

If the diffusion equation is solved for steady-state solidification it can be shown that the concentration profile in the liquid is given by

$$X_L = X_0 \left\{ 1 + \frac{1-k}{k} \exp \left[ -\frac{x}{(D/v)} \right] \right\} \quad (4.35)$$

i.e.  $X_L$  decreases exponentially from  $X_0/k$  at  $x = 0$ , the interface, to  $X_0$  at large distances from the interface. The concentration profile has a characteristic width of  $D/v$ .

When the solid/liquid interface is within  $\sim D/v$  of the end of the bar the bow-wave of solute is compressed into a very small volume and the interface composition rises rapidly leading to a final transient and eutectic formation, Fig. 4.22c.

In practice alloy solidification will usually possess features from all three of the cases discussed above. There will usually be some stirring either due to liquid turbulence caused by pouring, or because of convection currents, or gravity effects. However, stirring will not usually be sufficiently effective to prevent the formation of a boundary layer and some liquid diffusion will therefore be involved. Partial stirring does, however, have the effect of reducing the boundary layer thickness. The concentration profiles found in practice may thus exhibit features between those shown in Fig. 4.21d and 4.22c. In many cases diffusion in the solid must also be taken into account, e.g. when interstitial atoms or bcc metals are involved. In this case solute can diffuse away from the solidifying interface back into the solid as well as into the liquid, with the result that after solidification the alloy is more homogeneous.

Even when solidification is not unidirectional the above ideas can still often be applied at a microscopic level as will be discussed below. Unidirectional solidification has commercial importance in, for example, the production of creep resistant aligned microstructures for gas turbine blades. It is also used in the production of extremely pure metals (zone refining)<sup>7</sup>.

#### Cellular and Dendritic Solidification

So far we have considered solidification in which the growth front is planar. However, the diffusion of solute into the liquid during solidification of an alloy is analogous to the conduction of latent heat into the liquid during the solidification of a pure metal. At first sight therefore it would seem that the planar front should break up into dendrites. The problem is complicated, however, by the possibility of temperature gradients in the liquid.

Consider steady-state solidification at a planar interface as shown in Fig. 4.23. As a result of the varying solute concentration ahead of the solidification front there is a corresponding variation of the equilibrium solidification temperature, i.e. the liquidus temperature, as given by the line  $T_e$  in Fig. 4.23b. However, apart from the temperature of the interface, which is fixed by local equilibrium requirements, the actual temperature of the liquid

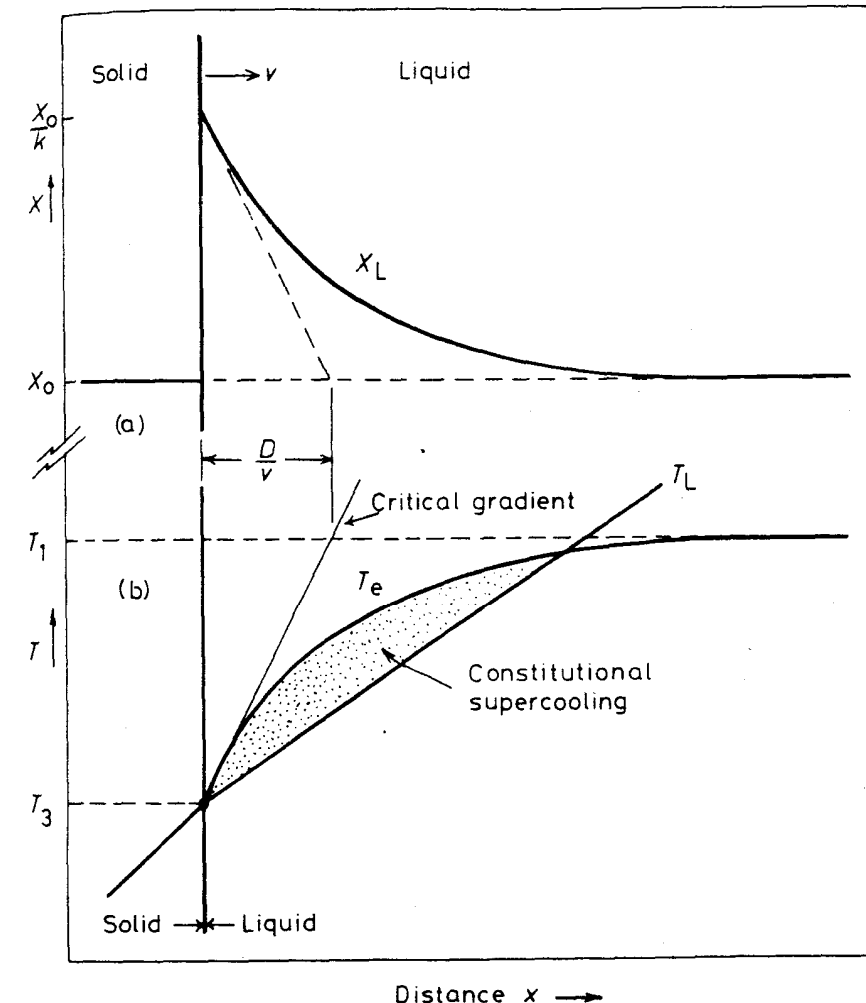


Fig. 4.23 The origin of constitutional supercooling ahead of a planar solidification front. (a) Composition profile across the solid/liquid interface during steady-state solidification. The dashed line shows  $dX_L/dx$  at the S/L interface. (b) The temperature of the liquid ahead of the solidification front follows line  $T_L$ . The equilibrium liquidus temperature for the liquid adjacent to the interface varies as  $T_e$ . Constitutional supercooling arises when  $T_L$  lies under the critical gradient.

can follow any line such as  $T_L$ . At the interface  $T_L = T_e = T_3$  (defined in Fig. 4.19). If the temperature gradient is less than the critical value shown in Fig. 4.23b the liquid in front of the solidification front exists below its equilibrium freezing temperature, i.e. it is supercooled. Since the supercooling arises from compositional, or constitutional effects it is known as *constitutional supercooling*.

A necessary condition for the formation of stable protrusions on a planar interface is that there must exist a region of constitutional supercooling in the liquid. Assuming the  $T_L$  variation in Fig. 4.23b the temperature at the tip of any protrusion that forms will be higher than that of the surrounding interface. (In contrast to pure metals the interface in alloys need not be isothermal.) However, provided the tip remains below the local liquidus temperature ( $T_e$ ) solidification is still possible and the protrusion can develop. On the other hand if the temperature gradient ahead of the interface is steeper than the critical gradient in Fig. 4.23b the tip will be raised above the liquidus temperature and the protrusion will melt back.

Under steady-state growth the critical gradient can be seen from Fig. 4.23 to be given by  $(T_1 - T_3)/(D/v)$  where  $T_1$  and  $T_3$  are the liquidus and solidus temperatures for the bulk composition  $X_0$ , Fig. 4.19. The condition for a stable planar interface is therefore

$$T'_L > \frac{(T_1 - T_3)}{(D/v)}$$

where  $T'_L$  stands for  $(dT_L/dx)$  at the interface. Or, regrouping the experimentally adjustable parameters  $T'_L$  and  $v$ , the condition for no constitutional supercooling is

$$(T'_L/v) > (T_1 - T_3)/D \quad (4.36)$$

$(T_1 - T_3)$  is known as the *equilibrium freezing range* of the alloy. Clearly planar front solidification is most difficult for alloys with a large solidification range and high rates of solidification. Except under well-controlled experimental conditions alloys rarely solidify with planar solid/liquid interfaces. Normally the temperature gradients and growth rates are not individually controllable but are determined by the rate at which heat is conducted away from the solidifying alloy.

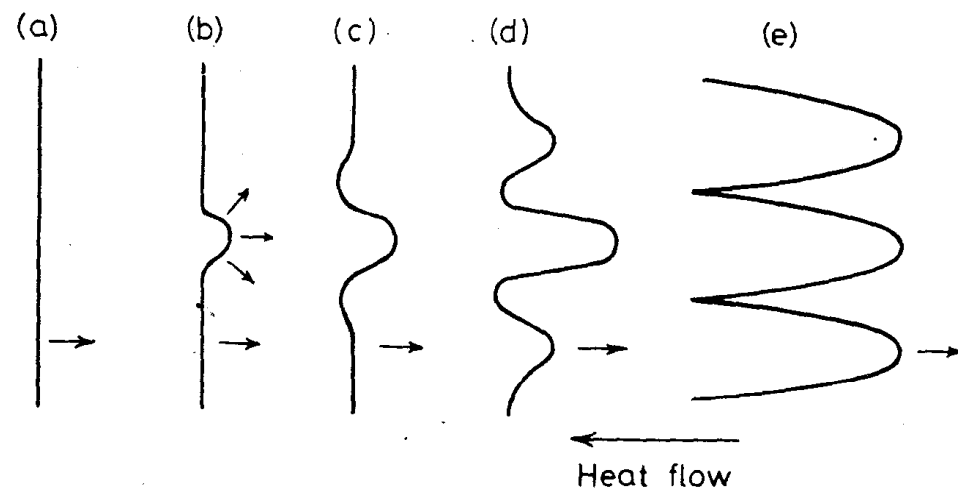


Fig. 4.24 The breakdown of an initially planar solidification front into cells.

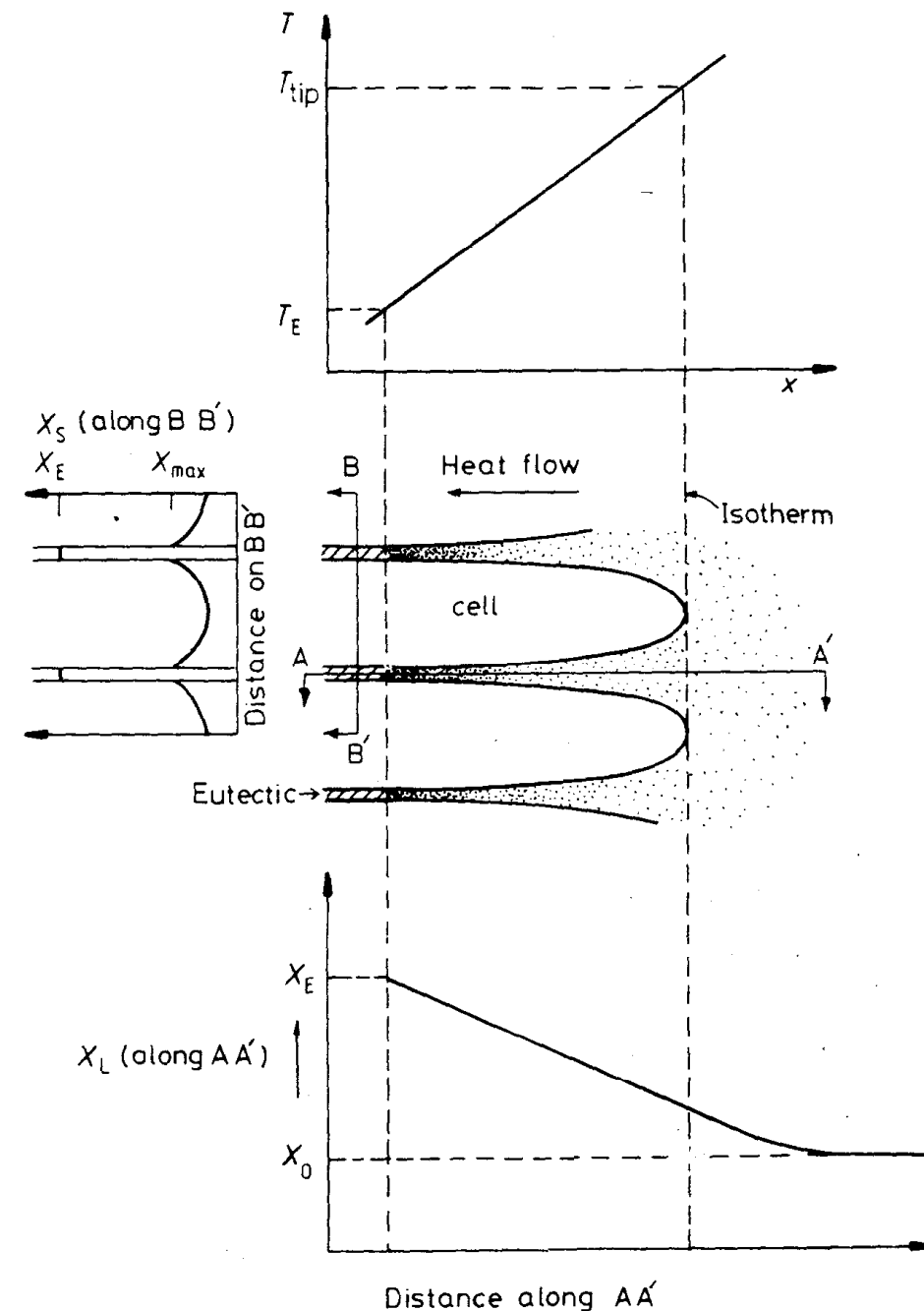


Fig. 4.25 Temperature and solute distributions associated with cellular solidification. Note that solute enrichment in the liquid between the cells, and coring in the cells with eutectic in the cell walls.

If the temperature gradient ahead of an initially planar interface is gradually reduced below the critical value the first stage in the breakdown of the interface is the formation of a cellular structure, Fig. 4.24. The formation of the first protrusion causes solute to be rejected laterally and pile up at the root of the protrusion (b). This lowers the equilibrium solidification temperature

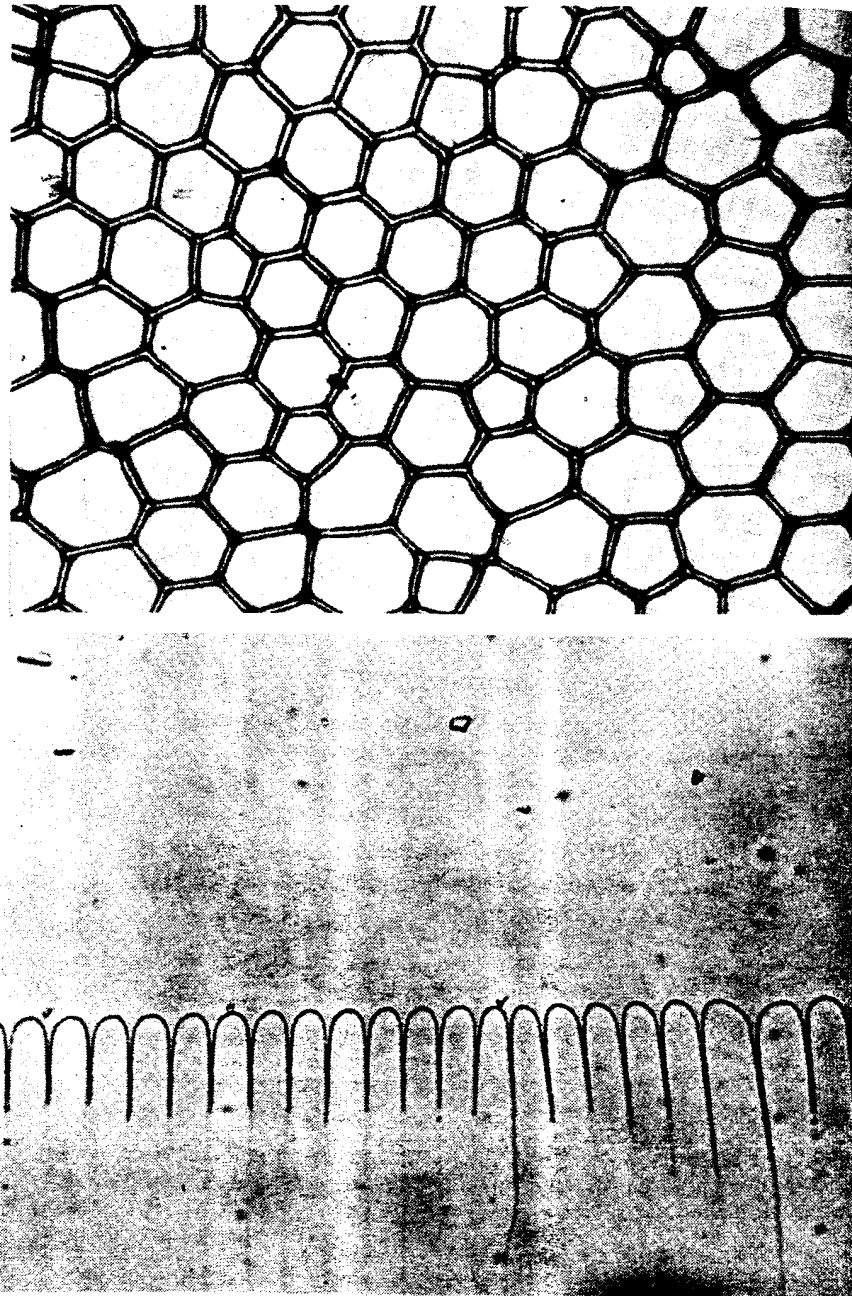


Fig. 4.26 Cellular microstructures. (a) A decanted interface of a cellularly solidified Pb-Sn alloy ( $\times 120$ ) (after J.W. Rutter in *Liquid Metals and Solidification*, American Society for Metals, 1958, p. 243). (b) Longitudinal view of cells in carbon tetrabromide ( $\times 100$ ) (after K.A. Jackson and J.D. Hunt, *Acta Metallurgica* **13** (1965) 1212).

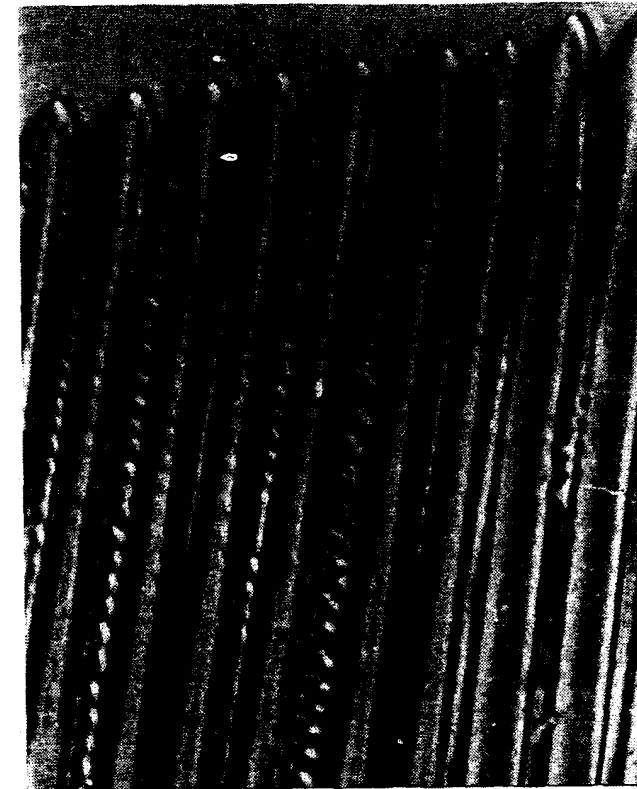


Fig. 4.27 Cellular dendrites in carbon tetrabromide. (After L.R. Morris and W.C. Winegard, *Journal of Crystal Growth* **6** (1969) 61.)

causing recesses to form (c), which in turn trigger the formation of other protrusions (d). Eventually the protrusions develop into long arms or *cells* growing parallel to the direction of heat flow (e). The solute rejected from the solidifying liquid concentrates into the cell walls which solidify at the lowest temperatures. The tips of the cells, however, grow into the hottest liquid and therefore contain the least solute. Even if  $X_0 \ll X_{\max}$  (Fig. 4.19) the liquid between the cells may reach the eutectic composition in which case the cell walls will contain a second phase. The interaction between temperature gradient, cell shape and solute segregation is shown in Fig. 4.25. Figure 4.26 shows the appearance of the cellular structure. Note that each cell has virtually the same orientation as its neighbours and together they form a single grain.

Cellular microstructures are only stable for a certain range of temperature gradients. At sufficiently low temperature gradients the cells, or primary arms of solid, are observed to develop secondary arms, and at still lower temperature gradients tertiary arms develop, i.e. dendrites form. Concomitant with

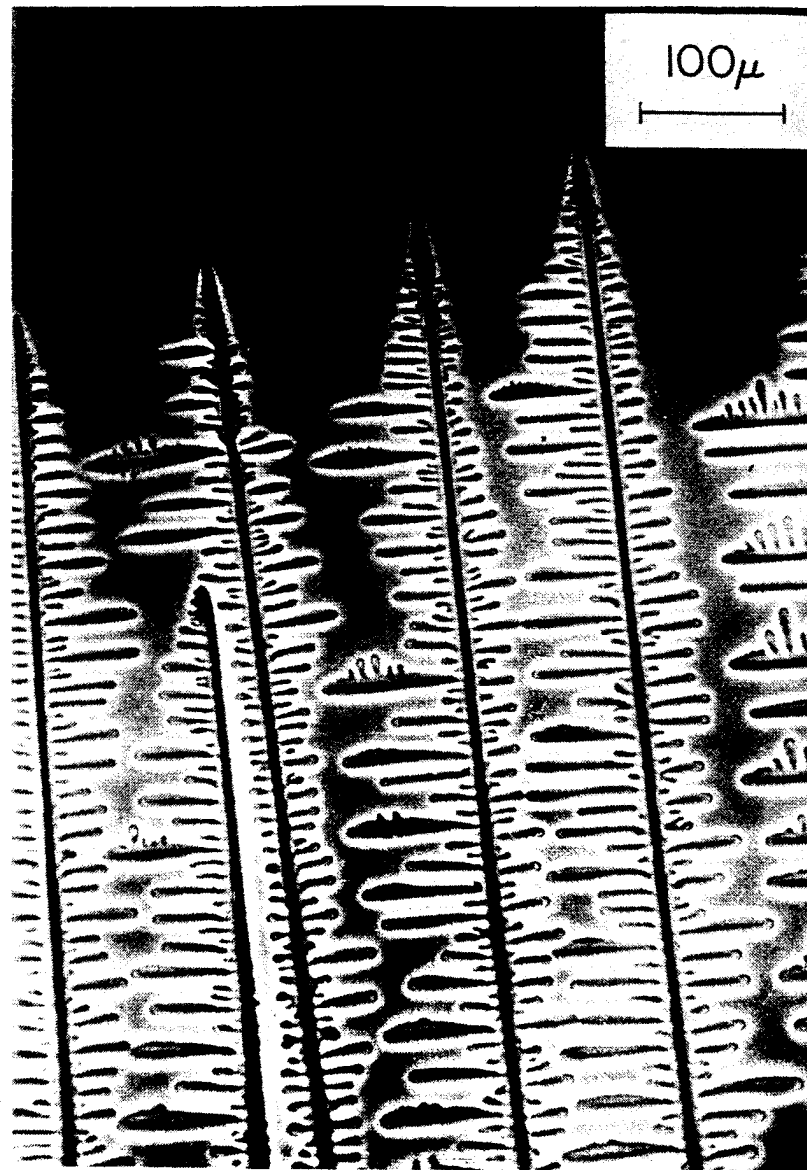


Fig. 4.28 Columnar dendrites in a transparent organic alloy. (After K.A. Jackson in *Solidification*, American Society for Metals, 1971, p. 121.)

this change in morphology there is a change in the direction of the primary arms away from the direction of heat flow into the crystallographically preferred directions such as  $\langle 100 \rangle$  for cubic metals. The change in morphology from cells to dendrites can be seen in Figs. 4.26b, 4.27 and 4.28. These pictures have been taken during *in situ* solidification of special transparent

organic compounds using a transmission light microscope<sup>8</sup>. The compounds used have low entropies of melting and solidify in the same way as metals. Alloys have been simulated by suitable combinations of such compounds.

In general the tendency to form dendrites increases as the solidification range increases. Therefore the effectiveness of different solutes can vary widely. For solutes with a very small partition coefficient ( $k$ ) cellular or dendritic growth can be caused by the addition of a very small fraction of a per cent solute.

The reason for the change from cells to dendrites is not fully understood. However it is probably associated with the creation of constitutional supercooling in the liquid between the cells causing interface instabilities in the transverse direction. Note that for unidirectional solidification there is approximately no temperature gradient perpendicular to the growth direction. The cell or dendrite arm spacing developing is probably that which reduces the constitutional supercooling in the intervening liquid to a very low level. This would be consistent with the observation that cell and dendrite arm spacings both decrease with increasing cooling rate: higher cooling rates allow less time for lateral diffusion of the rejected solute and therefore require smaller cell or dendrite arm spacings to avoid constitutional supercooling.

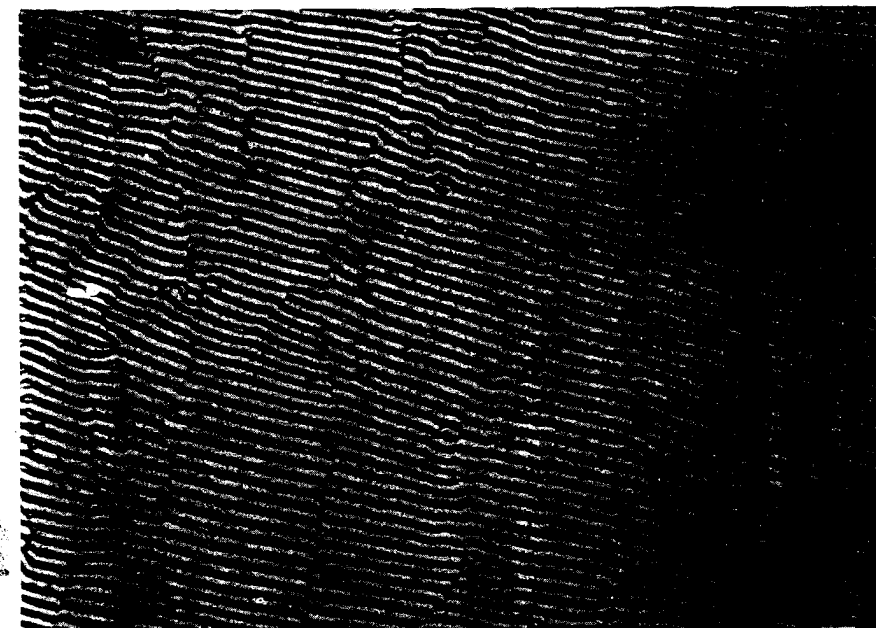


Fig. 4.29 Al-Cu Al<sub>2</sub> lamellar eutectic normal to the growth direction ( $\times 680$ ). (Courtesy of J. Strid, University of Luleå, Sweden.)



Fig. 4.30 Rod-like eutectic.  $\text{Al}_3\text{Fe}$  rods in Al matrix. Transverse section. Transmission electron micrograph ( $\times 70\,000$ ). (Courtesy of J. Strid, University of Luleå, Sweden.)

Finally it should be noted that although the discussion of alloy solidification has been limited to the case  $k < 1$ , similar arguments can be advanced for the case of  $k > 1$ . (See exercise 4.13.)

#### 4.3.2 Eutectic Solidification<sup>9</sup>

In the solidification of a binary eutectic composition two solid phases form cooperatively from the liquid, i.e.  $L \rightarrow \alpha + \beta$ . Various different types of eutectic solidification are possible and these are usually classified as *normal* and *anomalous*. In normal structures the two phases appear either as alternate lamellae, Fig. 4.29, or as rods of the minor phase embedded in the other phase, Fig. 4.30. During solidification both phases grow simultaneously behind an essentially planar solid/liquid interface. Normal structures occur when both phases have low entropies of fusion. Anomalous structures, on the other hand, occur in systems when one of the solid phases is capable of faceting, i.e. has a high entropy of melting. There are many variants of these structures the most important commercially being the flake structure of Al—Si alloys. This section will only be concerned with normal structures, and deal mainly with lamellar morphologies.

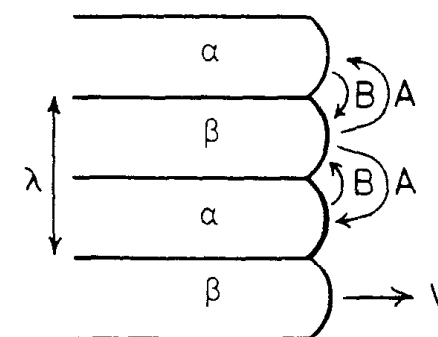


Fig. 4.31 Interdiffusion in the liquid ahead of a eutectic front.

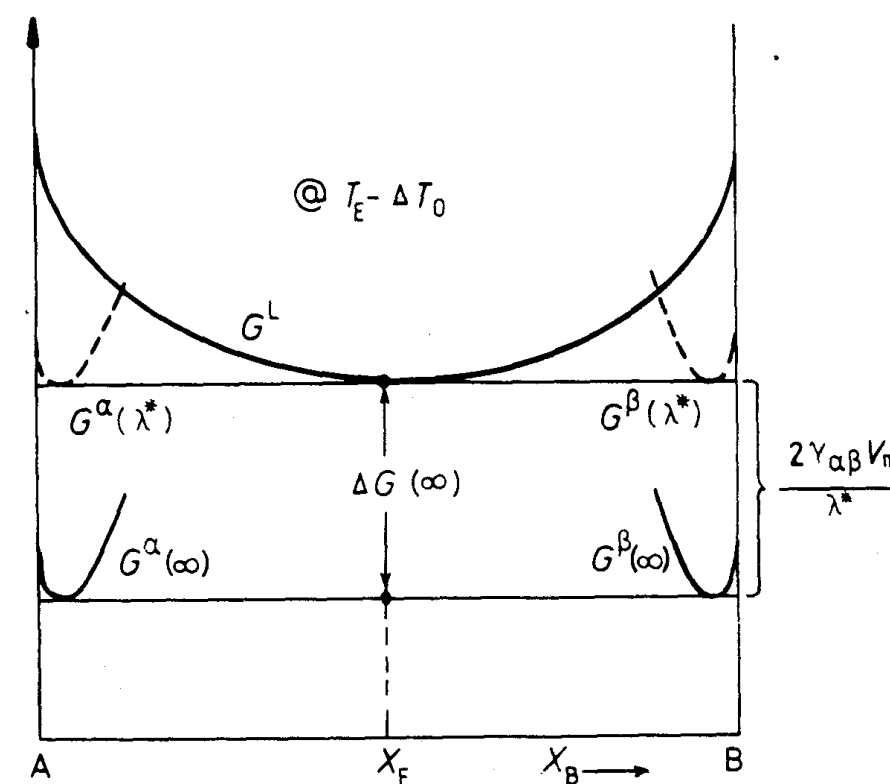


Fig. 4.32 Molar free energy diagram at a temperature  $\Delta T_0$  below the eutectic temperature, for the case  $\lambda = \lambda^*$ .

#### Growth of Lamellar Eutectics

Figure 4.31 shows how two phases can grow cooperatively behind an essentially planar solidification front. As the A-rich  $\alpha$  phase solidifies excess B diffuses a short distance laterally where it is incorporated in the B-rich  $\beta$  phase. Similarly the A atoms rejected ahead of the  $\beta$  diffuse to the tips of the adjacent  $\alpha$  lamellae. The rate at which the eutectic grows will depend on how fast this diffusion can occur and this in turn will depend on the interlamellar spacing  $\lambda$ . Thus small interlamellar spacings should lead to rapid growth.