes into account the surface tension and heat conduction while balancing energy in the phase-change boundary, and will be called *generalized Stefan condition* [51].

Consider a three-dimensional bounded region  $\bar{R}$  which is occupied by solid and liquid phases. There exists a time-dependent smooth singular nonmaterial surface  $\Gamma$  which divides  $\bar{R}$  into two parts  $R_S$  and  $R_L$ ,  $\bar{R} = R_S \cup R_L \cup \Gamma$ .  $R_S$  and  $R_L$  are solid and liquid regions such that  $R_S \cap$



$R_L$  is empty. The subscripts  $S$  and  $L$  stand for the solid and the liquid phases, respectively. The external surfaces of  $R_S$  and  $R_L$  will be denoted by  $\partial R_S$  and  $\partial R_L$ , respectively (see Fig. 2.4.1). Let  $(R_S)_b = \partial R_S \cup \Gamma$  and  $(R_L)_b = \partial R_L \cup \Gamma$ . The external surface of  $R$  is  $\partial R_S \cup \partial R_L \cup \partial \Gamma$  where the curve  $\partial \Gamma$  is the boundary of  $\Gamma$ . The surface  $\Gamma$  is orientable and the unit normal  $\vec{N}$  to  $\Gamma$  points into the liquid phase. Let  $\vec{V}$  be the velocity of  $\Gamma$  in the direction of  $\vec{N}$ , i.e.  $\vec{V} = |\vec{V}|\vec{N}$ . It may be noted that only the normal component of the velocity of the interface can be determined as in Eq. (1.4.15). The tangential component of the interface motion for a massless interface cannot be derived a priori by recourse to principles of general validity [52].

We shall first balance the forces in  $\bar{R}$ . These results will be used in balancing energy later.

### Conservation of Forces in $\bar{R}$

$$\int_{\bar{R}} \rho \vec{B} dv + \int_{\partial R_S \cup \partial R_L} \tau \vec{n} da + \int_{\partial \Gamma} \hat{\tau} \vec{v} dl = 0. \quad (2.4.1)$$

Here  $\vec{B}$  is the body force per unit mass,  $\vec{n}$  is the unit normal vector pointing outwards as the exterior boundary of a region is traversed in the anticlockwise direction,  $\tau$  is the bulk stress tensor and  $\hat{\tau}$  is the surface stress tensor, and  $\vec{v}$  is the outward unit vector normal to  $\partial \Gamma$  which is tangential to  $\Gamma$ .  $dv$ ,  $da$  and  $dl$  are elementary volume, elementary area and elementary length, respectively. We take  $\rho_S = \rho_L = \rho$  for simplicity:

$$\tau \vec{n} = \left( \sum_{i=1}^3 \tau_{ix} n_i, \sum_{i=1}^3 \tau_{iy} n_i, \sum_{i=1}^3 \tau_{iz} n_i \right), \quad \vec{n} = (n_1, n_2, n_3), \quad (2.4.2)$$

$\tau_{ij}$ ,  $i = 1, 2, 3, j = 1, 2, 3$  are components of bulk stress tensor  $\tau$ .

If it is assumed that both solid and liquid regions are in equilibrium independently of each other, the balancing of forces in the solid region gives

$$\int_{R_S} \rho \vec{B} dv + \int_{\partial R_S} \tau_S \vec{n} da + \int_{\Gamma} \tau_S \vec{N} da = 0. \quad (2.4.3)$$

Similarly balancing of forces in the liquid region gives

$$\int_{R_L} \rho \vec{B} dv + \int_{\partial R_L} \tau_L \vec{n} da - \int_{\Gamma} \tau_L \vec{N} da = 0. \quad (2.4.4)$$

The minus sign in the last term of Eq. (2.4.4) arises because the outward normal to the liquid region at the boundary  $\Gamma$  points in the direction opposite to  $\vec{N}$ . Adding Eqs (2.4.3), (2.4.4) and on subtracting the sum from Eq. (2.4.1), we obtain

$$\int_{\Gamma} \tau_L \vec{N} da - \int_{\Gamma} \tau_S \vec{N} da + \int_{\partial \Gamma} \hat{\tau} \vec{v} dl = 0. \quad (2.4.5)$$

Applying surface divergence theorem to the last term of Eq. (2.4.5) gives integration over  $\Gamma$  and then assuming local equilibrium, we obtain

$$(\tau_L - \tau_S) \vec{N} + \text{div}_{\Gamma} \hat{\tau} = 0, \quad \text{in } \Gamma. \quad (2.4.6)$$

Here  $\text{div}_\Gamma \hat{\boldsymbol{\tau}}$  is the surface divergence of  $\hat{\boldsymbol{\tau}}$  (cf. [47]). Surface stress tensor generalizes the usual notion of surface tension and is consistent with the atomistic calculations, indicating the presence of compressive surface stresses in certain crystals [47]. If  $\hat{\boldsymbol{\tau}} = \sigma \mathbf{1}$ , where  $\sigma$  is a scalar valued function called surface tension and  $\mathbf{1}$  is the inclusion mapping from the tangent space of  $\Gamma$  into the three-dimensional vector space [47], then

$$(\boldsymbol{\tau}_L - \boldsymbol{\tau}_S)\vec{N} + \bar{K}_c \sigma \vec{N} + \nabla_\Gamma \sigma = 0, \quad \text{in } \Gamma. \quad (2.4.7)$$

Here  $\bar{K}_c$  is the sum of principal curvatures of the singular surface.

The surface divergence of a smooth vector field  $\vec{u} : \Gamma \rightarrow G$ , where  $G$  is the translation space of a finite-dimensional Euclidean point space, is given by

$$\text{div}_\Gamma \vec{u} = t_r D \vec{u}, \quad (2.4.8)$$

where the r.h.s. in Eq. (2.4.8) is the trace of the tangential derivative  $D \vec{u}$  of  $\vec{u}$  [47]. Note that  $\vec{u}$  admits a unique decomposition.  $\vec{u} = \vec{u}_S + u_n \vec{N}$ , where  $\vec{u}_S$  is a vector in a smooth tangential field and  $u_n$  is a scalar in a smooth scalar field. If  $\boldsymbol{\tau}$  is a smooth tensor field, then for any scalar field  $\phi$

$$\text{div}_\Gamma(\phi \boldsymbol{\tau}) = \phi \text{div}_\Gamma \boldsymbol{\tau} + \boldsymbol{\tau} \nabla_\Gamma \phi. \quad (2.4.9)$$

Taking  $\phi = \sigma$  and  $\boldsymbol{\tau} = I$  ( $I$  is the identity tensor) in Eq. (2.4.9), we get

$$\text{div}_\Gamma(\hat{\boldsymbol{\tau}}) = \text{div}_\Gamma(\sigma I) = \sigma \text{div}_\Gamma I + \nabla_\Gamma \sigma. \quad (2.4.10)$$

Using the relation  $\text{div}_\Gamma \mathbf{1} = \text{div}_\Gamma I = \bar{K}_c \vec{N}$ , we obtain the last two terms on the r.h.s. of Eq. (2.4.7).

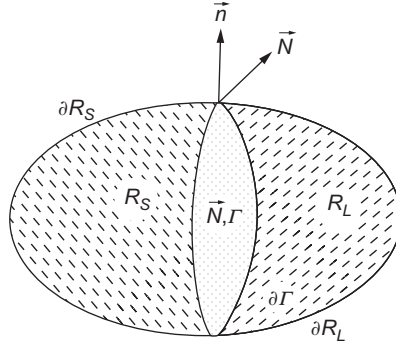
### Conservation of Energy in the Singular Surface $\Gamma$

In order to obtain conservation of energy in  $\Gamma$ , we shall first derive the equation of conservation of energy in  $\bar{R}$  followed by equations of conservation of energy in  $R_S$  and  $R_L$ . Subtracting the sum of energy equations for  $R_S$  and  $R_L$  from the energy equation for  $\bar{R}$ , we get the energy equation for  $\Gamma$ .

The equation of conservation of energy in  $\bar{R}$  is

$$\begin{aligned} \frac{d}{dt} \int_{R_S \cup R_L} \rho e dv + \frac{d}{dt} \int_\Gamma \bar{\epsilon} da = & - \int_{\partial R_S \cup \partial R_L} \vec{q} \cdot \vec{n} da - \int_{\partial \Gamma} \vec{\hat{q}} \cdot \vec{v} dl \\ & + \int_\Gamma (\boldsymbol{\tau}_L - \boldsymbol{\tau}_S) \vec{N} \cdot \vec{V} da + \int_{\partial \Gamma} \bar{\epsilon} U dl, \end{aligned} \quad (2.4.11)$$

where  $e$  is the specific internal energy,  $\bar{\epsilon}$  is the surface energy of  $\Gamma$  per unit area,  $\vec{q}$  is the heat flux vector of the bulk,  $\vec{\hat{q}}$  is the tangential heat conduction vector in  $\Gamma$ ,  $(\boldsymbol{\tau}_L - \boldsymbol{\tau}_S) \vec{N} \cdot \vec{V}$  is the work done by the body forces in  $\Gamma$  and  $U = -|\vec{V}| \vec{N} \cdot \vec{n}$  is the heat lost or gained due to geometry of  $R_S \cup R_L$  as  $\vec{N}$  may have a nonzero component along  $\vec{n}$ . Note that  $(\boldsymbol{\tau}_L - \boldsymbol{\tau}_S) \vec{N}$  appears as a body force in Eq. (2.4.7) and the tangential work done by this force is zero. The angle which  $\vec{N}$  makes with  $\vec{n}$  is called *contact angle*. It is still being debated on how to prescribe the boundary conditions at the contact point [53, 54]. By calculating the time derivative of the first term on the l.h.s. of Eq. (2.4.11) by first principles, it can be proved that



**Fig. 2.4.1** Geometry in generalized Stefan condition.

$$\frac{d}{dt} \int_{R_S \cup R_L} \rho e dv = \int_{R_S \cup R_L} \rho \frac{\partial e}{\partial t} + \int_{\Gamma} \rho (e_S - e_L) \vec{V} \cdot \vec{N} da. \quad (2.4.12)$$

It may be noted that the region  $\bar{R}$  is time independent but  $R_S$  and  $R_L$  vary with time in  $\bar{R}$  and this point should be taken care in calculating the time derivative to get the last term in Eq. (2.4.12).

On balancing the energy separately in  $R_S$  and  $R_L$ , we get

$$\int_{R_S} \rho \frac{\partial e_S}{\partial t} dv = - \int_{\partial R_S} \vec{q}_S \cdot \vec{n} da - \int_{\Gamma} \vec{q}_S \cdot \vec{N} da, \quad (2.4.13)$$

$$\int_{R_L} \rho \frac{\partial e_L}{\partial t} dv = - \int_{\partial R_L} \vec{q}_L \cdot \vec{n} da + \int_{\Gamma} \vec{q}_L \cdot \vec{N} da. \quad (2.4.14)$$

Adding Eqs (2.4.13), (2.4.14) and subtracting the sum from Eq. (2.4.11), we obtain

$$\begin{aligned} \int_{\Gamma} \rho (e_S - e_L) |\vec{V}| da + \frac{d}{dt} \int_{\Gamma} \bar{\epsilon} da &= - \int_{\Gamma} (\vec{q}_L - \vec{q}_S) \cdot \vec{N} da - \int_{\partial \Gamma} \vec{\hat{q}} \cdot \vec{v} dl \\ &+ \int_{\Gamma} (\tau_L - \tau_S) \vec{N} \cdot \vec{V} da - \int_{\partial \Gamma} \bar{\epsilon} |\vec{V}| \vec{N} \cdot \vec{n} dl. \end{aligned} \quad (2.4.15)$$

The second term and the last term on the r.h.s in Eq. (2.4.15) should be converted to a surface integral over  $\Gamma$  to obtain an equation for local energy balance in  $\Gamma$ . The conversion of the second term to the surface integral is straight forward. In [51], the contribution of the last term on the r.h.s. of Eq. (2.4.15) has been included as the third term in Eq. (2.4.16).

Local balance of energy in  $\Gamma$  gives

$$\rho (e_S - e_L) |\vec{V}| + \bar{\epsilon}' - \bar{K}_c \bar{\epsilon} \vec{V} \cdot \vec{N} + \text{div}_{\Gamma} \vec{\hat{q}} + (\vec{q}_L - \vec{q}_S) \cdot \vec{N} - (\tau_L - \tau_S) \vec{N} \cdot \vec{V} = 0, \quad (2.4.16)$$

$$\bar{\epsilon}' = \frac{\partial \bar{\epsilon}}{\partial t} + \vec{V} \cdot \text{grad } \bar{\epsilon}. \quad (2.4.17)$$

With the help of Eq. (2.4.6), the last term in Eq. (2.4.16) can be rewritten as

$$(\boldsymbol{\tau}_L - \boldsymbol{\tau}_S) \vec{N} \cdot \vec{V} = -(\operatorname{div}_\Gamma \hat{\boldsymbol{\tau}}) \cdot \vec{V}. \quad (2.4.18)$$

Eq. (2.4.16) is called a *generalized Stefan condition*.

Let us now briefly describe surface tension and its relation to  $\bar{\epsilon}$ . The effect of surface tension or capillarity can be explained on the basis of the assumption that on the outer surface of the liquid there exists a surface layer which could be a few molecules thick and whose properties differ from those of the bulk liquid. The surface film and the liquid can be considered as two phases of the liquid in equilibrium. The atoms in the free surface of a solid or a liquid have higher free energy than those inside because they have no neighbours and hence no cohesive bonds, on one side. Therefore, in equilibrium, a tension develops on the surface of the liquid. This tension is related to pressure by a relation of the form (2.2.12).  $\sigma$  is often assumed to be identical to the free energy of the surface. From the relation (2.1.15), we get

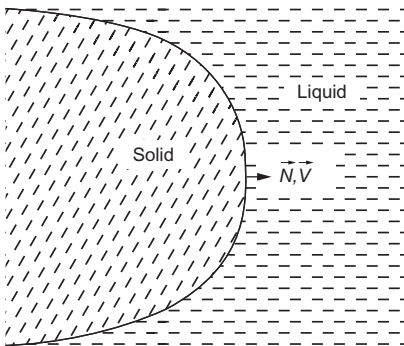
$$\sigma = \bar{\epsilon} - T\hat{S}, \quad (2.4.19)$$

where  $T$  is the phase-change temperature and  $\hat{S}$  is the entropy.

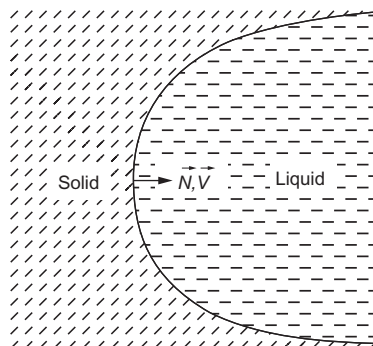
The Stefan condition (1.4.8) can be easily derived as a particular case of Eq. (2.4.16). For the derivation of Gibbs–Thomson effect from Eq. (2.4.16), see [51]. Some other observations made in [51] are as follows. A simple criterion for the instability of the interface can be derived using Eq. (2.4.16). Let  $\bar{\epsilon}' = 0$ ,  $\bar{\epsilon} \neq 0$ ,  $\vec{q} = 0$  and  $\hat{\boldsymbol{\tau}} = \sigma \mathbf{1}$  where the surface tension  $\sigma$  is constant. Under these assumptions, the following relation can be obtained:

$$|\vec{V}| = \frac{(\vec{q}_L - \vec{q}_S) \cdot \vec{N}}{l\rho + \bar{K}_c(\bar{\epsilon} - \sigma)}. \quad (2.4.20)$$

Here  $l$  is the latent heat per unit mass (for simplicity take  $C_S = C_L$ ). Consider a very small solid growth protruding into the liquid (see Fig. 2.4.2) at the solid–liquid interface. In this case  $\bar{K}_c$  is negative and if  $(\bar{\epsilon} - \sigma) > 0$ , then  $|\vec{V}|$  is increasing. This is an ideal situation for the dendritic growth as any solid protrusion in the liquid will grow. If  $(\bar{\epsilon} - \sigma) < 0$ , then there is retardation. If  $l\rho + \bar{K}_c(\bar{\epsilon} - \sigma) \rightarrow 0$ , then  $|\vec{V}| \rightarrow \infty$  and dendrites will grow indicating



**Fig. 2.4.2** Mean curvature  $\bar{K}_c$  is negative.



**Fig. 2.4.3** Mean curvature  $\bar{K}_c$  is positive.

instability of the solid–liquid interface. If  $l\rho + \bar{K}_c(\bar{\epsilon} - \sigma) \rightarrow \infty$ , then  $|\bar{V}| \rightarrow 0$ . This criterion may indicate branching or side protrusion in the dendrite. If the mean curvature is positive (see Fig. 2.4.3) and  $\bar{\epsilon} - \sigma > 0$ , then the surface  $\Gamma$  is locally retarded and for  $\epsilon - \sigma < 0$  it would be advanced.

In the derivation of Eqs (2.4.6), (2.4.16), both the solid and liquid phases have been considered at rest. The motion of phases has been taken into account in [49] and a more general solidification theory has been presented which takes into account the coupling between thermal fields and kinematic fields. The liquid region is an ordinary Newtonian liquid and the solid phase an elastic material. The specific internal energy, specific entropy, stress tensor and the heat flux vector in the bulk are considered as functions of temperature, temperature gradient, deformation gradient and the rate of deformation gradient.

In Clapeyron's equation (2.1.27), it is assumed that Gibbs free energies of liquid and solid phases (two different phases of the same substance) are the same and that the system is in thermodynamic equilibrium. This means that neither phase can grow nor decrease. In [50], a new Clapeyron's equation has been derived, which holds in the presence of nonuniform fields of pressure, temperature, density and velocity, and which does not require the equality of Gibbs functions across the interface as long as their difference is a function of time only, or in particular a constant along the interface. It was shown that even in the presence of constant pressure along the interface, the interface temperature can be changed by increasing or decreasing the velocity at which the process of solidification is taking place.