Physics of Materials

Dr. Thomas LaGrange

LUMES

Chapter 11
Phase Transformations 1: Solidification

Masters Course PHYS-307

Fall 2024

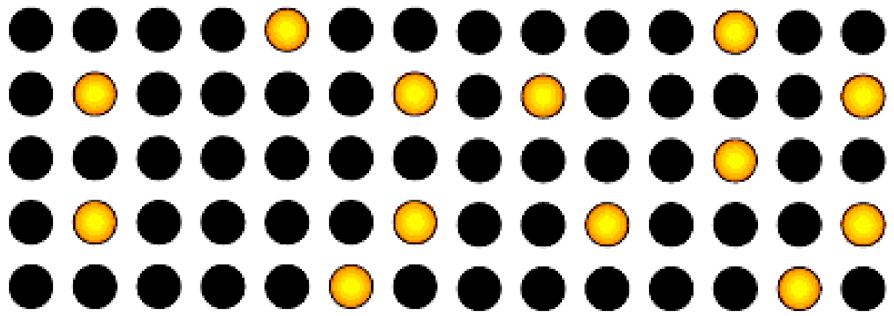
Thermodynamics: mixing energy

Concentration $X_A = \frac{N_A}{N_A + N_B}$

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

Ideal solution $\Delta H_m = 0$

Calculation of the mixing entropy ΔS_m



$$T\Delta S_m = kT \ln\left(\frac{(N_A + N_B)!}{N_A!N_B!}\right)$$

Stirling formula: $\ln N! \approx N \ln N - N$

$$T\Delta S_m = kT\left[(N_A + N_B)\ln(N_A + N_B) - N_A \ln N_A - N_B \ln N_B\right] \qquad \boxed{N_A = X_A n_a}$$

$$T\Delta S_m = kT\left[n_a(X_A + X_B)\left[\ln n_a + \ln(X_A + X_B)\right] - n_a\left(X_A(\ln n_a + \ln X_A) + X_B(\ln n_a + \ln X_B)\right)\right]$$

$$T\Delta S_m = kT\left[-n_a(X_A \ln X_A + X_B \ln X_B)\right] = -RT(X_A \ln X_A + X_B \ln X_B) \qquad \boxed{X_A + X_B = 1}$$

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Thermodynamics: mixing energy

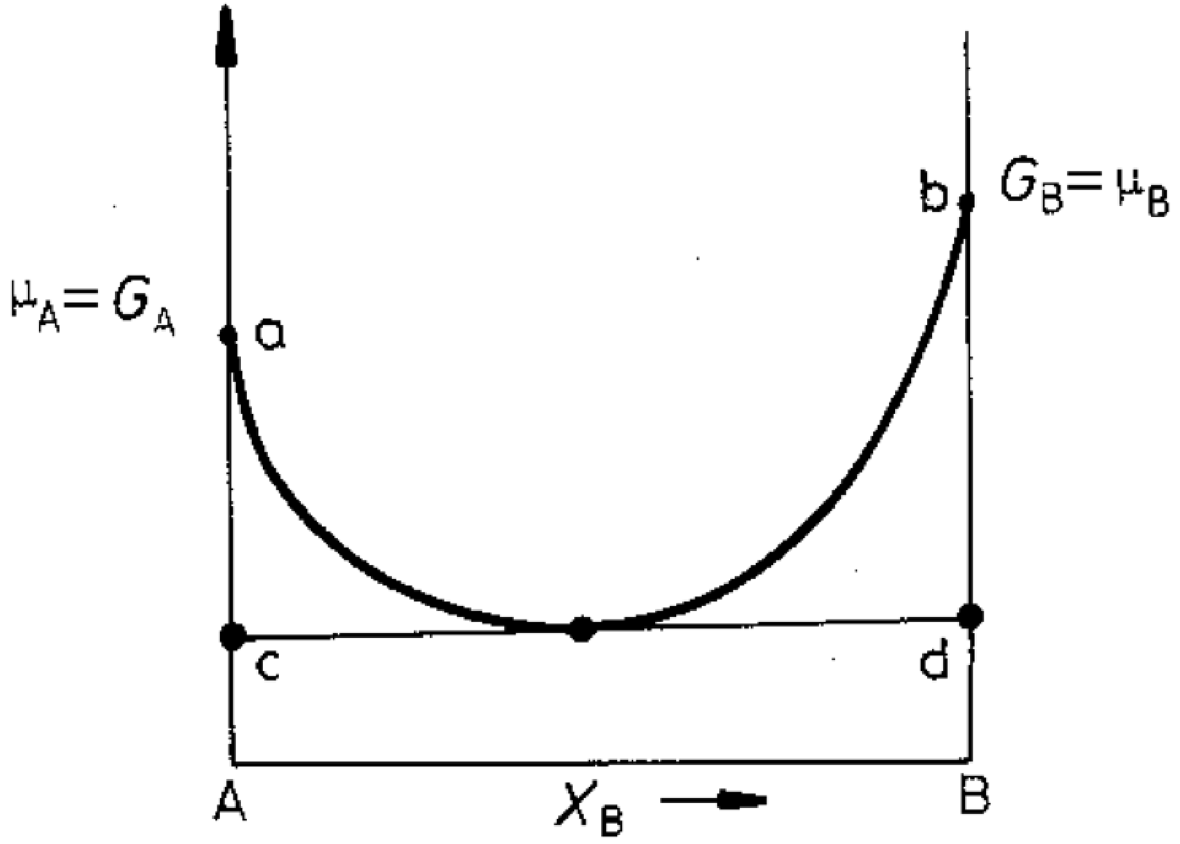
Total free energy of the mixture: $\Delta H_m = 0$

$$G = G_A X_A + G_B X_B + RT\left(X_A \ln X_A + X_B \ln X_B\right)$$

$$G = \mu_A X_A + \mu_B X_B$$

$$\mu_A = G_A + RT \ln X_A$$

$$\mu_B = G_B + RT \ln X_B$$



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Calculation of the mixing enthalpy $\Delta H_m \neq 0$

V_{AA} = potential of interaction *A*-*A*

V_{BB} = potential of interaction *B*-*B*

V_{AB} = potential of interaction *A*-*B*

$$\Delta H_m \approx \Delta E_m = N_{AA}V_{AA} + N_{BB}V_{BB} + N_{AB}V_{AB}$$

number of pairs *A*-*A* $\quad N_{AA} = \frac{1}{2} N X_A \cdot z X_A$

$$X_A = X \qquad X_B = 1 - X$$

$$N_{AA} = \frac{1}{2} N z X^2 \qquad N_{BB} = \frac{1}{2} N z (1-X)^2 \qquad N_{AB} = N z X (1-X)$$

$$\Delta H_m \cong \Delta E_m = \frac{1}{2} N z X^2 V_{AA} + \frac{1}{2} N z (1-X)^2 V_{BB} + N z X (1-X) V_{AB}$$

$$= \frac{1}{2} N z \left[X V_{AA} - X(1-X) V_{AA} + (1-X) V_{BB} - X(1-X) V_{BB} + 2X(1-X) V_{AB} \right]$$

Calculation of the mixing enthalpy

$$\Delta H_m = \frac{1}{2} Nz\left[XV_{AA} + (1-X)V_{BB} + 2X(1-X)\left(V_{AB} - \frac{V_{AA}+V_{BB}}{2} \right) \right]$$

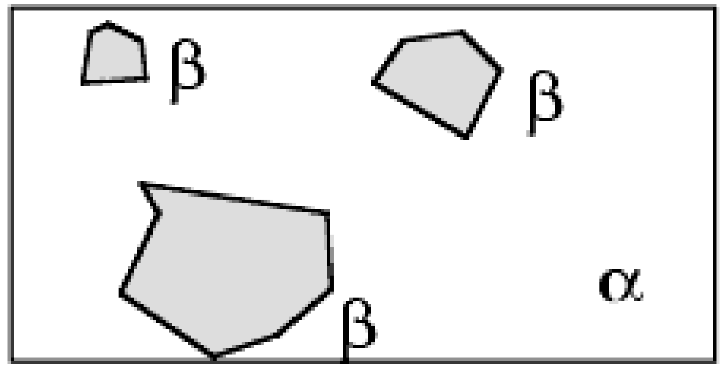
$$\Delta H_m = \frac{1}{2} Nz\left[XV_{AA} + (1-X)V_{BB} + 2X(1-X)V \right] \quad V = V_{AB} - \frac{V_{AA}+V_{BB}}{2}$$

3 possible cases

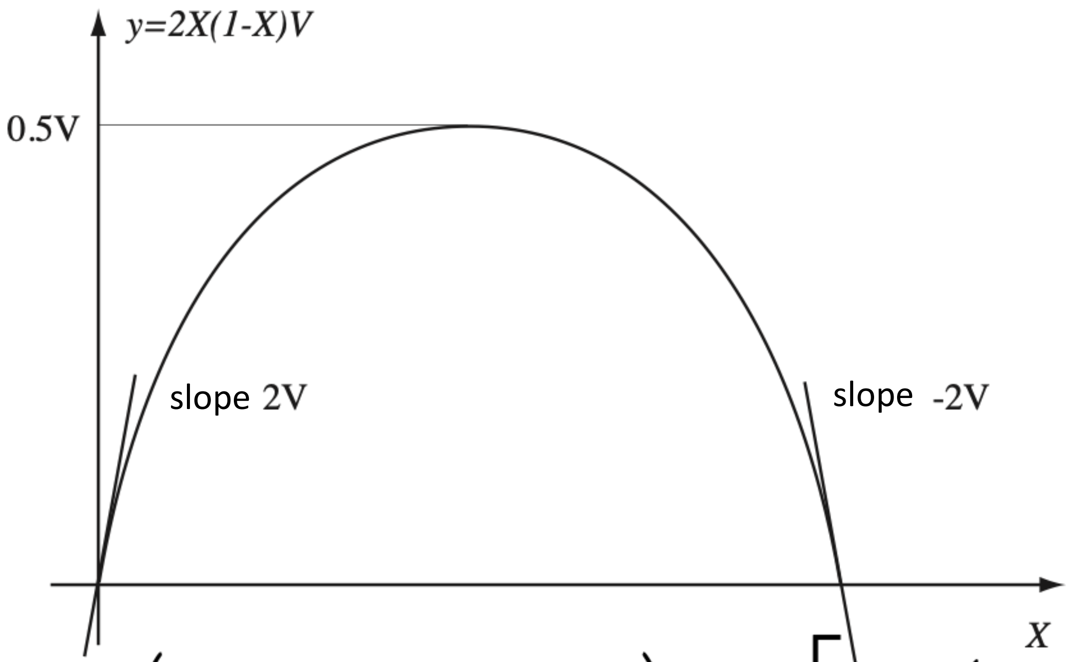
1) $V = 0$ that is $V_{AA} \sim V_{AB} \sim V_{BB}$ Disordered solution

2) $V > 0$ or $V_{AB} > \frac{V_{AA}+V_{BB}}{2}$ Separation of phases (precipitation)

3) $V < 0$ or $V_{AB} < \frac{V_{AA}+V_{BB}}{2}$ Alloy



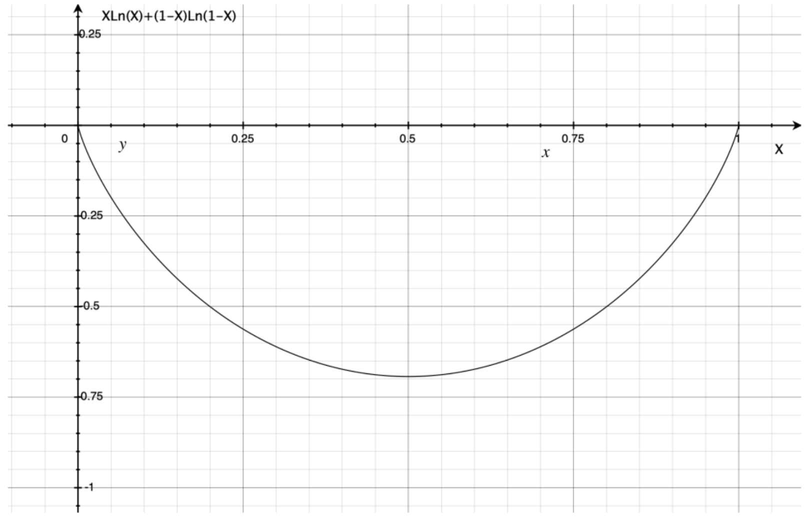
The interaction potential V (Ω)



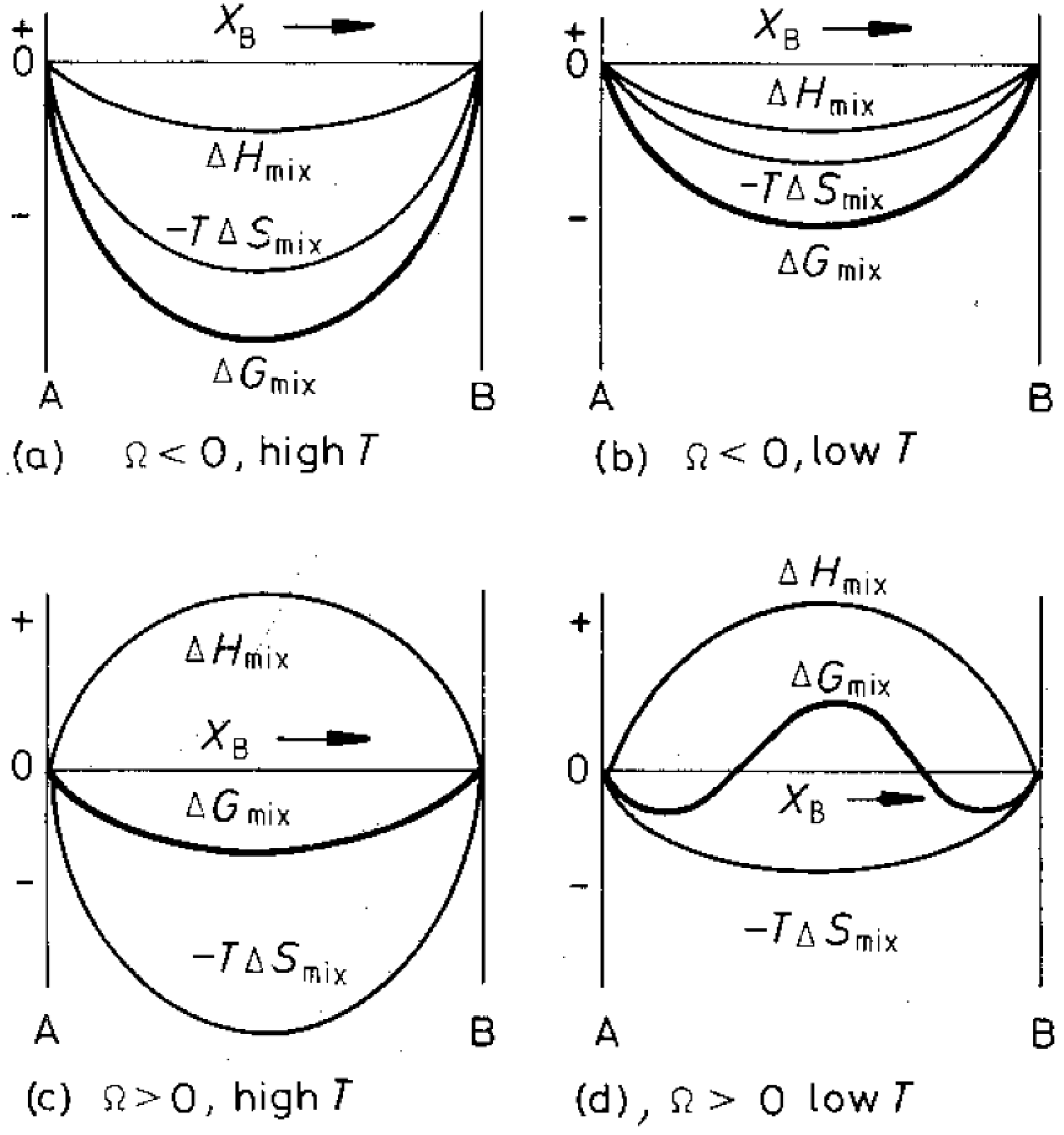
$$NzX(1-X)V = \Omega X_A X_B = \Omega\left(X_A^2 X_B + X_A X_B^2\right) = \Omega\left[X_A\left(1-X_A\right)^2 + X_B\left(1-X_B\right)^2\right]$$

$$\Delta H_m = \Omega X_A X_B$$

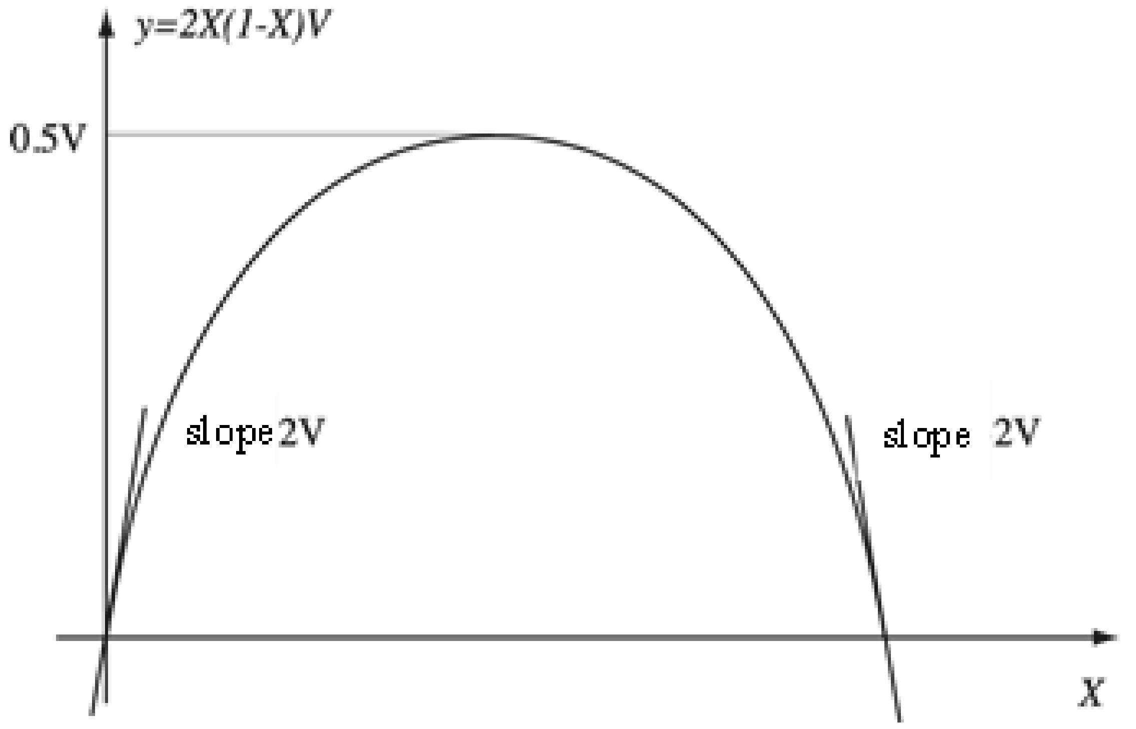
$$\Delta G_m = \Delta H_m - T\,\Delta S_m = G_A X_A + G_B X_B + \Omega X_A X_B + RT\left(X_A \ln X_A + X_B \ln X_B\right)$$



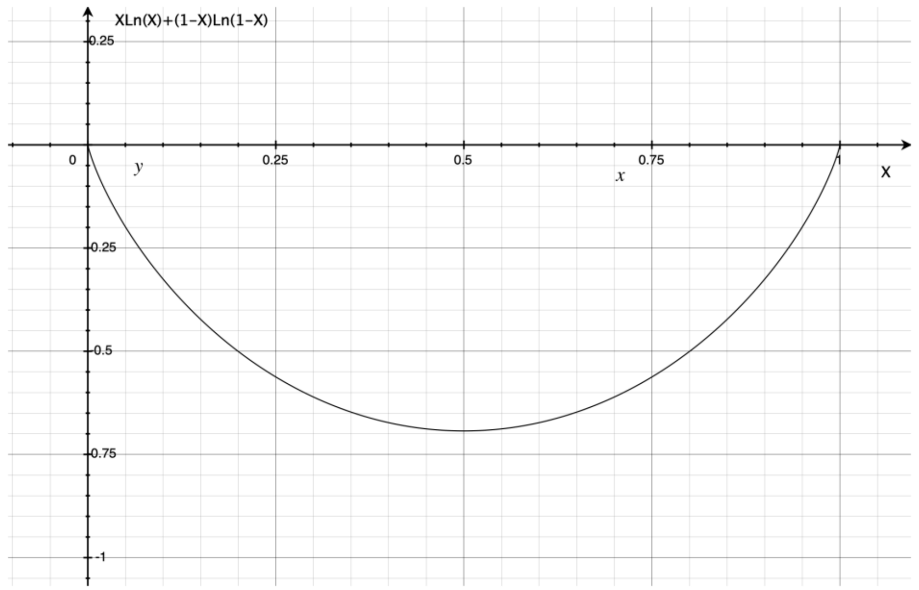
The interaction potential V (Ω)



$$\Delta H_m = \Omega X_A X_B$$



$$-T\Delta S_m = RT\left(X\ln X + (1-X)\ln(1-X)\right)$$



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Chemical potential and activity (real solutions)

$$\Delta G_m = \Delta H_m - T\Delta S_m = G_A X_A + G_B X_B + \Omega X_A X_B + RT\left(X_A \ln X_A + X_B \ln X_B\right)$$

$$\Omega X_A X_B = \Omega\left[X_A\left(1 - X_A\right)^2 + X_B\left(1 - X_B\right)^2\right]$$

$$\mu_A = G_A + \Omega\left(1 - X_A\right)^2 + RT\ln X_A \qquad \mu_B = G_B + \Omega\left(1 - X_B\right)^2 + RT\ln X_B$$

ideal solution

$$\mu_A = G_A + RT\ln X_A$$

$$\mu_B = G_B + RT\ln X_B$$

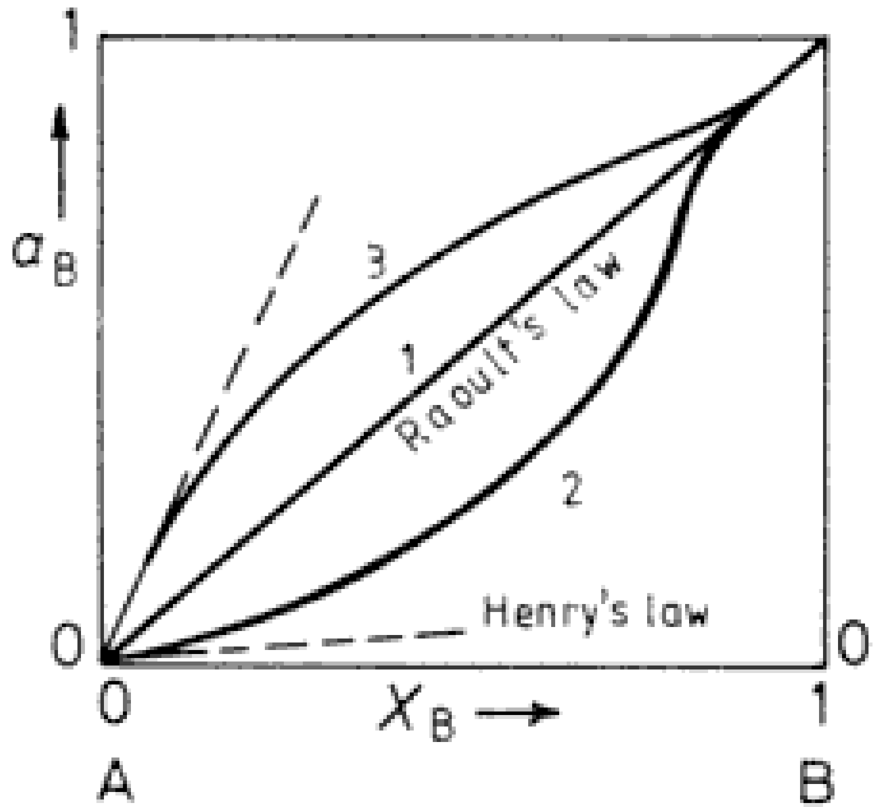
$$\mu_A = G_A + RT\ln a_A$$

$$\mu_B = G_B + RT\ln a_B$$

$$\frac{a_A}{X_A} = \gamma_A$$

activity coefficient

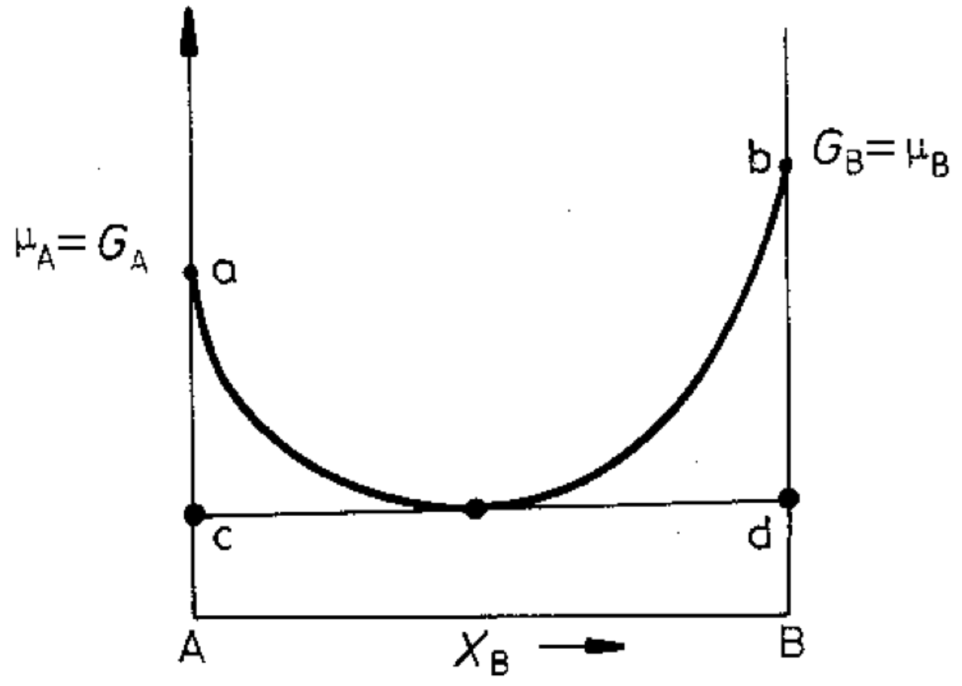
$$\ln\frac{a_A}{X_A} = \frac{\Omega}{RT}\left(1 - X_A\right)^2$$



Binary phase diagram

Ideal solution

$$\mu_A^\alpha = G_A^\alpha + RT\ln X_A^\alpha \qquad \mu_A^\beta = G_A^\beta + RT\ln X_A^\beta$$



Equilibrium (minimum)

$$\mu_A^\alpha = \mu_A^\beta \qquad \mu_B^\alpha = \mu_B^\beta$$

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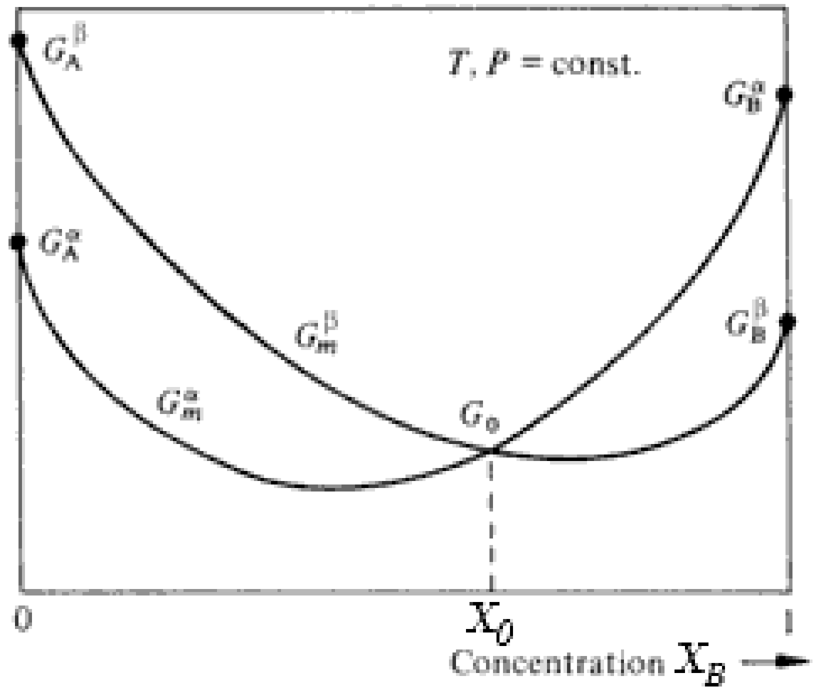
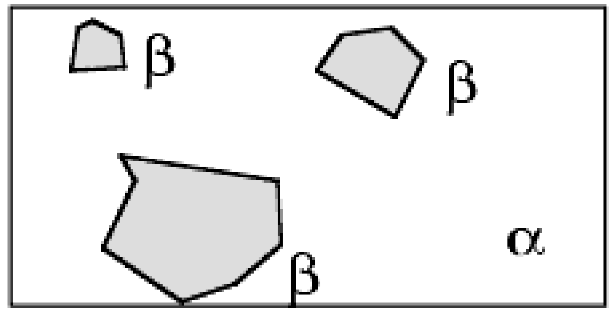
Binary phase diagram





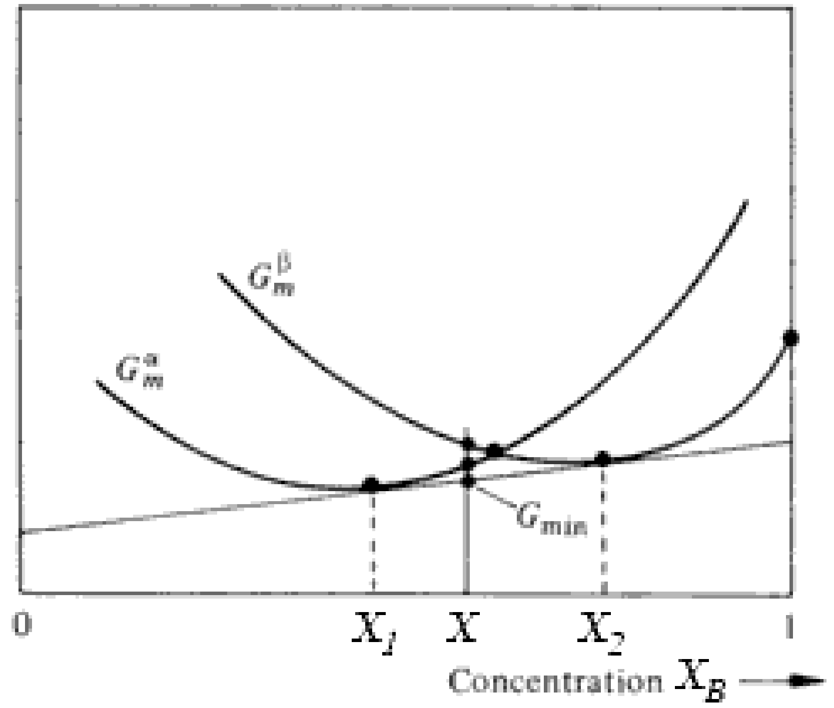
Concentration $X = X_A$

$$X = f^\alpha X^\alpha + f^\beta X^\beta = f^\alpha X^\alpha + \left(1 - f^\alpha\right) X^\beta$$

$$f^\alpha = \frac{X^\beta - X}{X^\beta - X^\alpha} \qquad f^\beta = 1 - f^\alpha = \frac{X - X^\alpha}{X^\beta - X^\alpha}$$

$$G = f^\alpha G^\alpha + f^\beta G^\beta = \frac{X^\beta - X}{X^\beta - X^\alpha} G^\alpha + \frac{X - X^\alpha}{X^\beta - X^\alpha} G^\beta$$

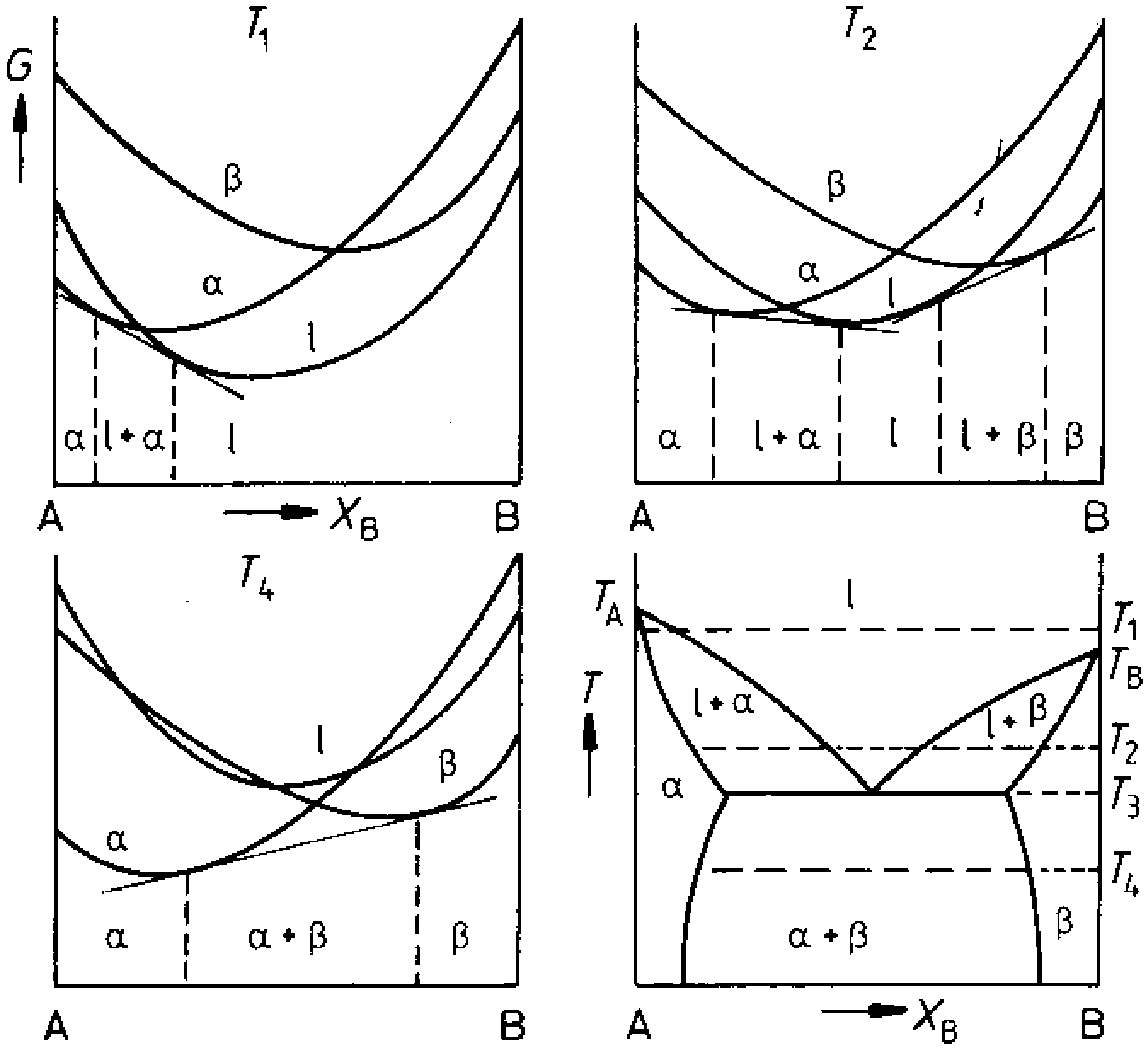
$$G = G^\alpha + \frac{G^\beta - G^\alpha}{X^\beta - X^\alpha}\left(X - X^\alpha\right)$$



$$G_{\min} = G^\alpha_{c1} + \frac{G^\beta_{c2} - G^\alpha_{c1}}{X^\beta - X^\alpha}\left(X - X^\alpha\right)$$

construction of the common tangent

Eutectic binary phase diagram



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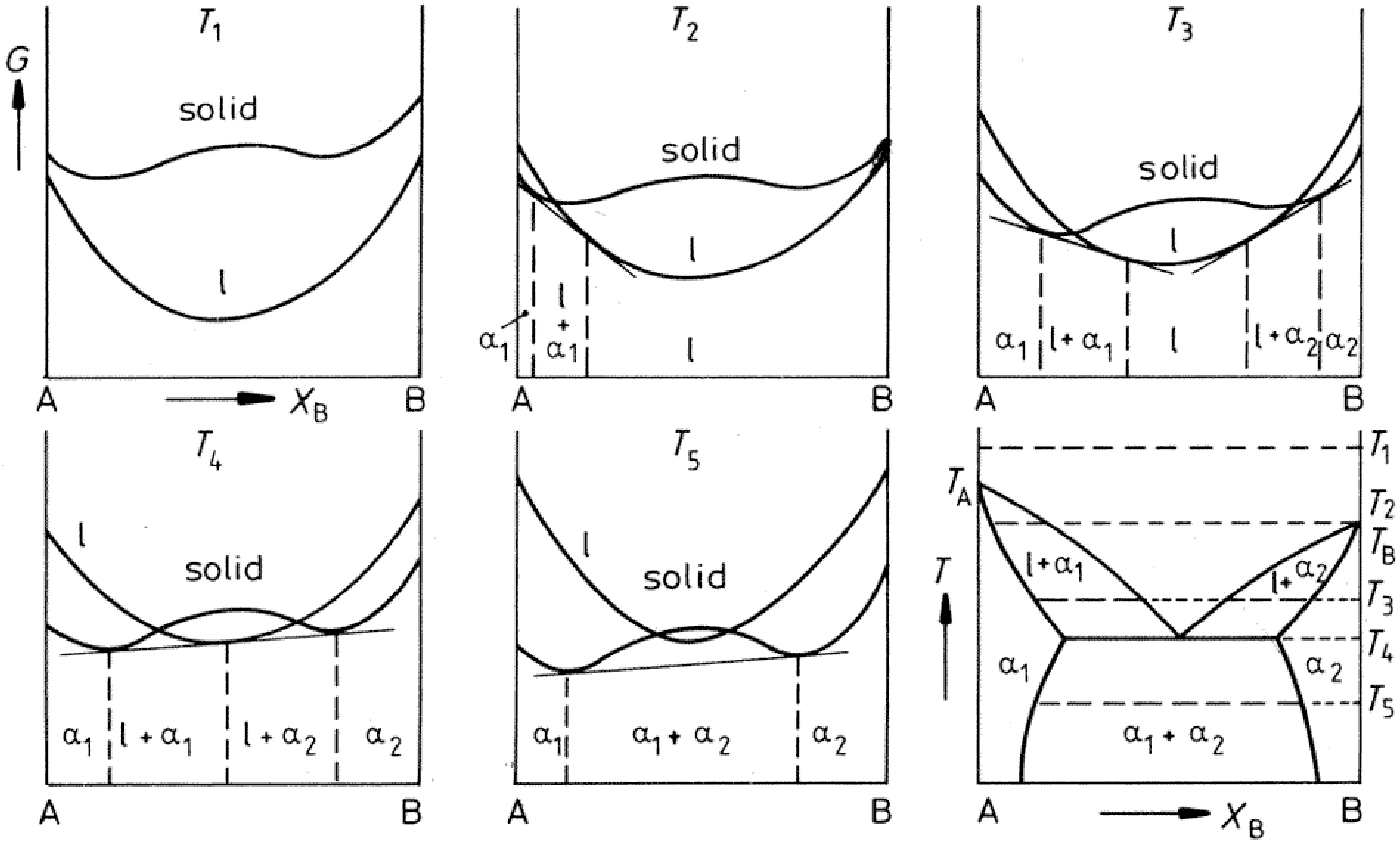
Binary phase diagram (alpha₁ and alpha₂ phases)



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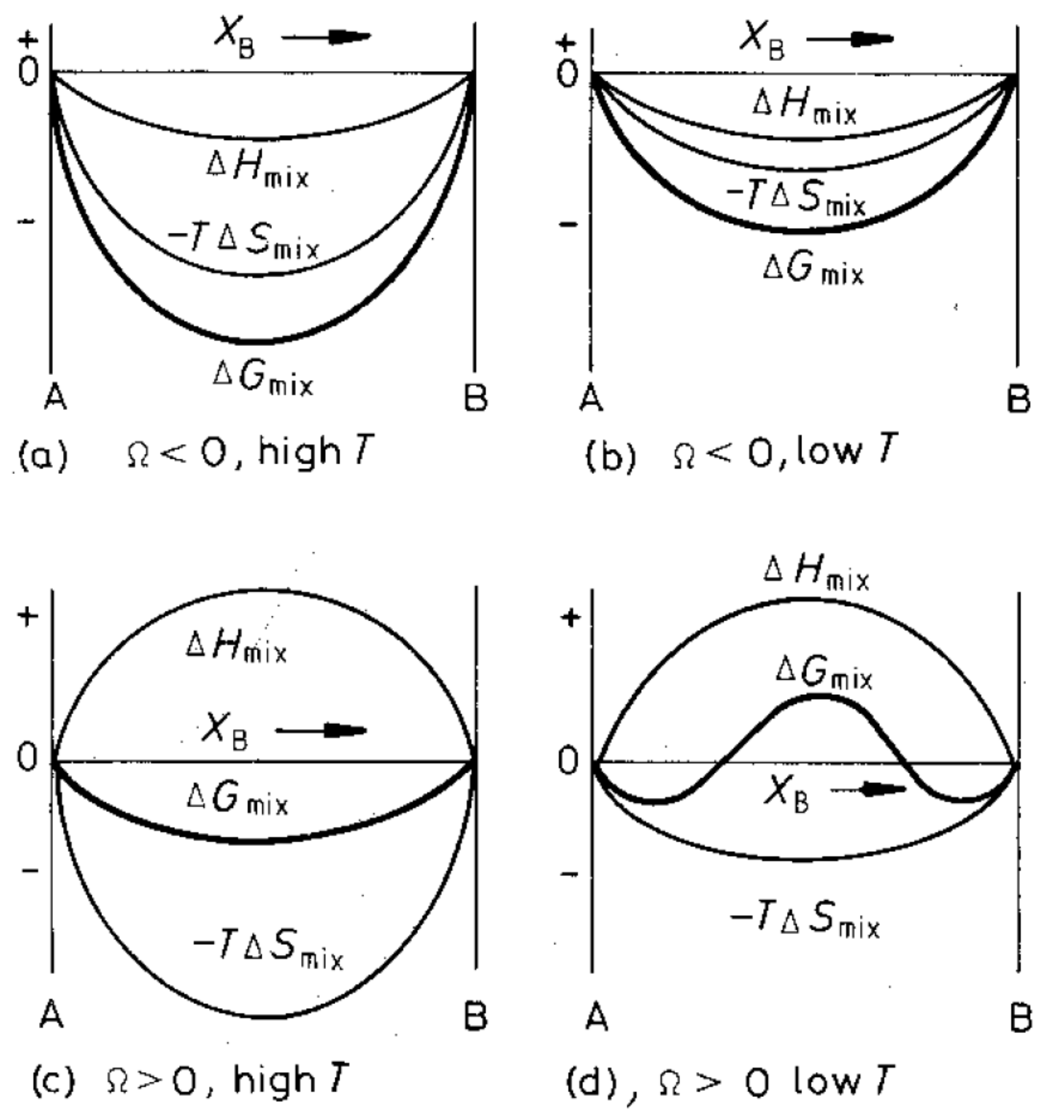
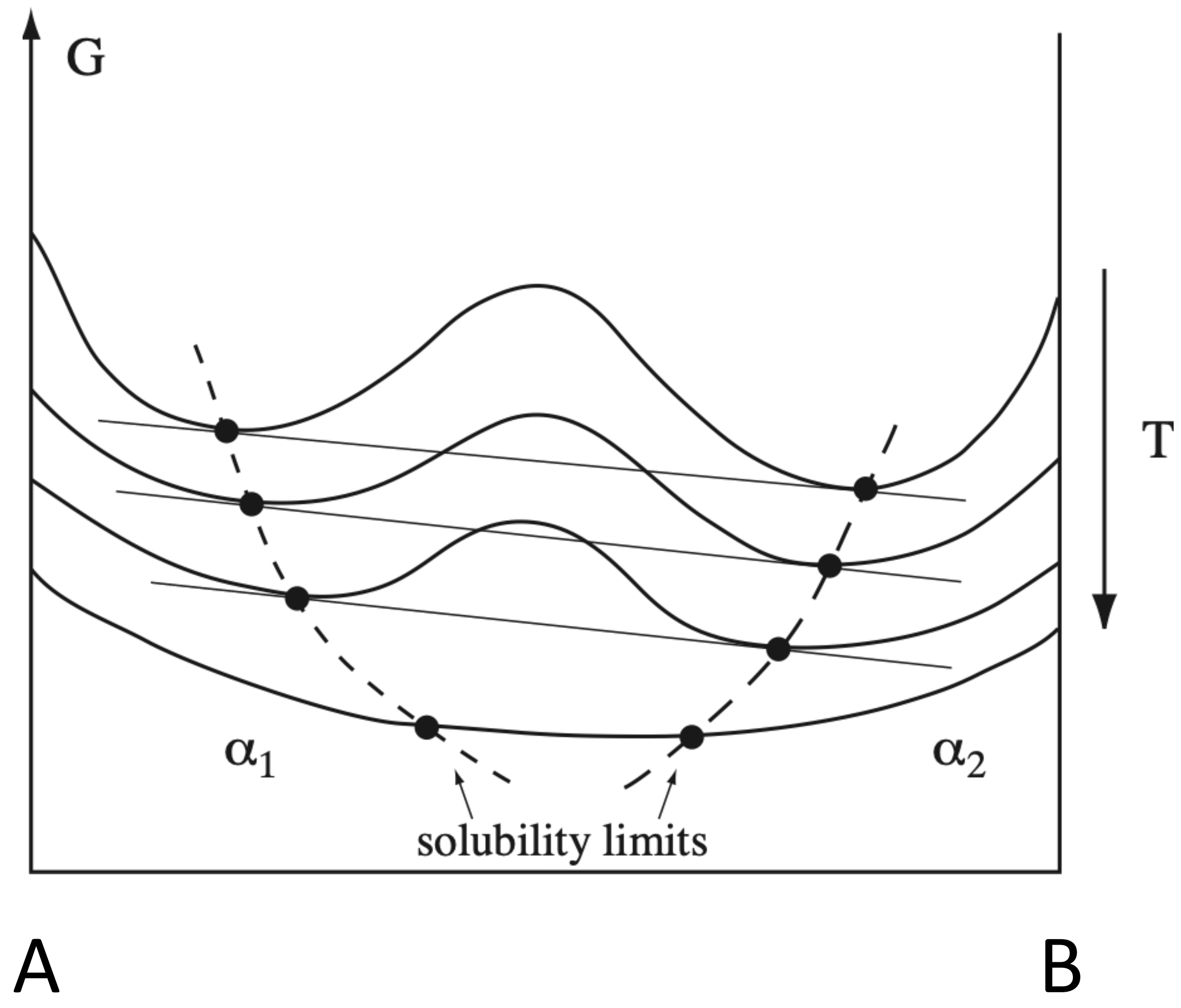
Spinodal diagram

miscibility gap





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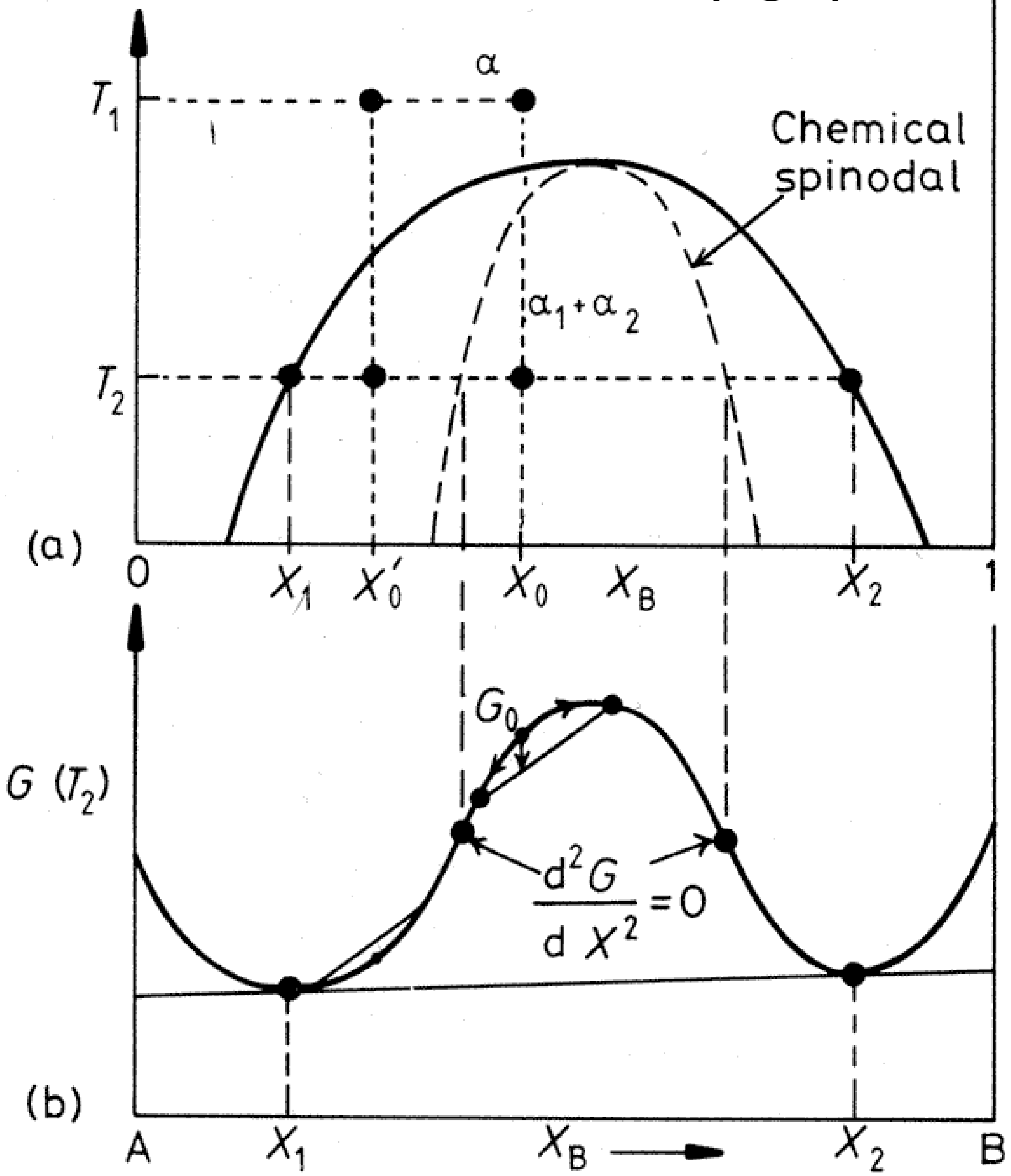
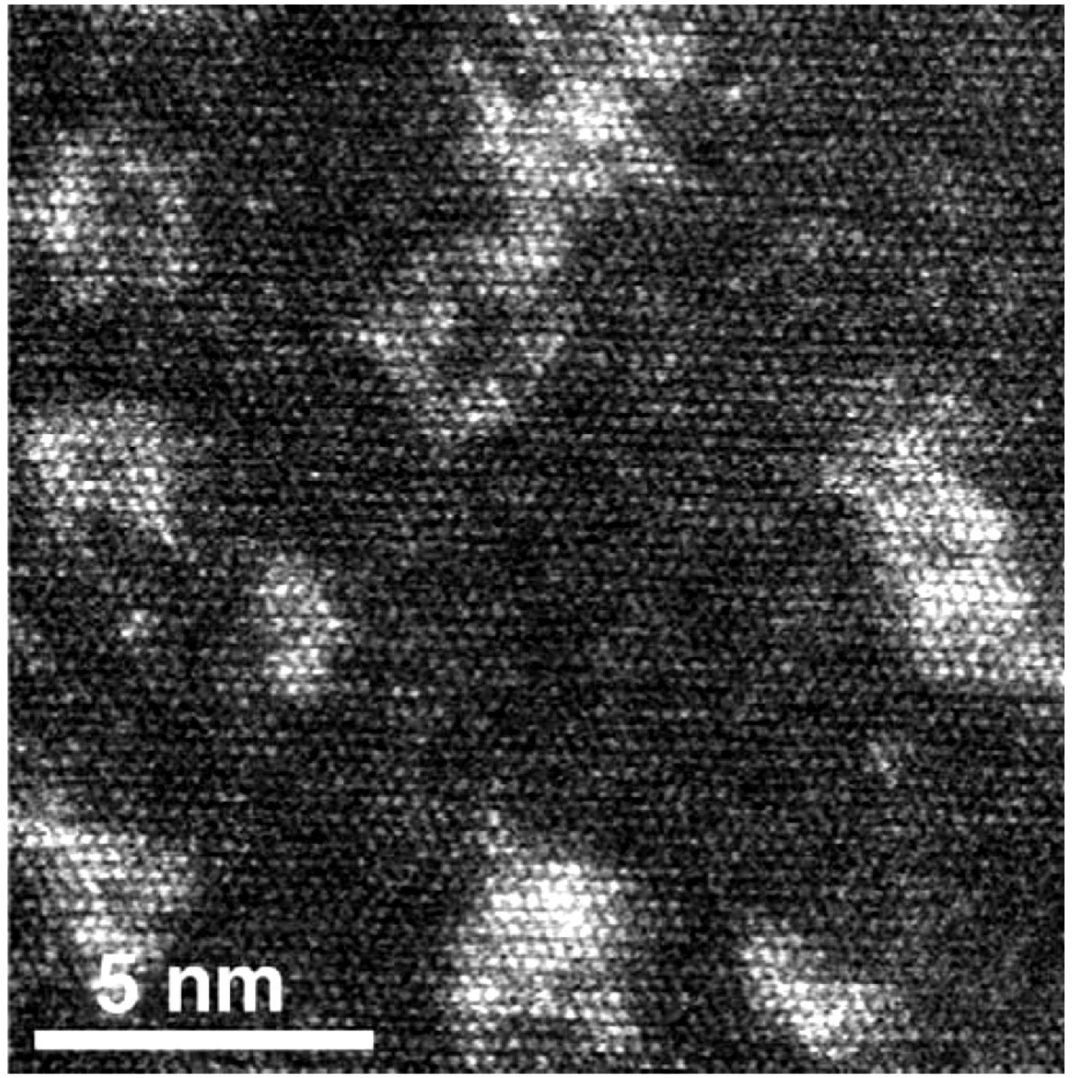
Spinodal diagram

miscibility gap

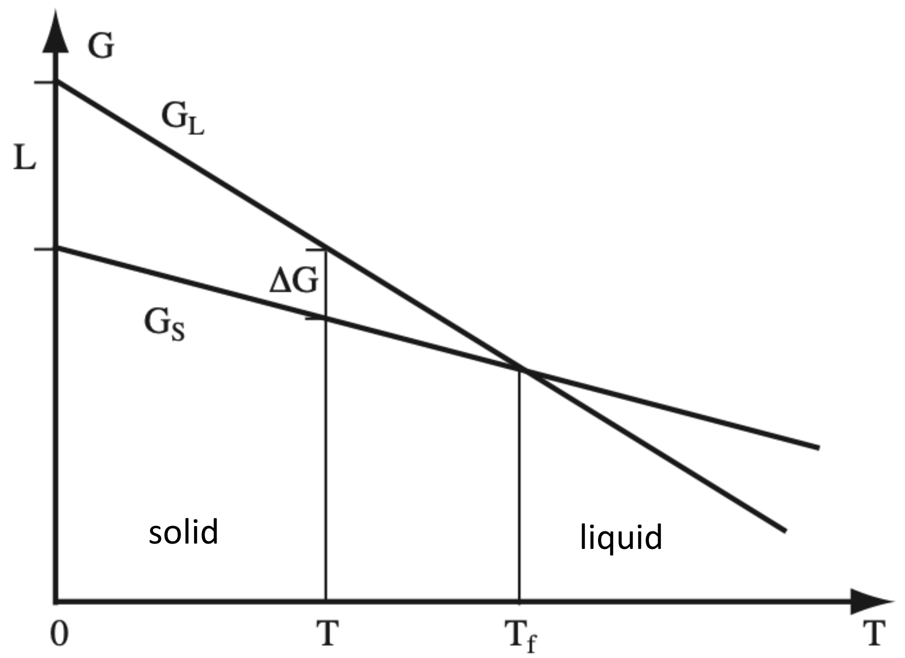




GP zones in Al-Ag

Spinodal decomposition

Solidification



$$G_L = H_L - TS_L$$

$$G_S = H_S - TS_S$$

$$G_L = G_S \Rightarrow H_L - T_F S_L = H_S - T_F S_S$$

$$\Delta H_F = H_L - H_S = T_F(S_L - S_S) = T_F \Delta S_F$$

$$\Delta H_F = H_L - H_S = L$$ Latent heat

$$\Delta S_F = \frac{L}{T_F}$$

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Clausius-Clapeyron equation

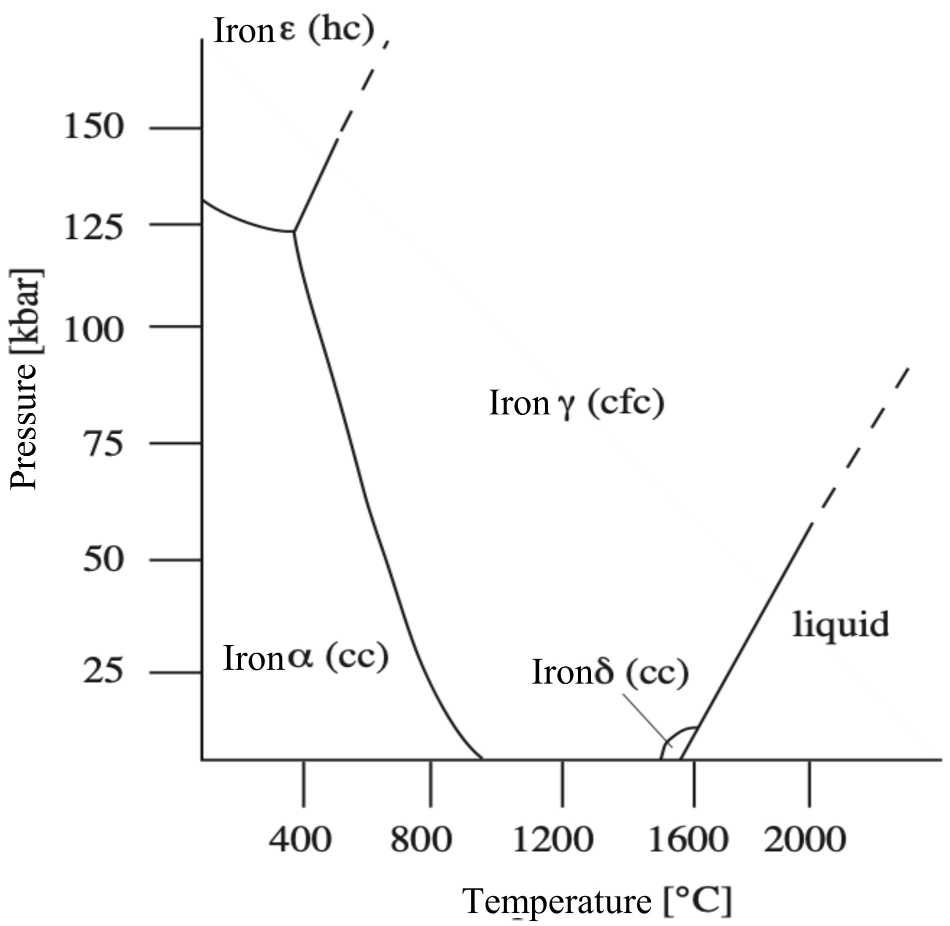
$$dG^{\alpha} = V^{\alpha}dP - S^{\alpha}dT$$

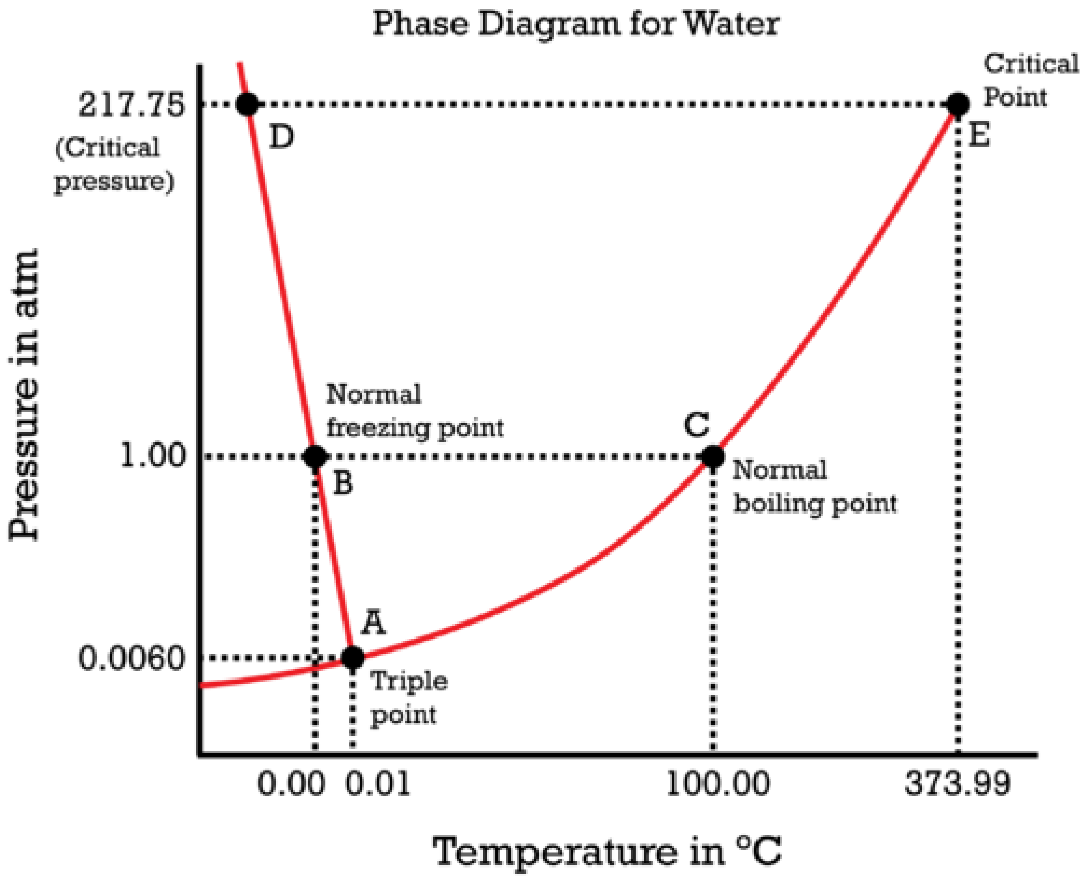
$$dG^{\beta} = V^{\beta}dP - S^{\beta}dT$$

$$dG^{\alpha} = dG^{\beta}$$

$$\left(\frac{dP}{dT}\right)_{eq} = \frac{S^{\beta} - S^{\alpha}}{V^{\beta} - V^{\alpha}} = \frac{\Delta S}{\Delta V}$$

$$\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta H}{T_{eq}\Delta V}$$





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Nucleation

$$T < T_F$$

$$\Delta G = G_L - G_S = \Delta H_F - T\left(S_L - S_S\right) = L - T\Delta S$$

$$\Delta G == L - T\frac{L}{T_F} = \frac{L}{T_F}\left(T_F - T\right) = \Delta S_F \Delta T$$ Supercooling energy

Energy due to the formation of an interface

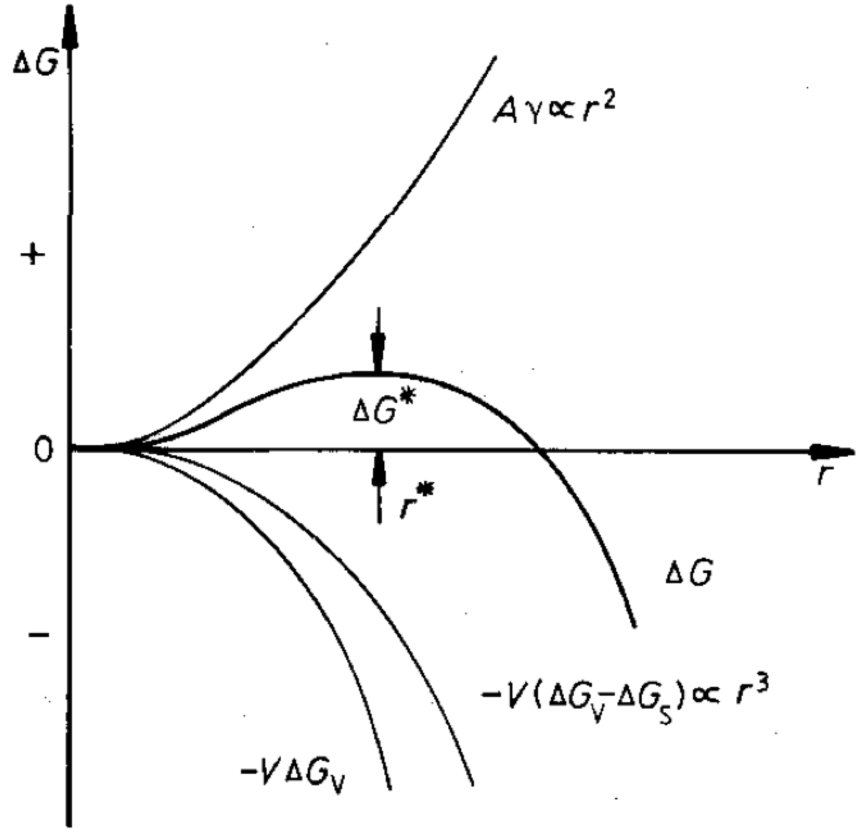
1) homogeneous nucleation

$$\Delta G_g = \Delta g_V V + \Delta g_s s$$

$$\Delta G_g = (g_S - g_L)\frac{4}{3}\pi r^3 + 4\pi r^2\gamma = -\frac{4}{3}\pi r^3\frac{L}{T_F}\Delta T + 4\pi r^2\gamma$$

$$r^* = \frac{2\gamma T_F}{L\Delta T}$$

$$\Delta G^* = \frac{16}{3}\pi\gamma^3\frac{T_F^2}{L^2\Delta T^2} = \frac{16}{3}\pi\frac{\gamma^3}{\Delta G^2}$$



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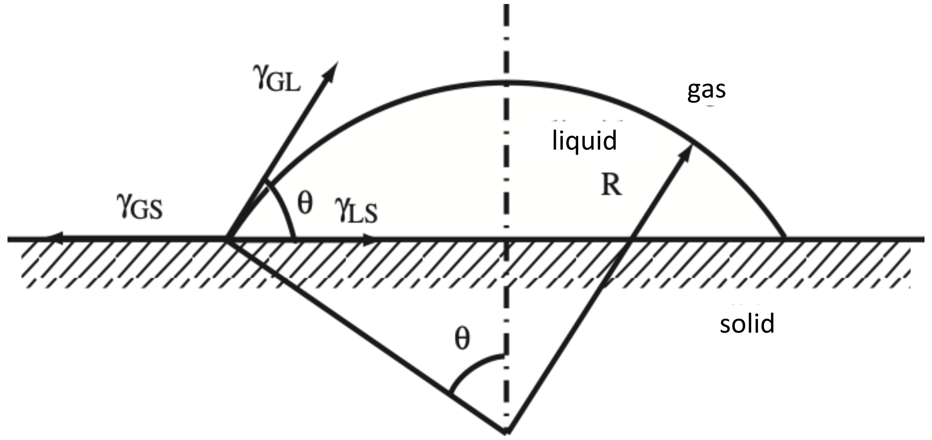
Nucleation

1) localized (heterogeneous) nucleation



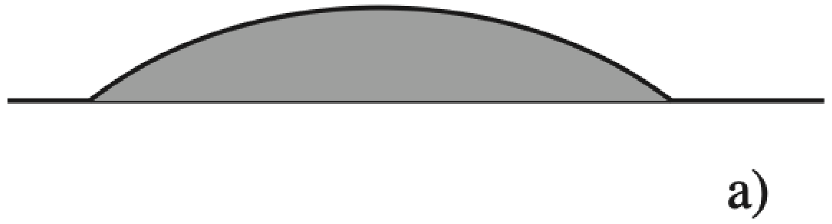
$$\gamma_{GS} = \gamma_{LS} + \gamma_{GL} cos\theta$$

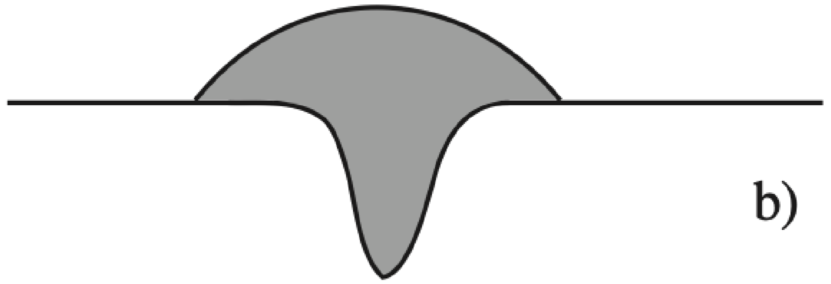
$$R_c^{loc} = -\frac{2\gamma_{LS}}{\Delta g_V}$$

$$\Delta G_c^{loc} = \frac{4}{3}\pi \frac{\gamma_{LS}^3}{\Delta g_V^2}\left(2 - 3\cos\theta + \cos^3\theta\right)$$

$\theta = \pi : \Delta G_c^{loc} = \Delta G_c^{gen}$

$\theta = 0 : \Delta G_c^{loc} = 0$





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Nucleation statistics

$$N^* = N_\alpha e^{-\frac{\Delta G^*}{kT}} \qquad \Delta G^* = \frac{16}{3}\pi\gamma^3 \frac{T_F^2}{L^2\left(T_F - T\right)^2}$$

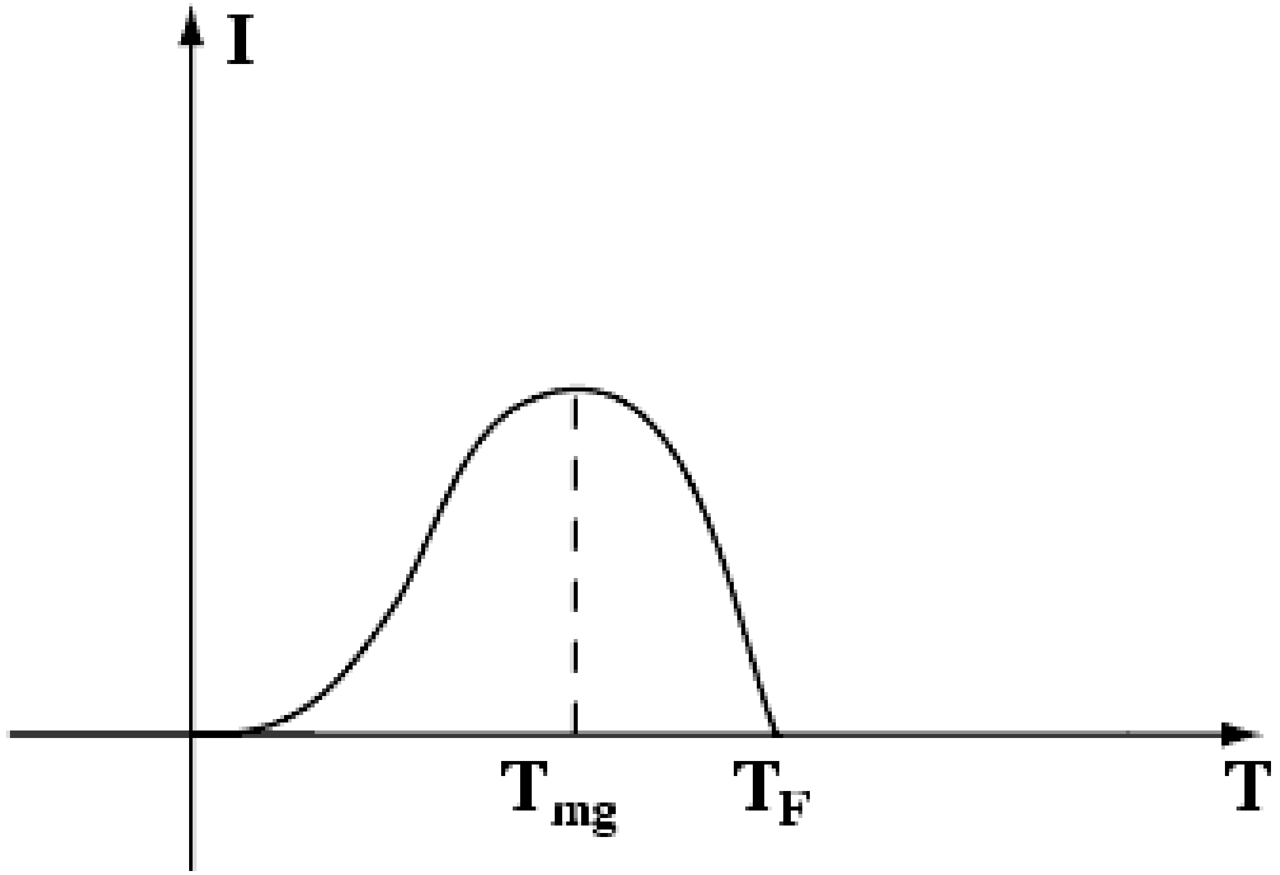
Nucleation rate

$$I = N^* n_s \nu_c \qquad \nu_c = \nu_D z e^{-\frac{\Delta G^S}{kT}}$$

$$I = I_0 e^{-\frac{\Delta G^* + \Delta G^S}{kT}}$$

$$T \to T_F \quad \Delta G^* \to \infty \quad I \to 0$$

$$T \to 0 \quad I \to 0$$



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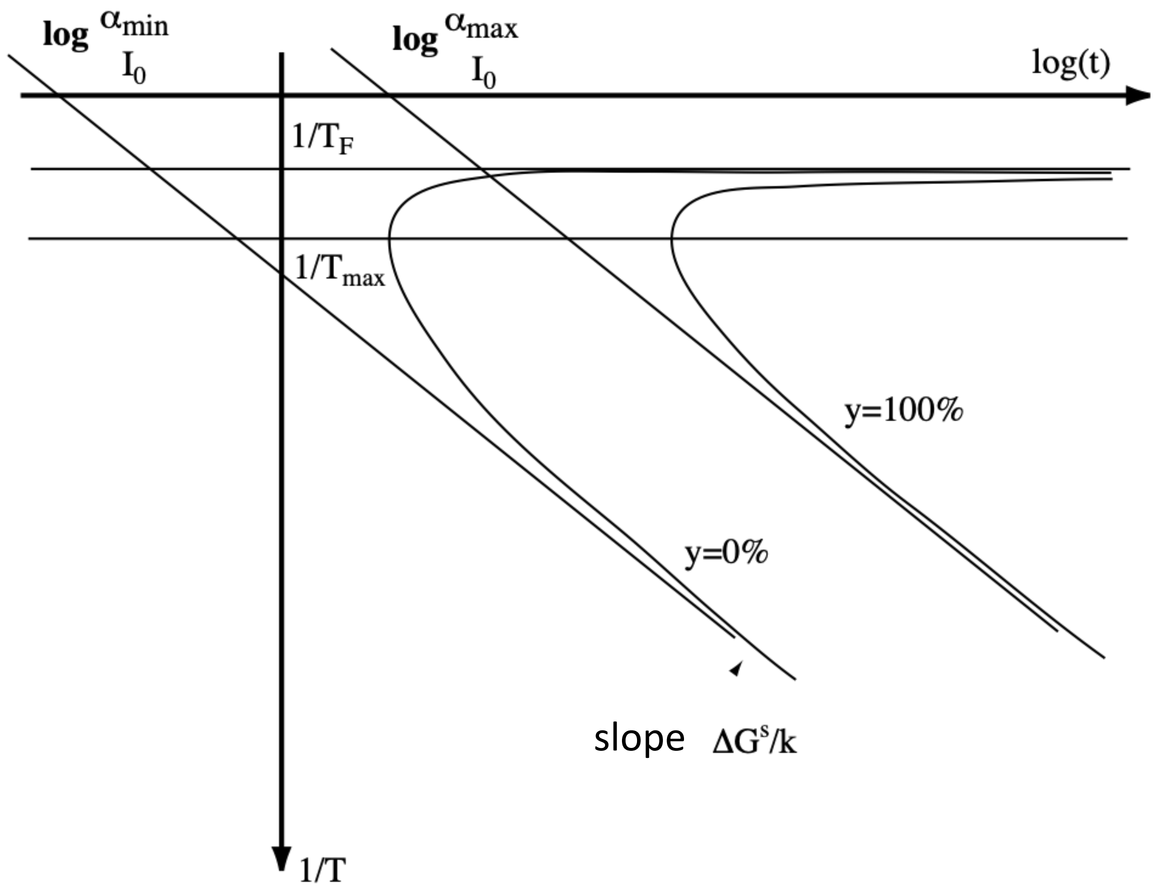
Nucleation statistics

$\alpha = I \cdot t$ number of nuclei/cm^3

$$I = I_0 e^{-\frac{\Delta G^* + \Delta G^S}{kT}} \qquad \log t = \log\frac{\alpha}{I_0} + \frac{\Delta G^*}{kT} + \frac{\Delta G^S}{kT}$$

$$T \to 0 \;\; \Delta G^* \; is \; small \;\; \log t \simeq \log\frac{\alpha}{I_0} + \frac{\Delta G^S}{kT} \qquad T \to T_F \quad \Delta G^* \to \infty \;\; \log t \to \infty$$

Diagram Temperature-Transformation Time (TTT)



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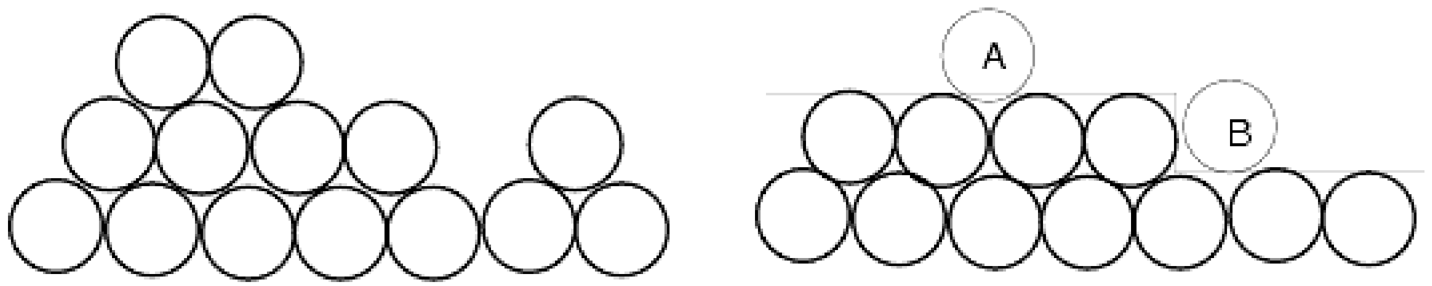
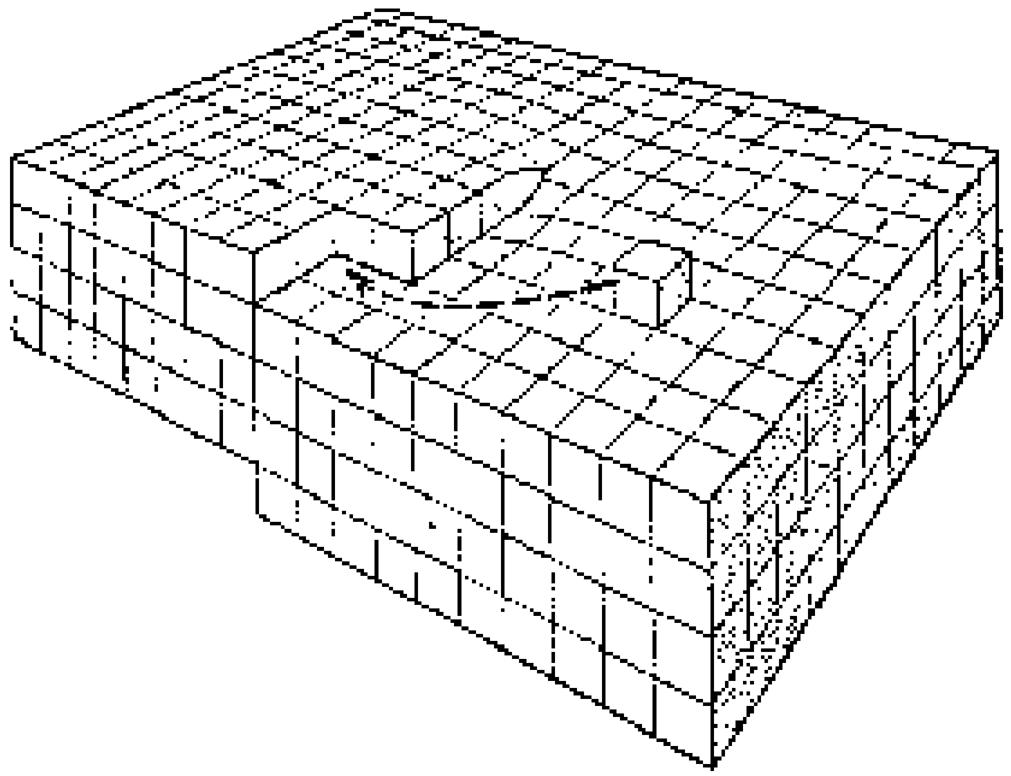
Crystalline growth

a-rough   b-smooth



b   a

$$G_{surf} = H_{surf} - TS_{surf}$$



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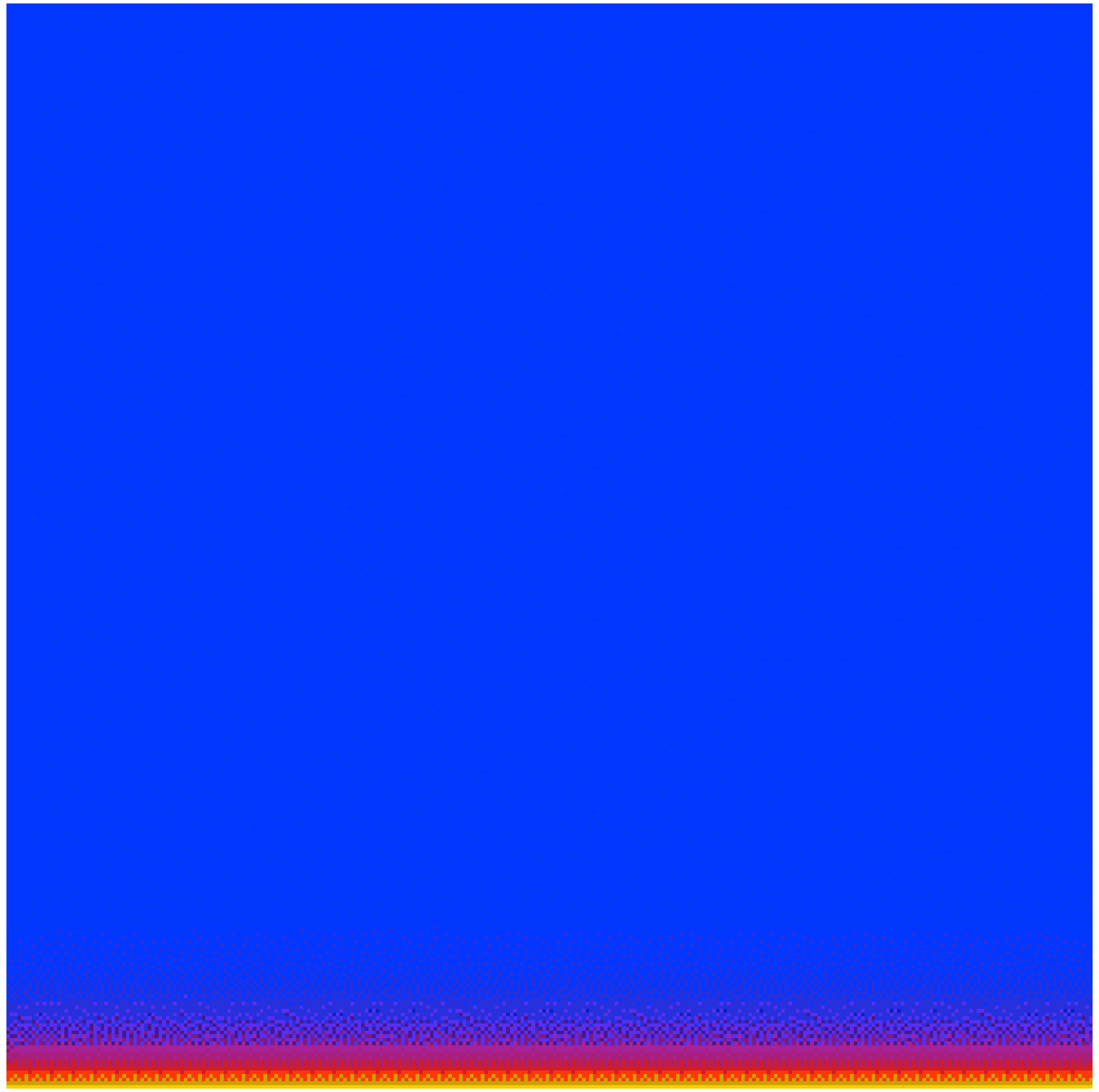
Dendritic growth



Thermal balance

$$\vec{J} = \lambda \overrightarrow{grad T}$$

λ=thermal conductivity

$$\lambda_S \left.\frac{\partial T}{\partial x}\right)_S = L_V v_i + \lambda_L \left.\frac{\partial T}{\partial x}\right)_L$$

L_V latent heat/ volume unit

$$v_i = \frac{1}{L_V}\left(\lambda_S \left.\frac{\partial T}{\partial x}\right)_S - \lambda_L \left.\frac{\partial T}{\partial x}\right)_L \right)$$

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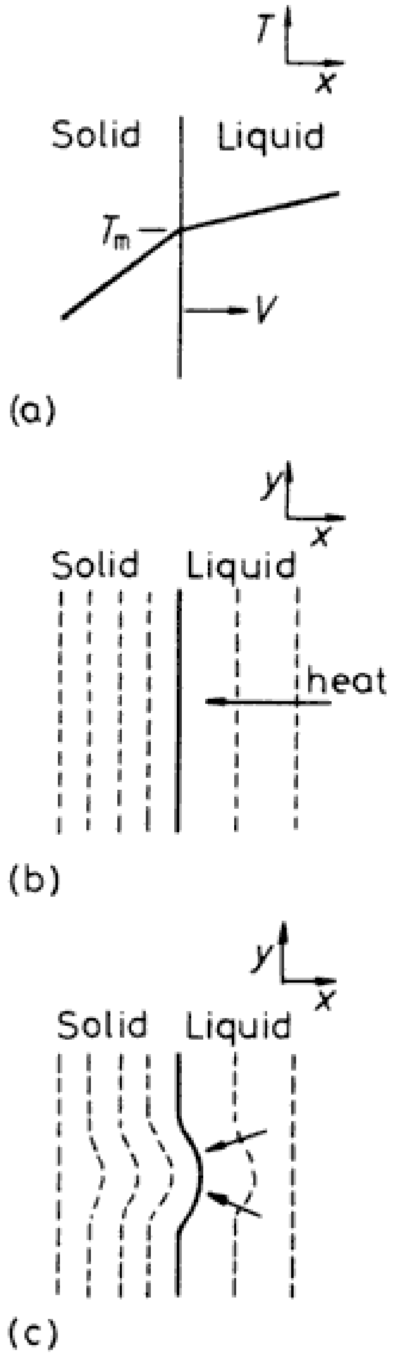
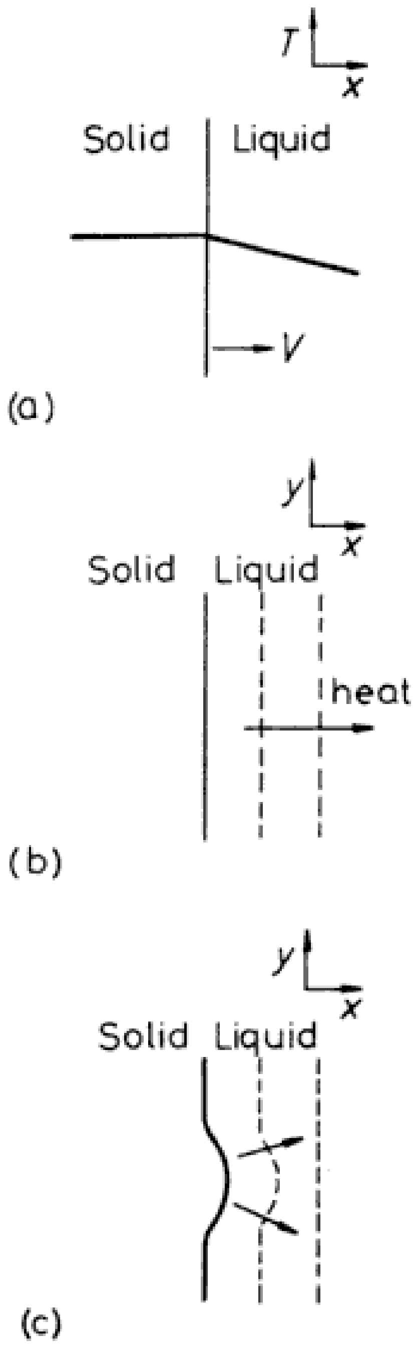
Dendritic growth

$$v_i = \frac{1}{L_V}\left(\lambda_S \left(\frac{\partial T}{\partial x}\right)_S - \lambda_L \left(\frac{\partial T}{\partial x}\right)_L\right)$$

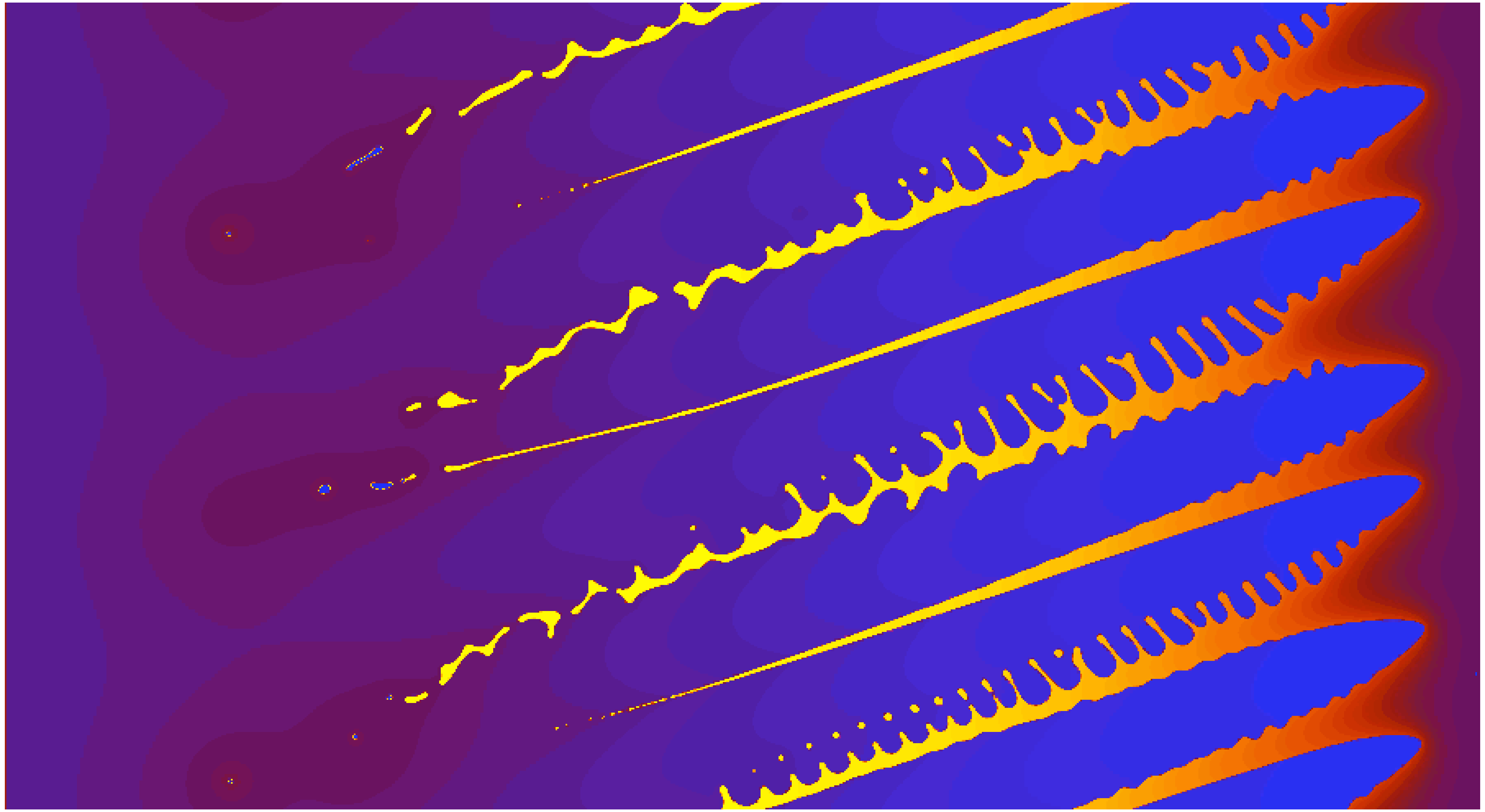




Dendritic growth: simulations

V. Pavlik, U. Dilthey, Aachen University

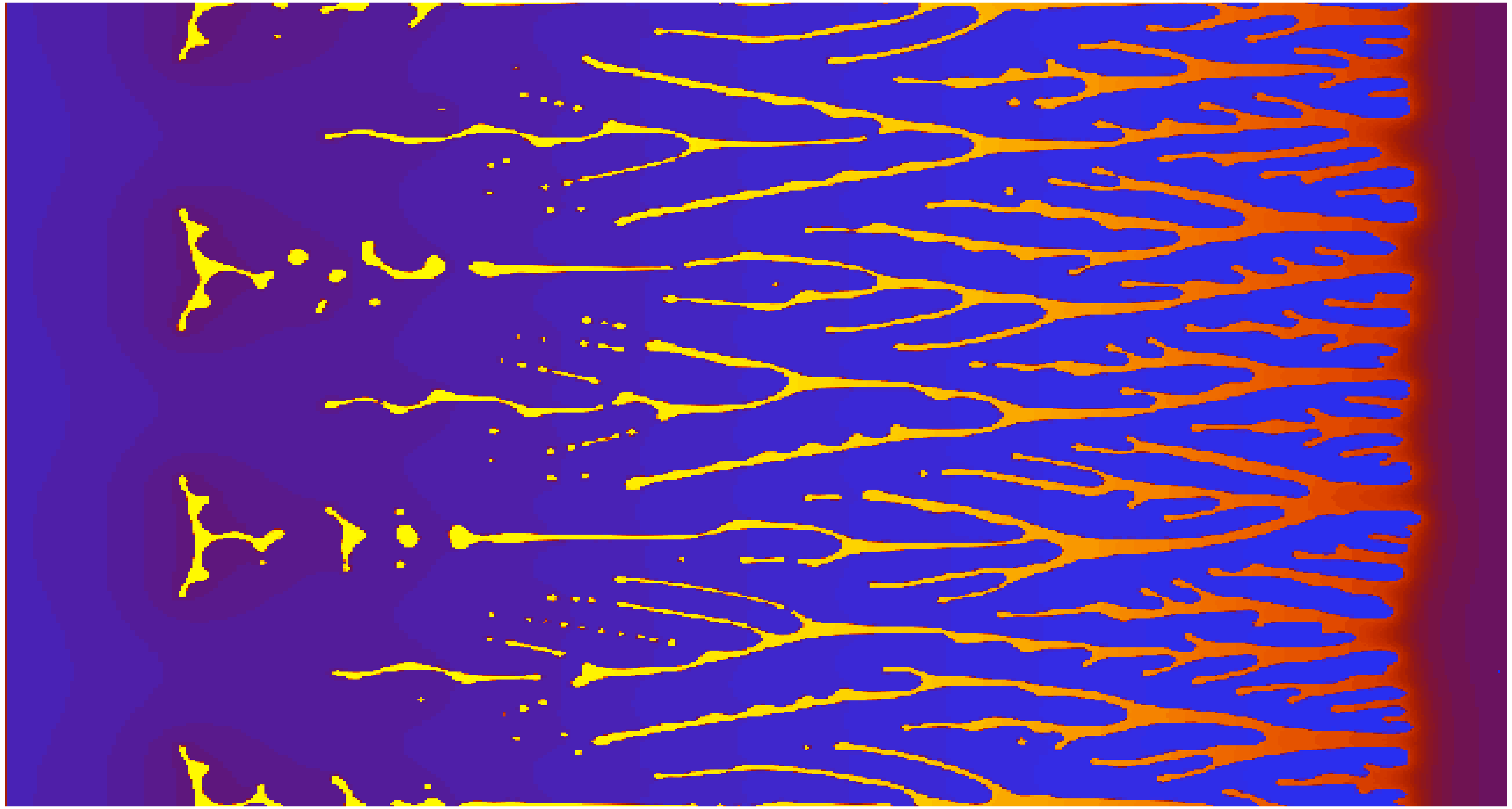
Fe-0.11%C v=10 mm/s, grad(T)=100 K/mm



Dendritic growth: simulations

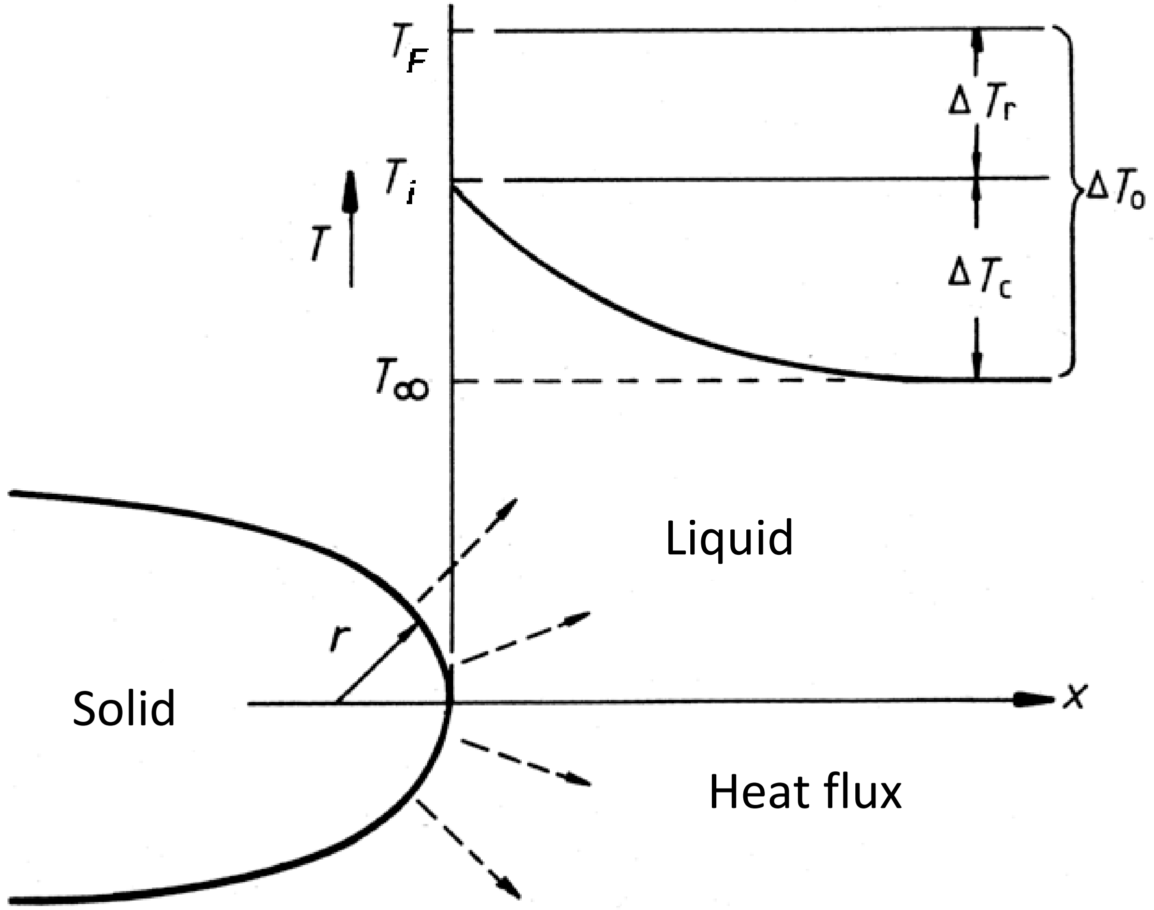
V. Pavlik, U. Dilthey, Aachen University

Fe-0.11%C v=0.1 mm/s, grad(T)=15 K/mm



Dendritic growth: effect of the curvature radius, $\lambda_S << \lambda_L$

$$\left.\frac{\partial T}{\partial x}\right)_L = \frac{T_\infty - T_i}{\alpha r} = -\frac{\Delta T_c}{\alpha r} \qquad v_i = -\frac{\lambda_L}{L_V}\left.\frac{\partial T}{\partial x}\right)_L \qquad v_i = -\frac{\lambda_L}{L_V}\frac{\Delta T_c}{\alpha r}$$



$$r^* = \frac{2\gamma T_F}{L\Delta T} \Rightarrow r = \frac{2\gamma_{SL} T_F}{L_V\left(T_F - T_i\right)} = \frac{2\gamma_{SL} T_F}{L_V \Delta T_r}$$

$T_i \rightarrow T_\infty \Rightarrow r$ minimum

$T_i \rightarrow T_F \Rightarrow r \rightarrow \infty$

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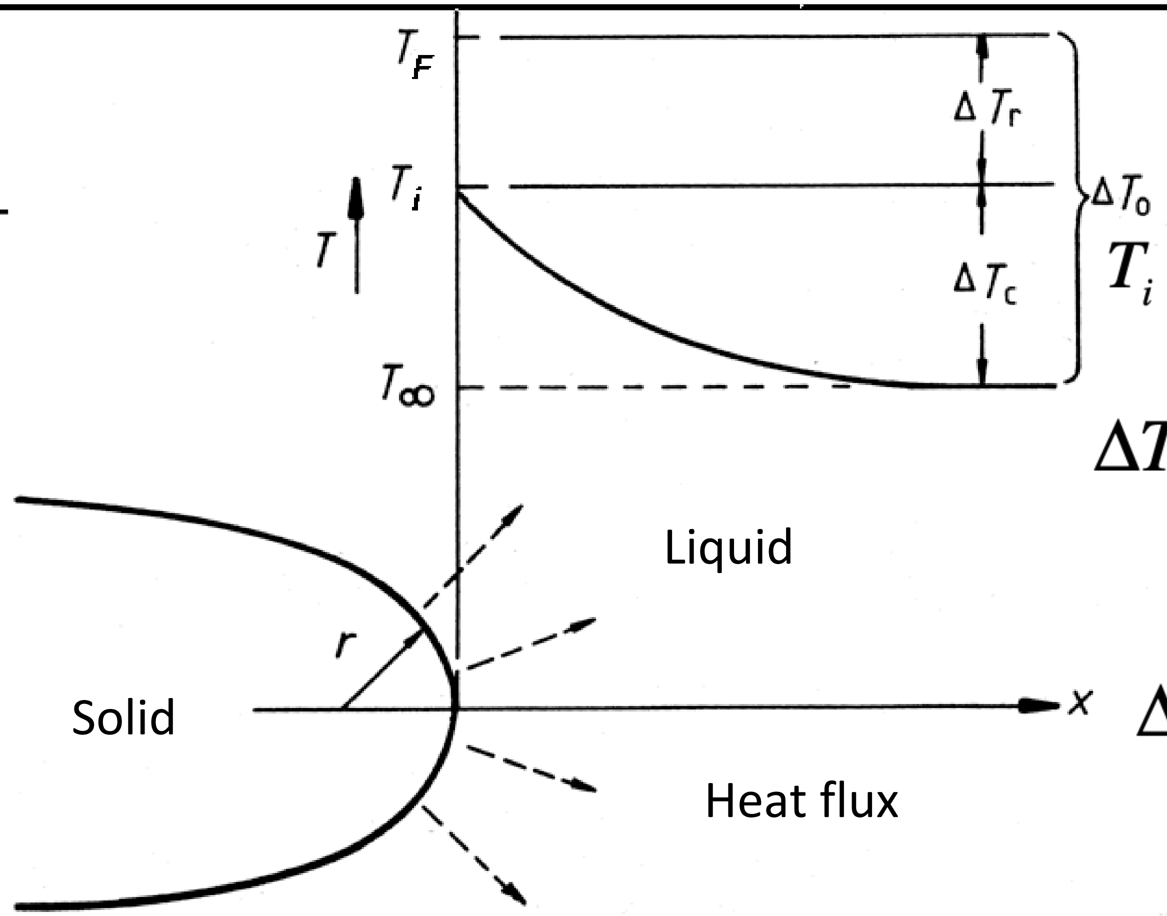
Dendritic growth: effect of the curvature radius, $\lambda_S << \lambda_L$

$$r = \frac{2\gamma_{SL} T_F}{L_V \Delta T_r}$$



$T_i \to T_\infty \Rightarrow r$ minimum

$T_i \to T_F \Rightarrow r \to \infty$ *and* $\Delta T_r \to 0$

$$\Delta T_r = \Delta T_0 \frac{r_c}{r}$$

$$\Delta T_c = \Delta T_0 \left(1 - \frac{r_c}{r}\right)$$

$r > r_c \Rightarrow T_i > T_\infty$ solidification produces heat

$r < r_c \Rightarrow T_i < T_\infty$ melting absorbs heat: the dendrite melts

$$v_i = -\frac{\lambda_L}{L_V} \frac{\Delta T_0}{\alpha r}\left(1 - \frac{r_c}{r}\right)$$ max for $r = 2r_c$

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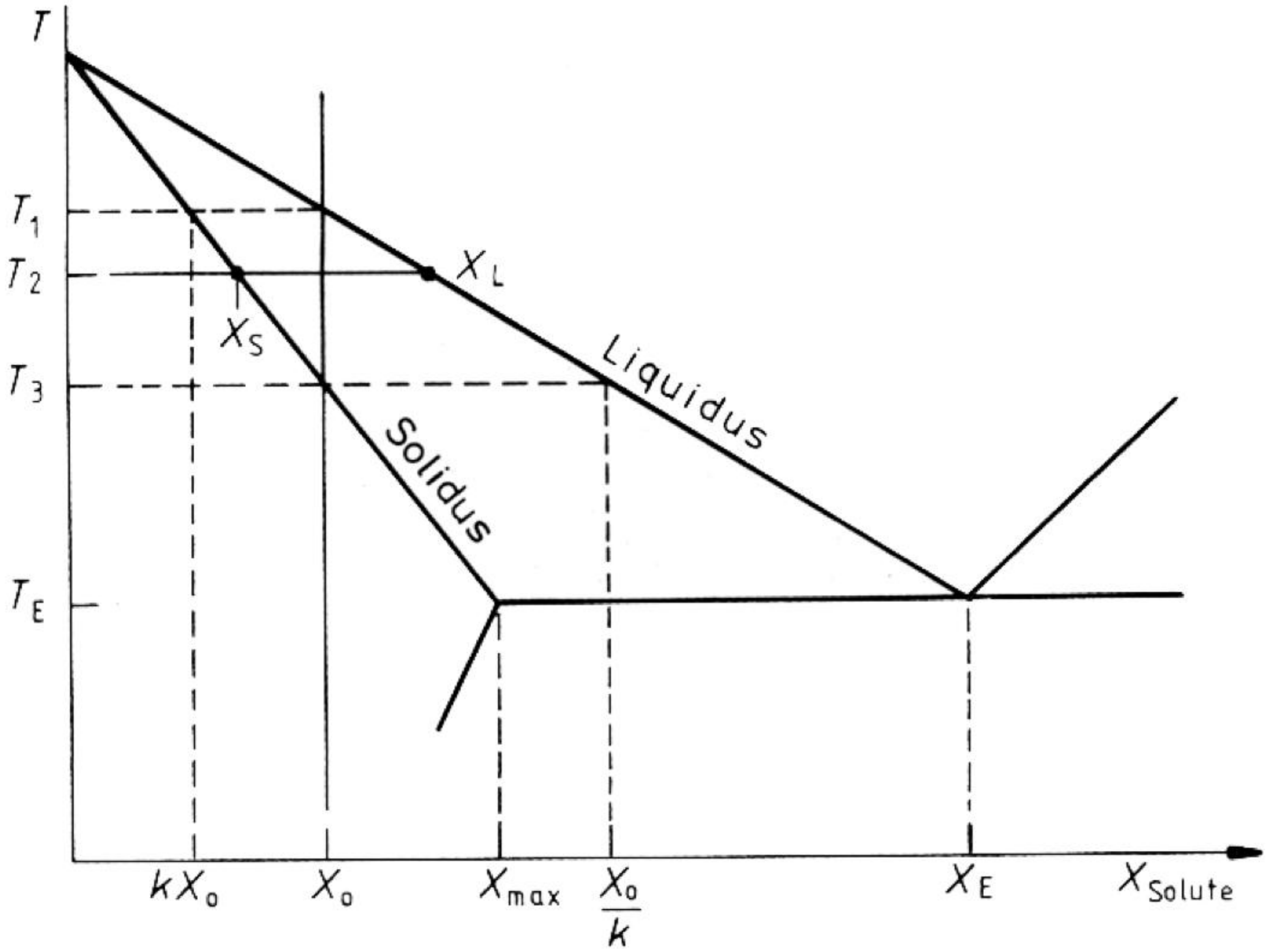
Solidification of two component alloys

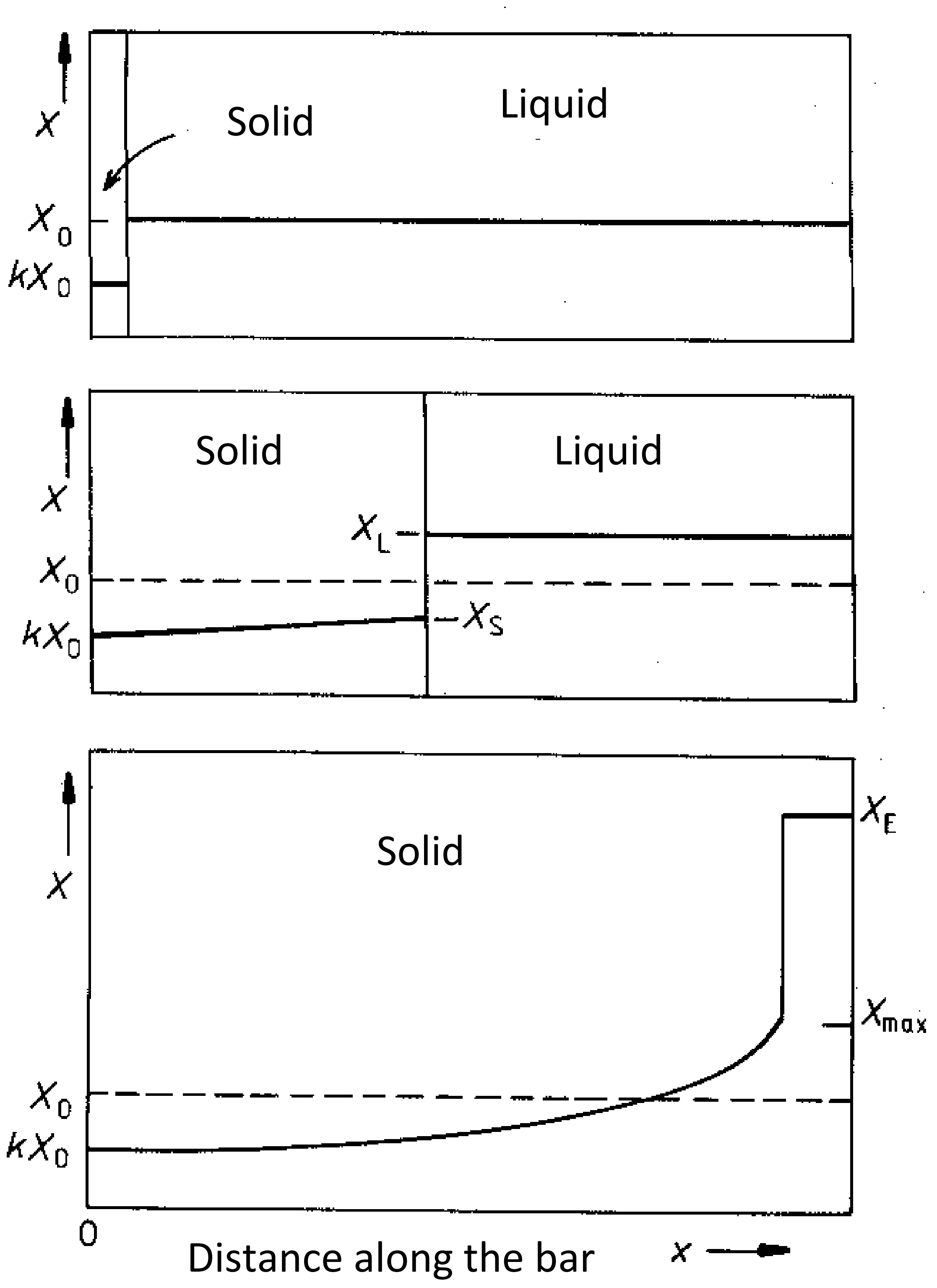


$$T = k_S X_S + T_0$$

$$T = k_L X_L + T_0$$

$$X_S = \frac{k_L}{k_S} X_L = k X_L$$

Thermodynamic equilibrium in a liquid - no diffusion in the solid (Scheil law)



$$X_S = kX_0\left(1-f_s\right)^{(k-1)}$$

$$X_L = X_0\left(f_L\right)^{(k-1)}$$

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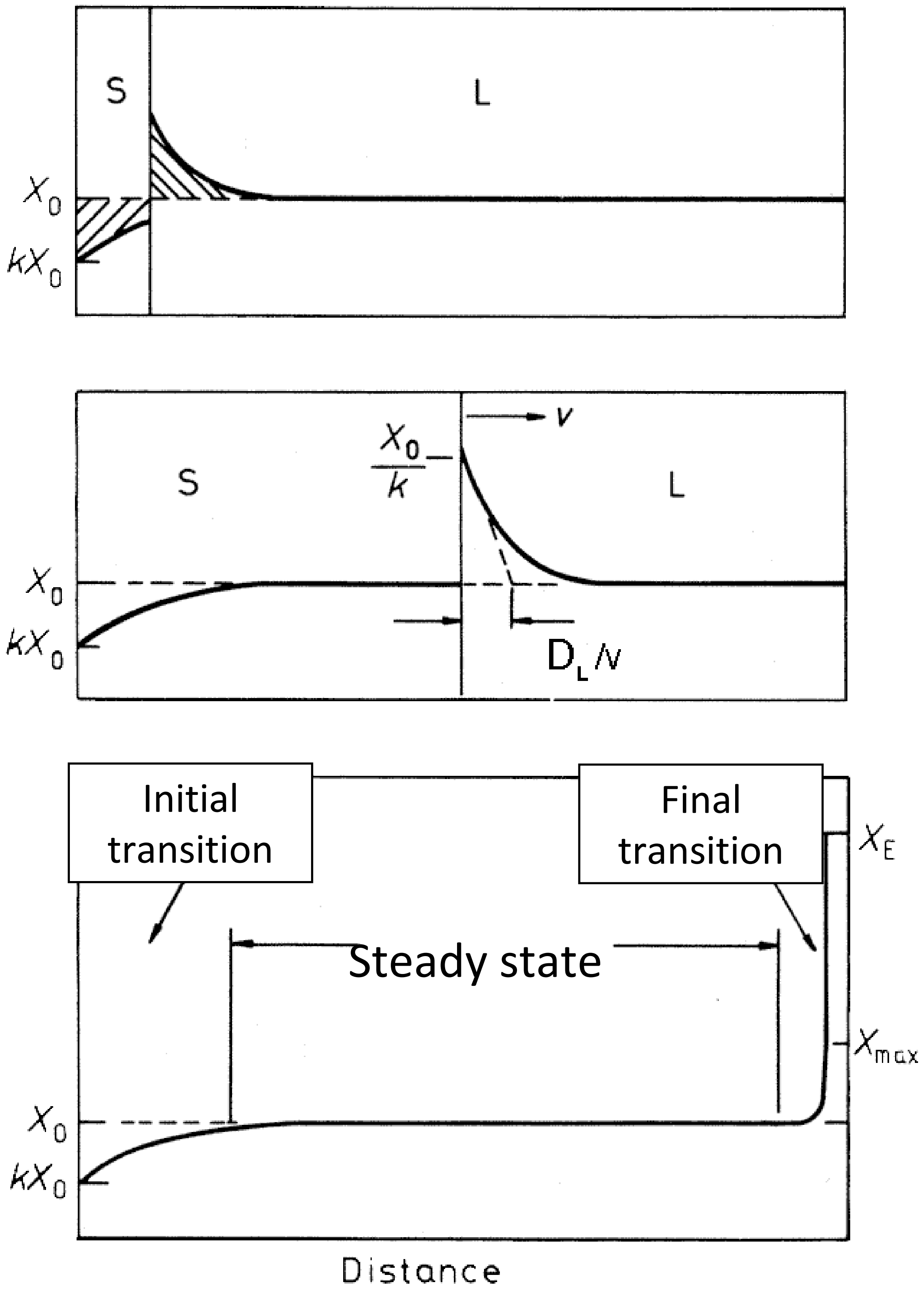
Controlled solidification by diffusion in the liquid phase



$$vX_S = vX_L + D_L \frac{\partial X_L}{\partial x}$$

$$v\left(X_S - X_L\right) = D_L \frac{\partial X_L}{\partial x}$$

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

$$X_S = kX_L \quad \text{with} \quad k < 1$$

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Constitutional supercooling

$$T_e = T_0 + k_L X_L$$

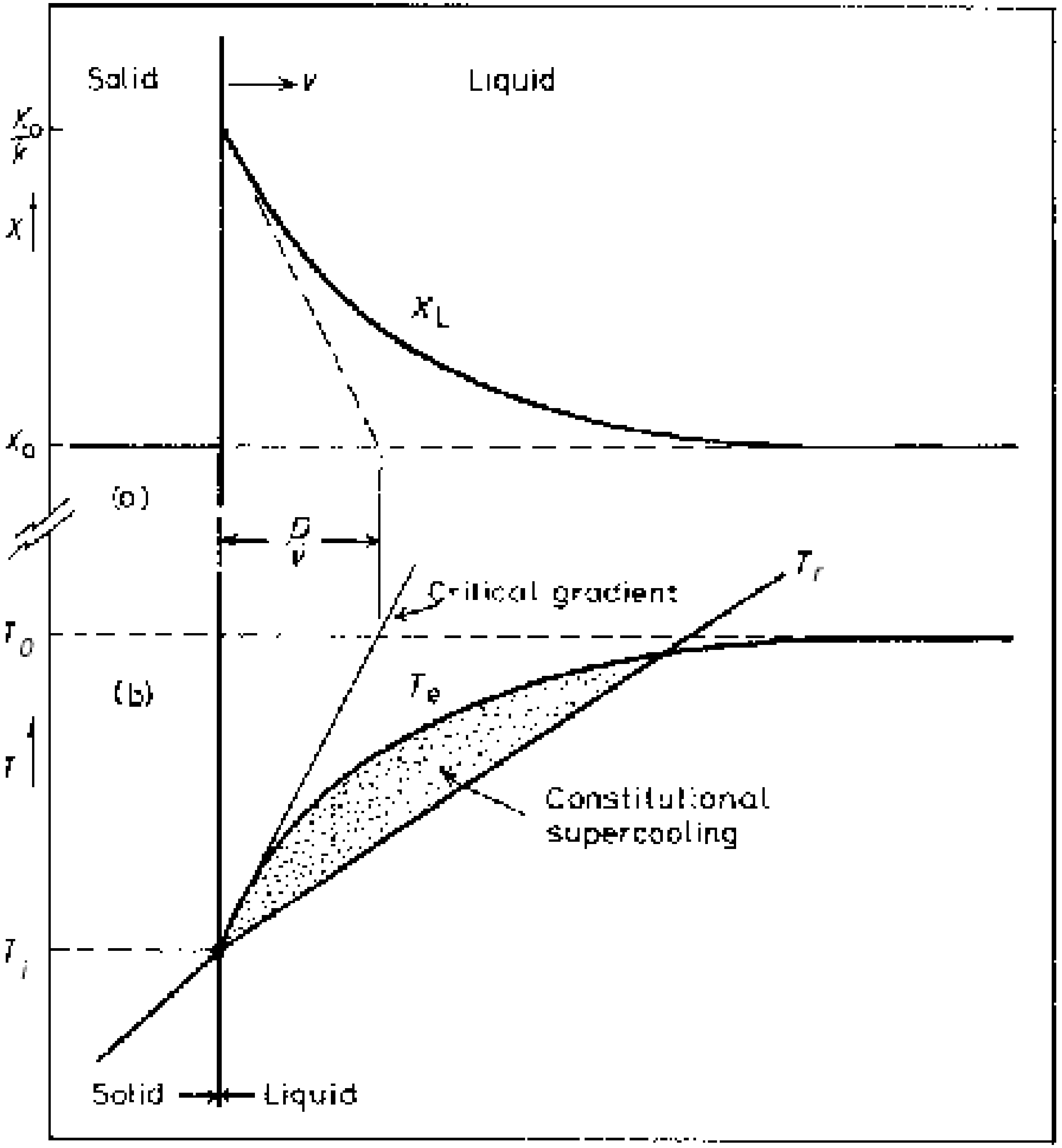
$$T_e = T_0 + k_L X_0 \left[1 + \frac{1-k}{k} \exp\left(-\frac{(1-k)x}{D_L / v} \right) \right]$$

At the solidification front

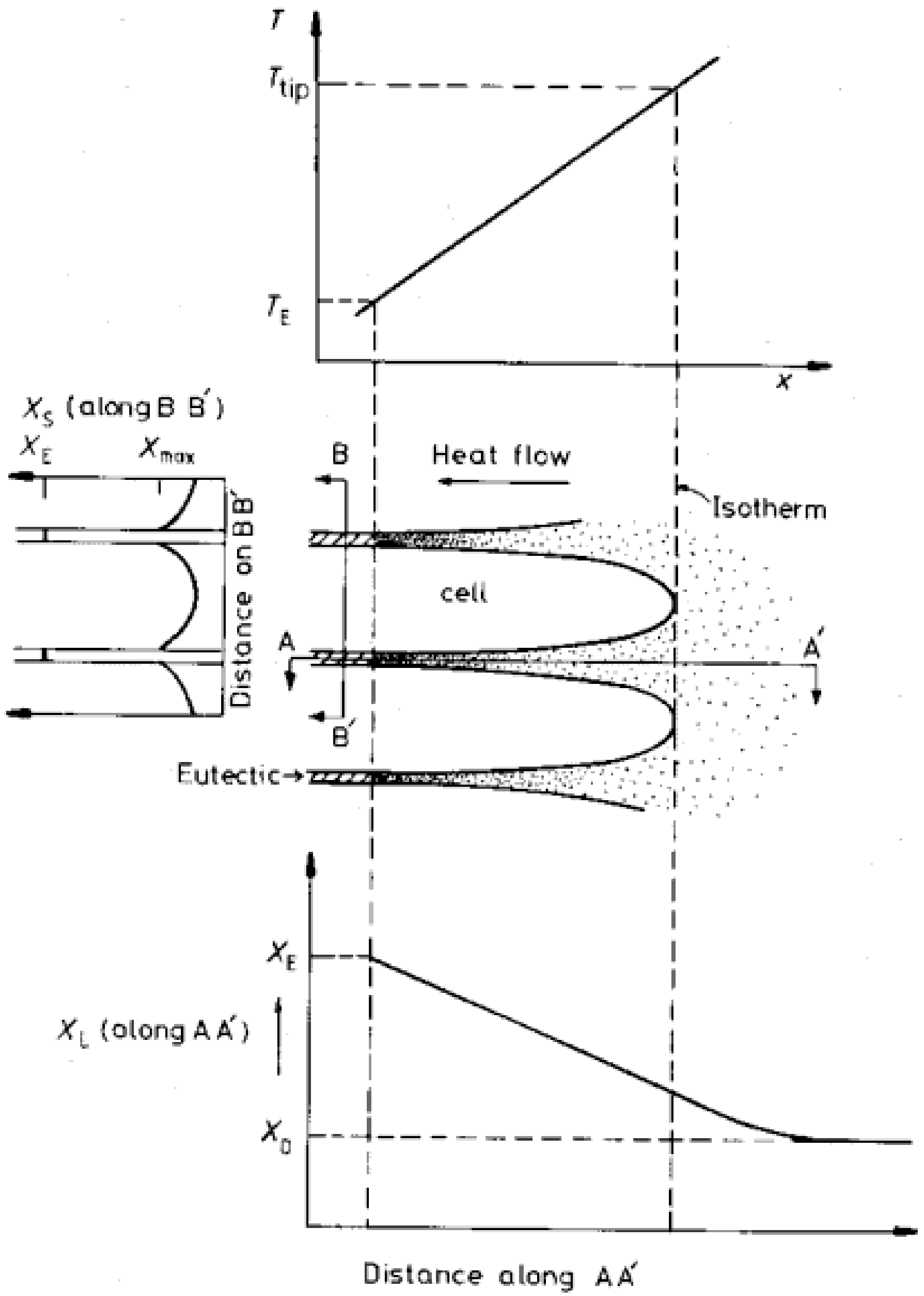
$$T_r = T_i + \left.\frac{\partial T}{\partial x}\right)_L x = T_0 + k_L \left(\frac{X_0}{k} \right) + \left.\frac{\partial T}{\partial x}\right)_L x$$

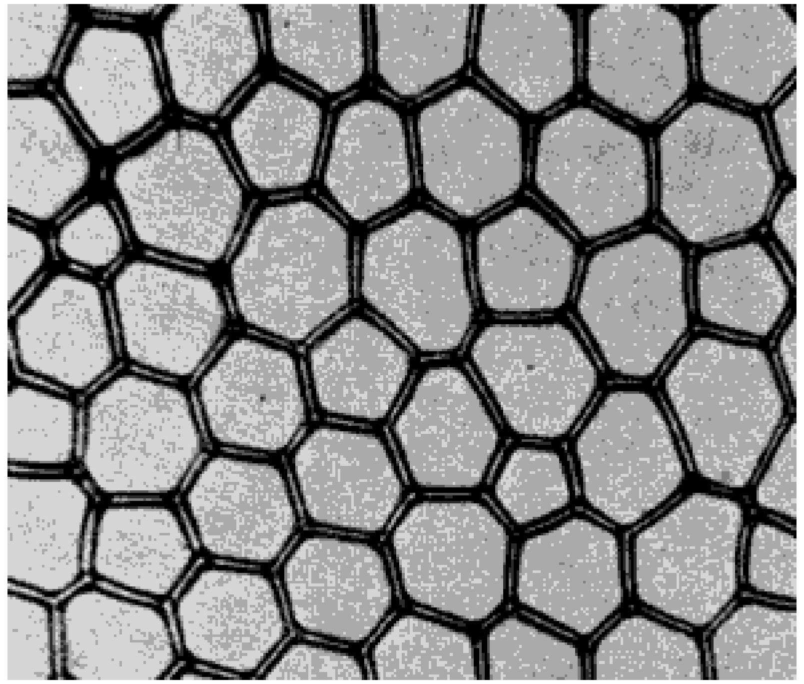
progress condition of the solidification front

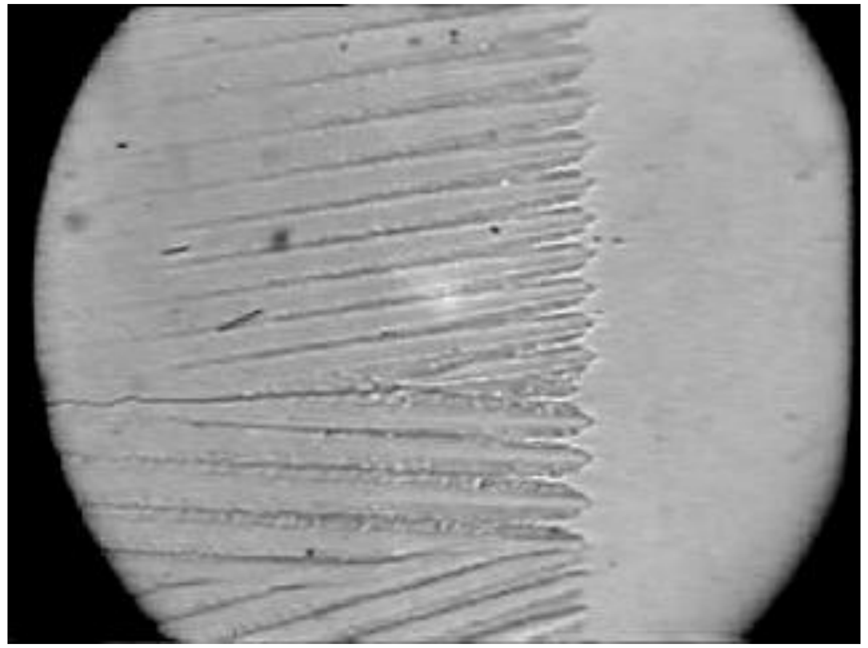
$$\left.\frac{\partial T}{\partial x}\right)_L < \frac{k_L X_0 v (1-k)^2}{k D_L}$$



Growth of a cellular structure



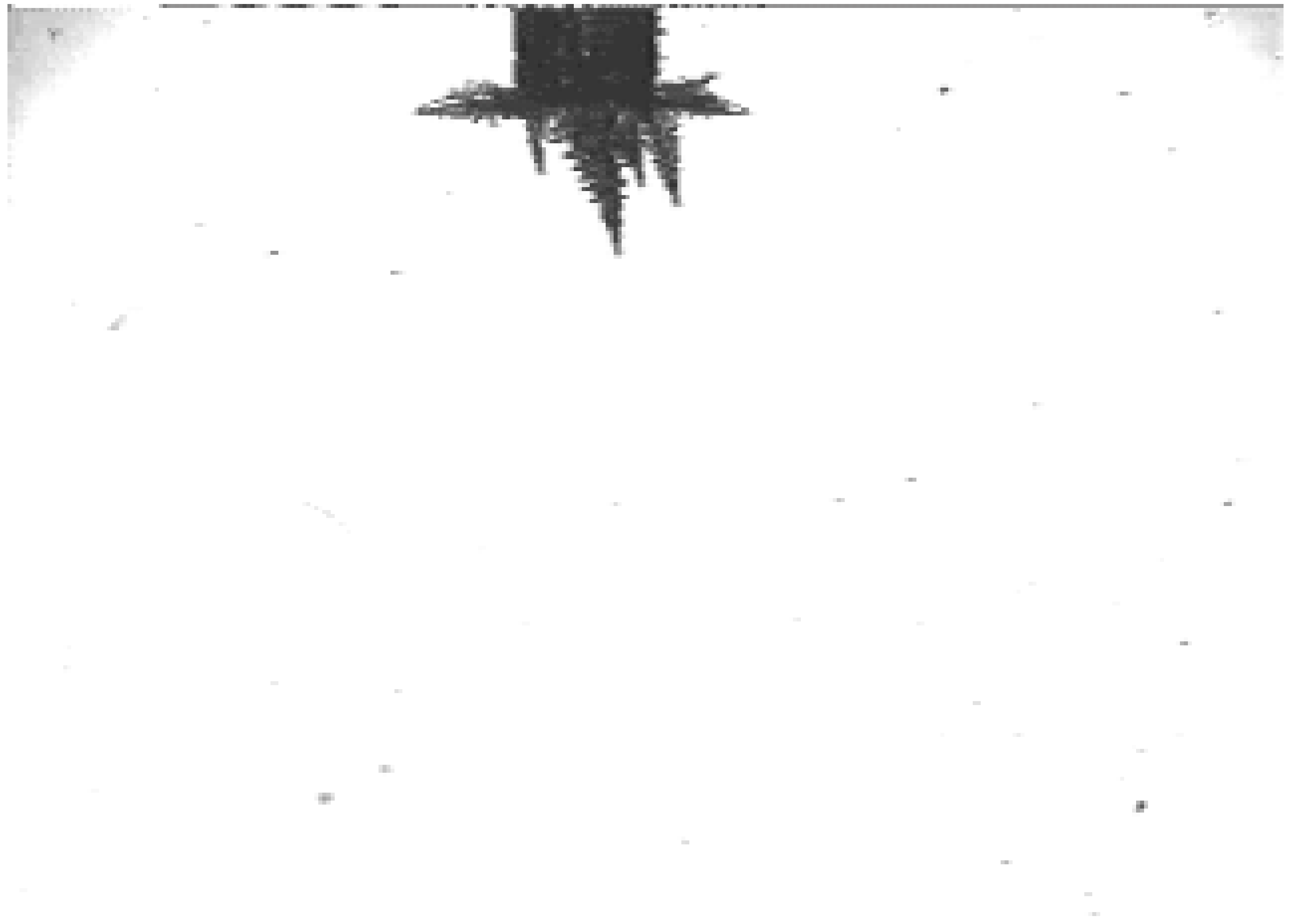




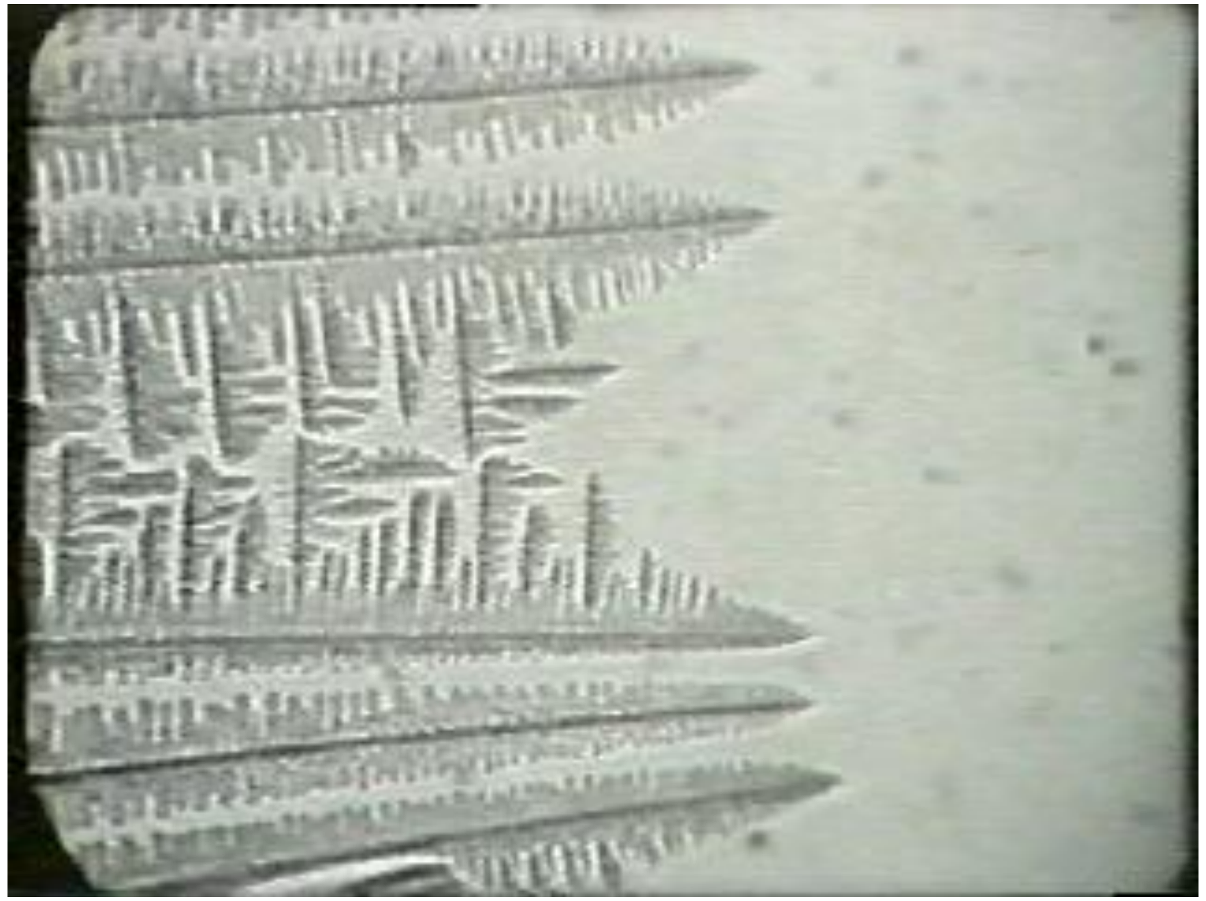
Cellular growth in succinonitrile-acetone (H. Esaka, J. Stramke and W. Kurz DMX-EPFL)

Dendritic structure

$$v = \frac{D_L}{(X_S - X_L)} \frac{\partial X_L}{\partial x}$$

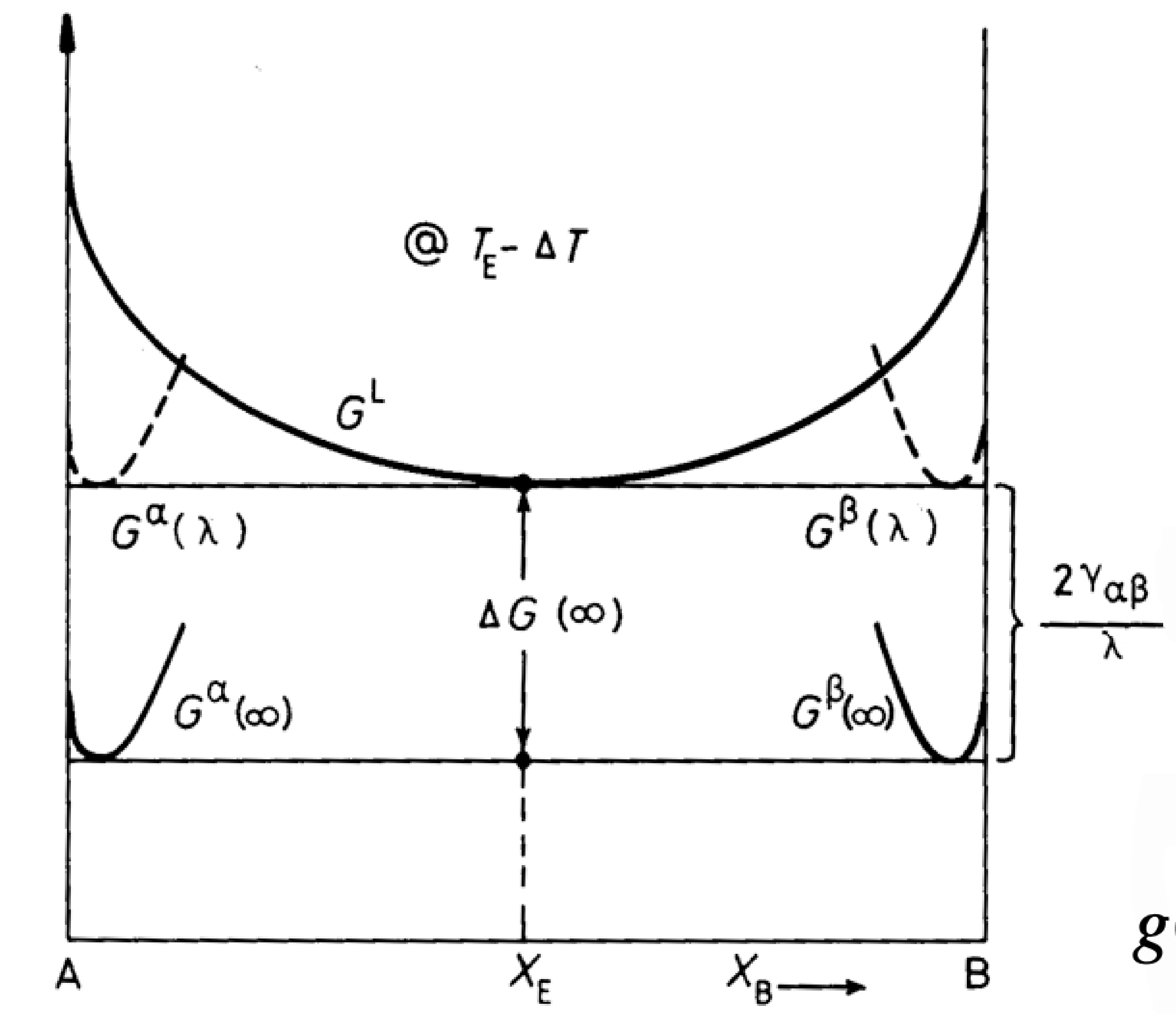


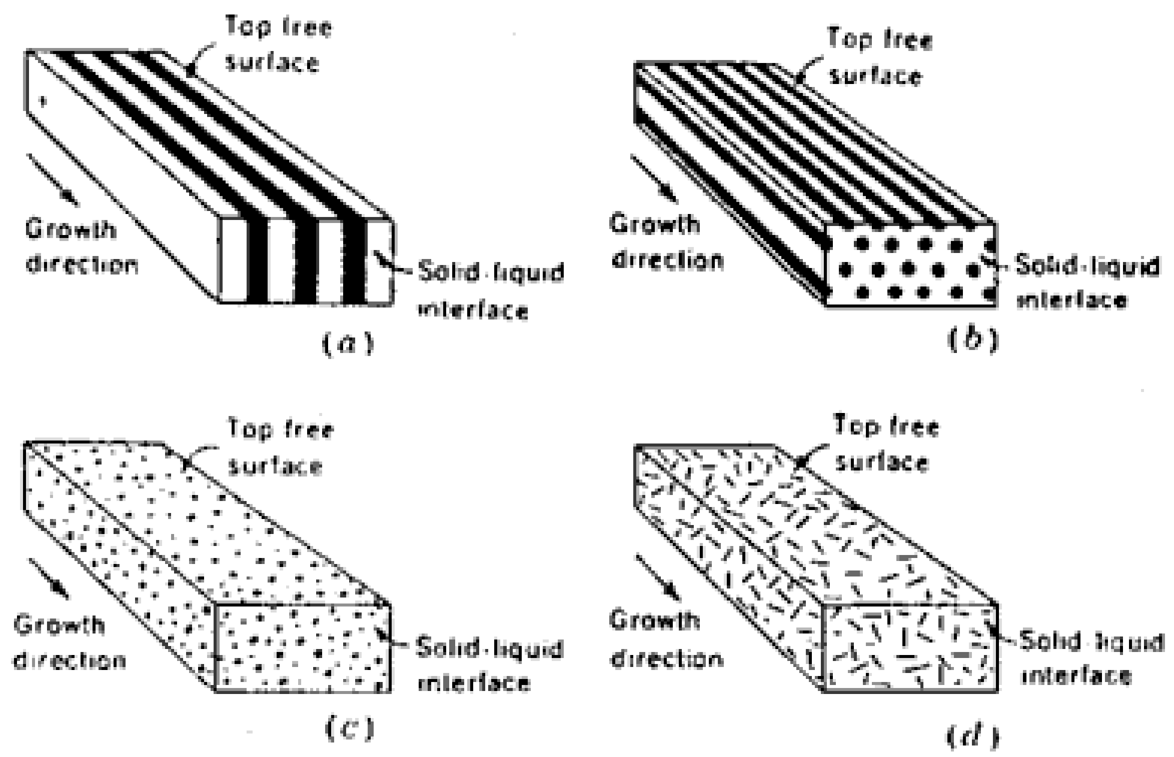
Growth of pivalic acid in microgravity (NASA)



Cellular growth in succinonitrile-acetone (H. Esaka, J. Stramke et W. Kurz DMX-EPFL)

Eutectic solidification

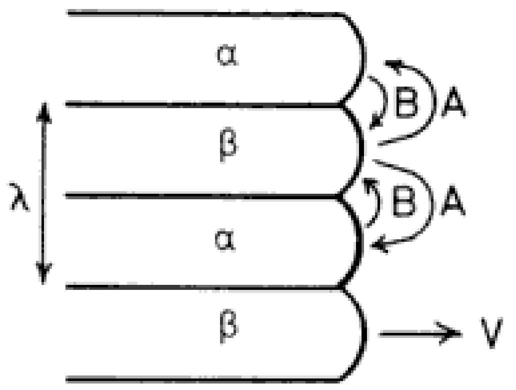


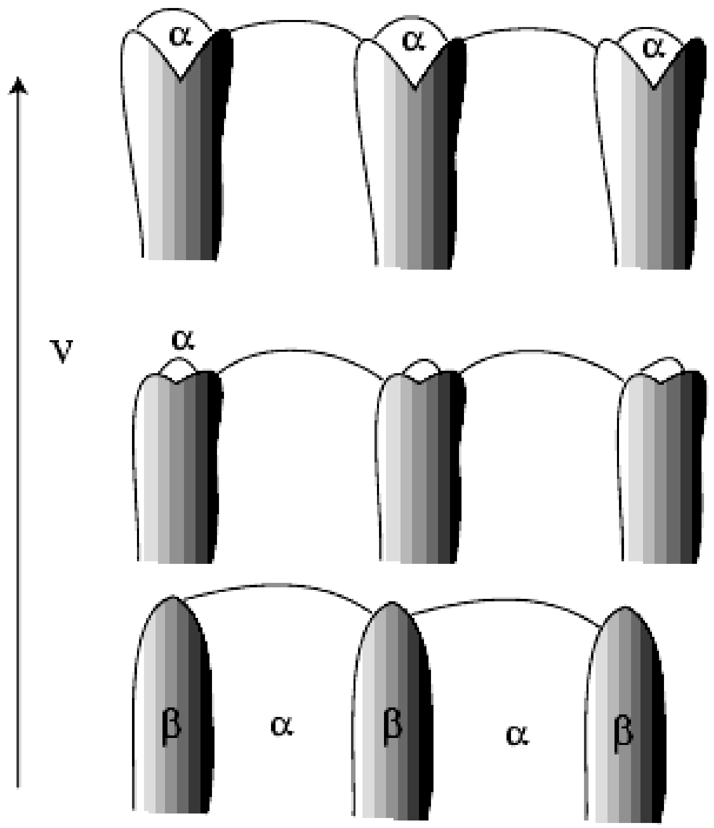


$$g(\lambda) = g(\infty) + \frac{\gamma_{\alpha\beta} S_{\alpha\beta}}{V} = g(\infty) + \frac{2\gamma_{\alpha\beta}}{\lambda}$$

Eutectic solidification

$$v\left(X_S - X_L\right) = D_L \frac{\partial X_L}{\partial x}$$





gradient of mean concentration

$$\frac{\Delta X}{\lambda/2} = 2\frac{\left(X_B^{L-\beta} - X_B^{L-\alpha}\right)}{\lambda}$$

$$v\left(X_B^{\alpha} - X_B^{L-\alpha}\right) = 2D_L \frac{\left(X_B^{L-\beta} - X_B^{L-\alpha}\right)}{\lambda}$$

$$v_\alpha = v_\beta = 2D_L \frac{\left(X_B^{L-\beta} - X_B^{L-\alpha}\right)}{\lambda\left(X_B^{\alpha} - X_B^{L-\alpha}\right)}$$

$\lambda = \lambda_c$ that is $X_B^{L-\alpha} = X_B^{L-\beta} \Rightarrow v_\alpha \to 0$

$$\Delta X = \Delta X_0 \left(1 - \frac{\lambda_c}{\lambda}\right)$$

$$v_\alpha = v_\beta = 2D_L \frac{\Delta X_0}{\lambda\left(X_B^{L-\alpha} - X_B^{\alpha}\right)}\left(1 - \frac{\lambda_c}{\lambda}\right)$$

Maximum speed $\lambda = 2\lambda_c$

$$\lambda_c v_{\max} = const.$$

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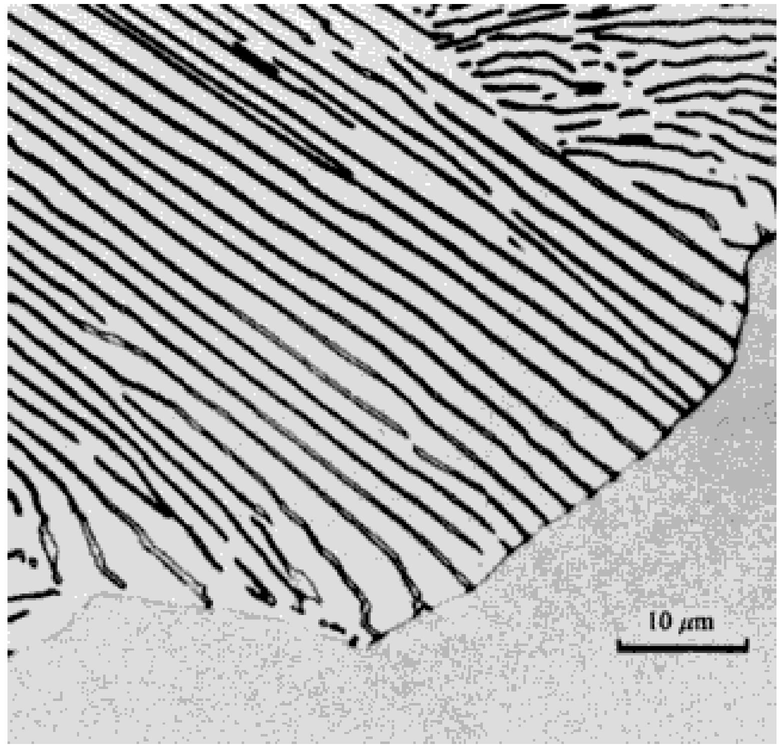
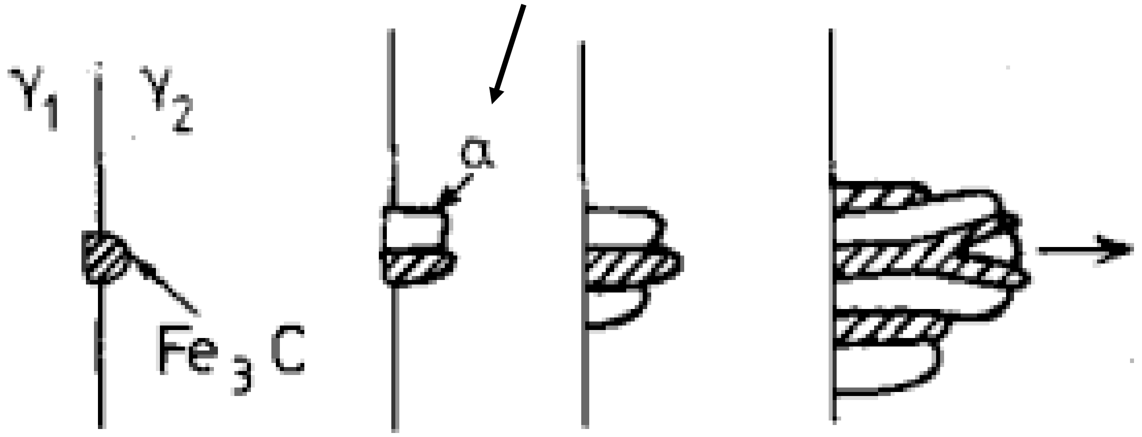
Pearlite structure in steels



Ferrite
(dilute carbon Steel
(C<0.02%)phase)



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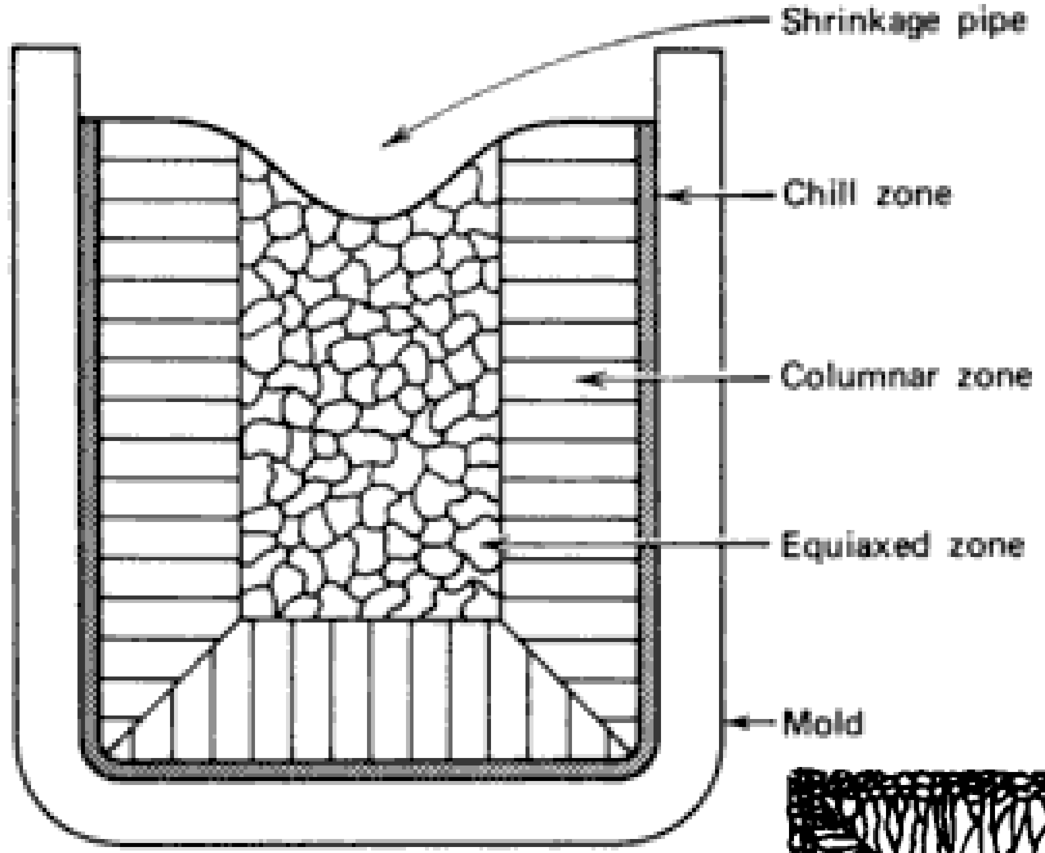
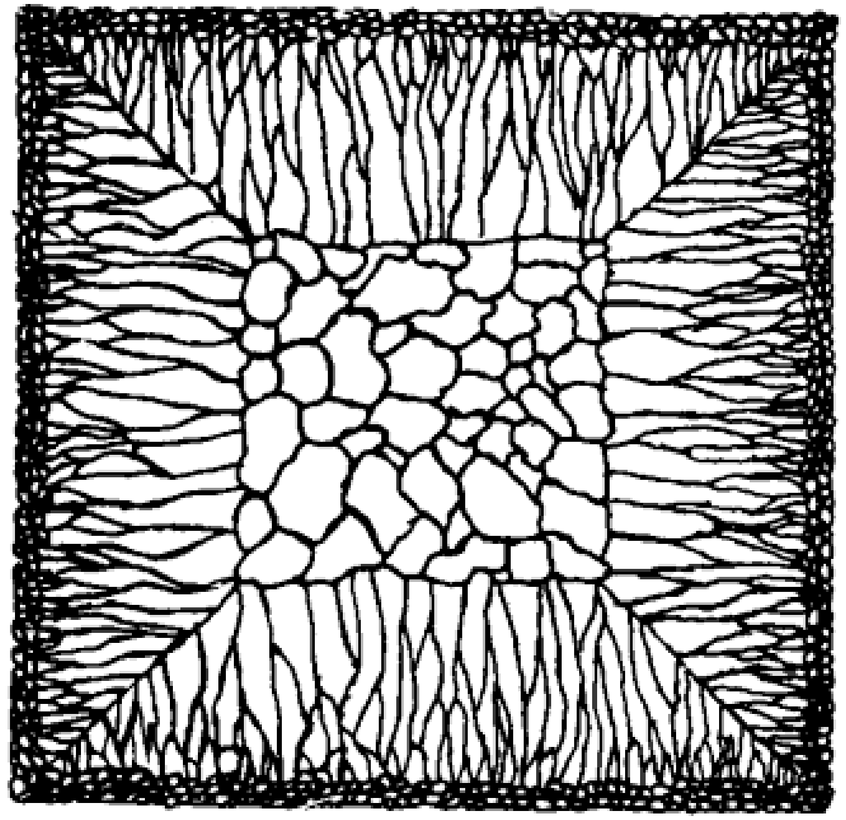
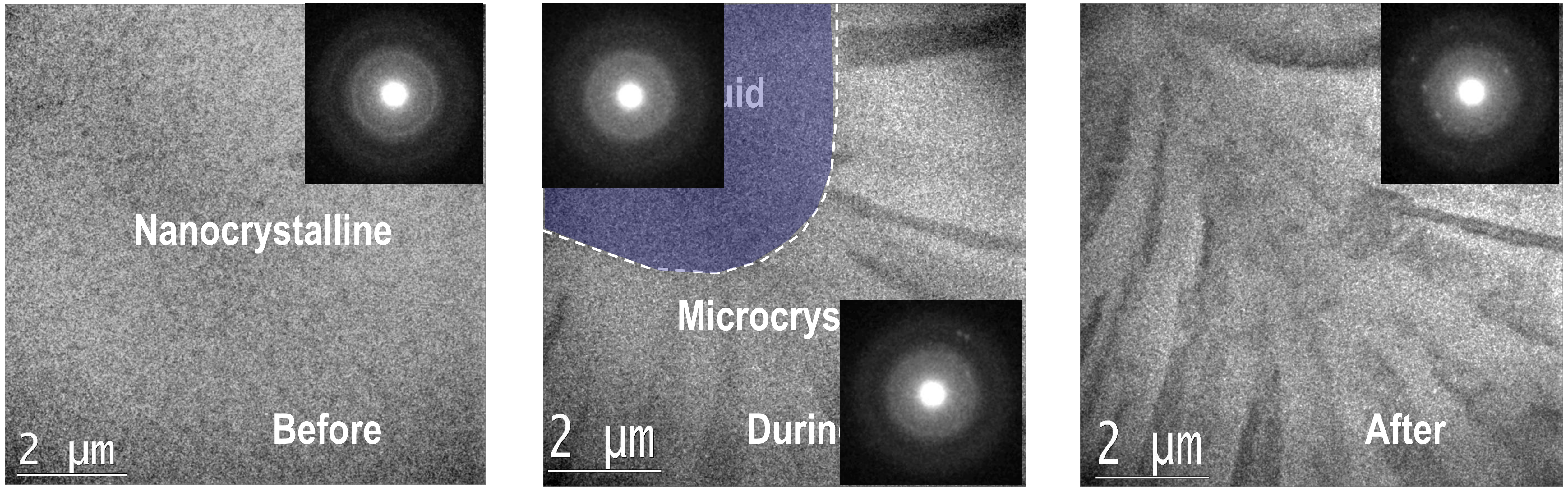
Solidification of a bar

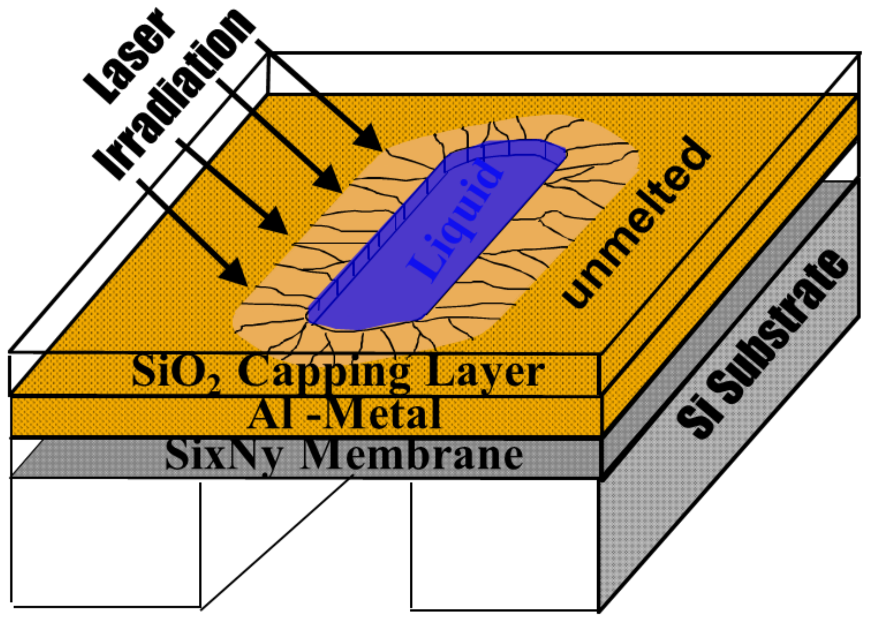




Time-resolved Electron Microscopy (DTEM)

Series of nanosecond bright field TEM images and diffraction patterns showing the rapid dynamics solidification processes after laser melting





We can observe morphological changes in liquid-solid interface of rapid lateral solidification (RLS) of molten metal films and quantitatively measure interface velocities moving at ~3.5 m/s.

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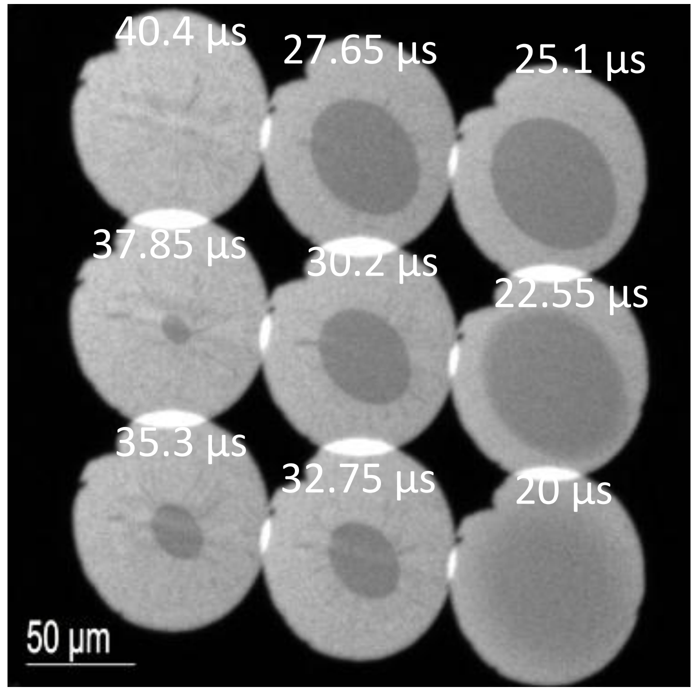
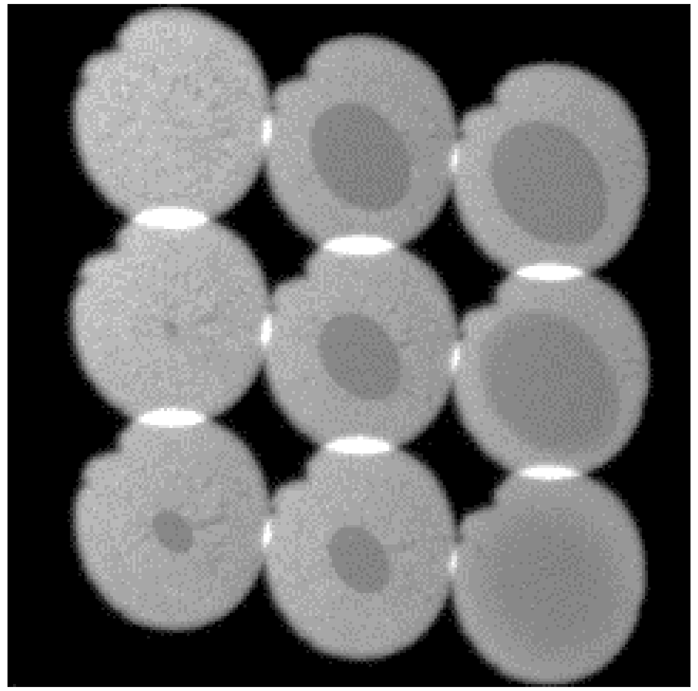
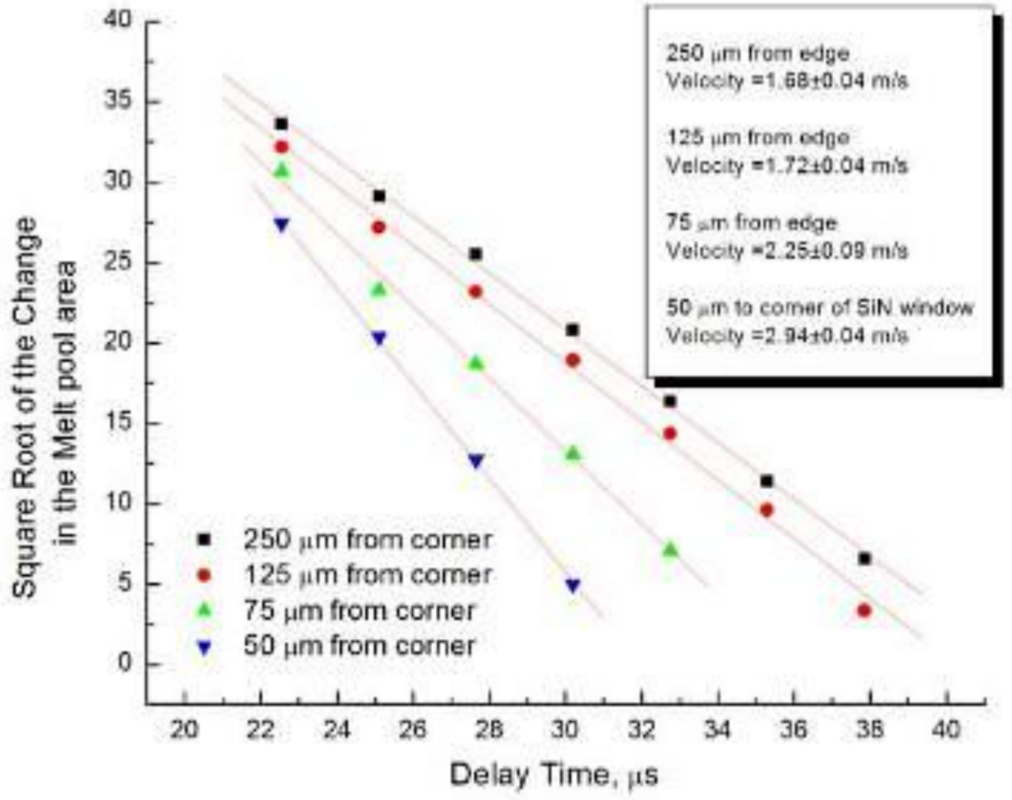
Heat extraction controls the solidification velocities

250 µm from corner

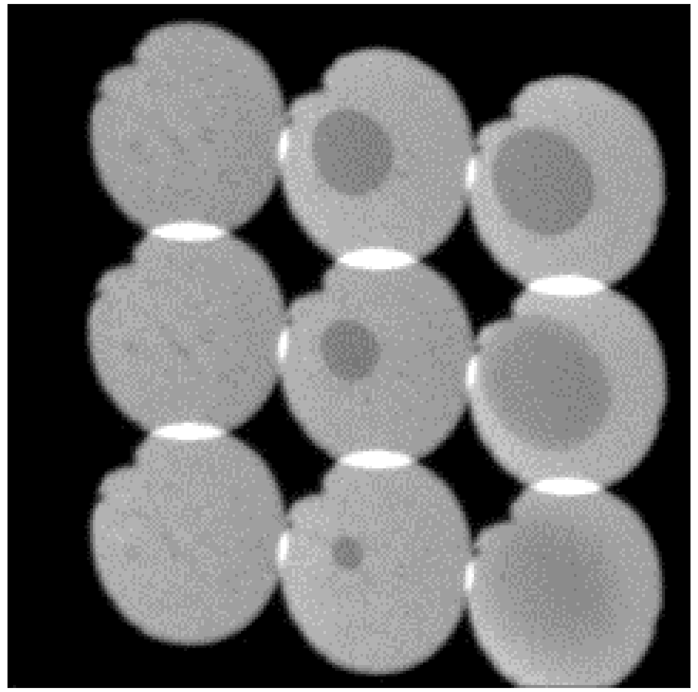


125 µm from corner

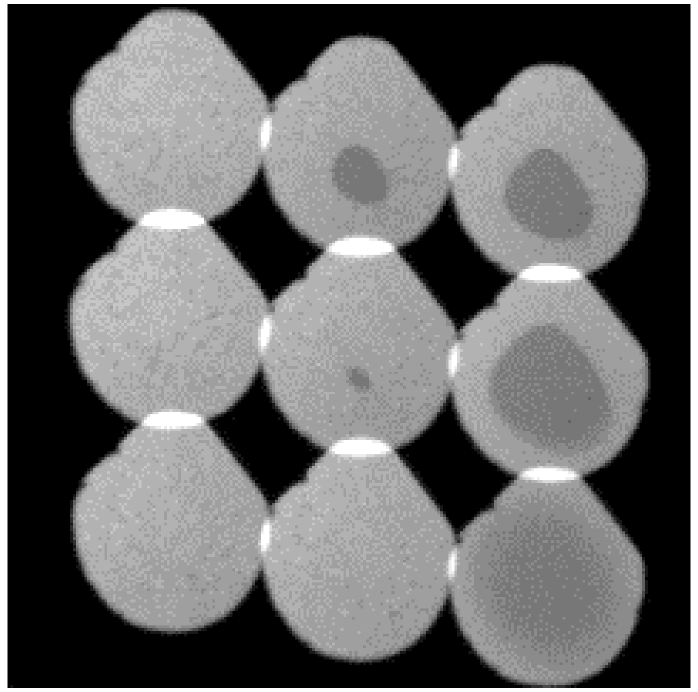




75 µm from corner



50 µm from corner



$$v_i = \frac{1}{L_V}\left(\lambda_S \left(\frac{\partial T}{\partial x}\right)_S - \lambda_L \left(\frac{\partial T}{\partial x}\right)_L \right)$$

Only planar front are observed in this thin film geometries

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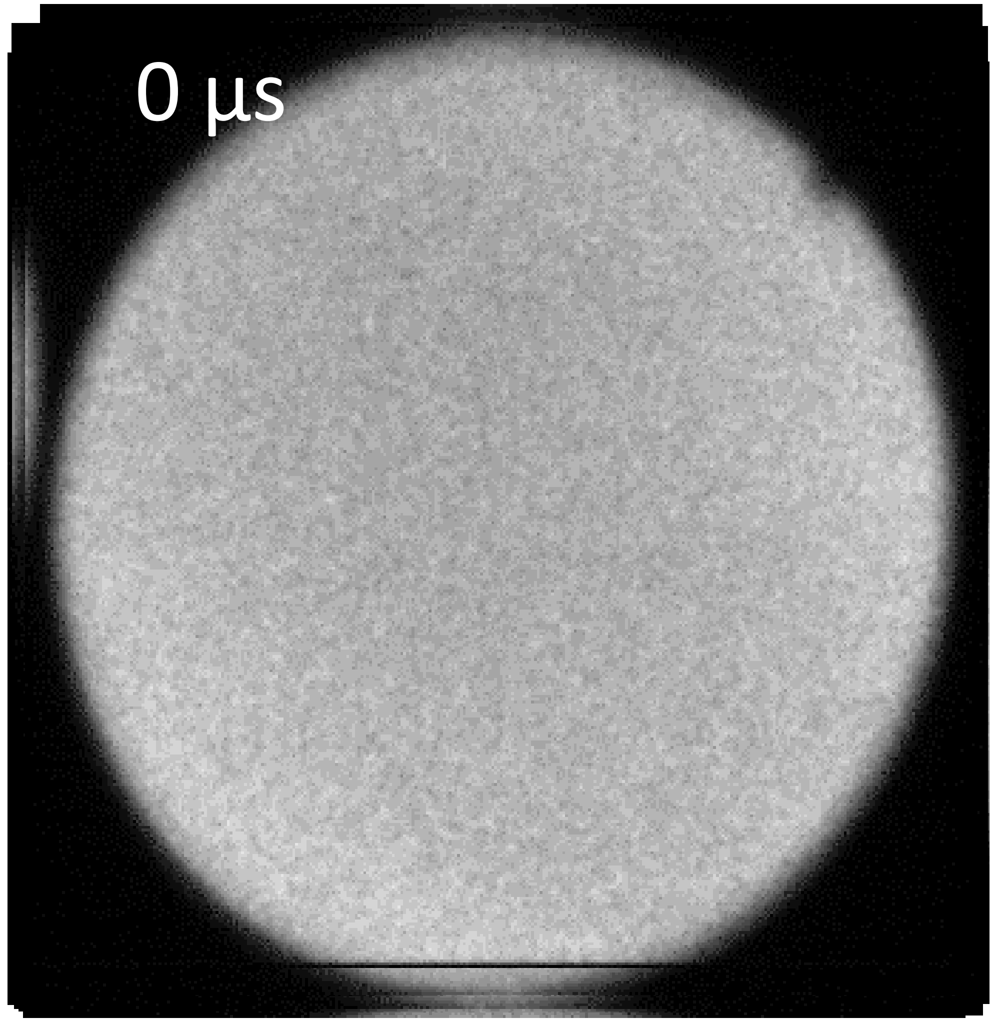
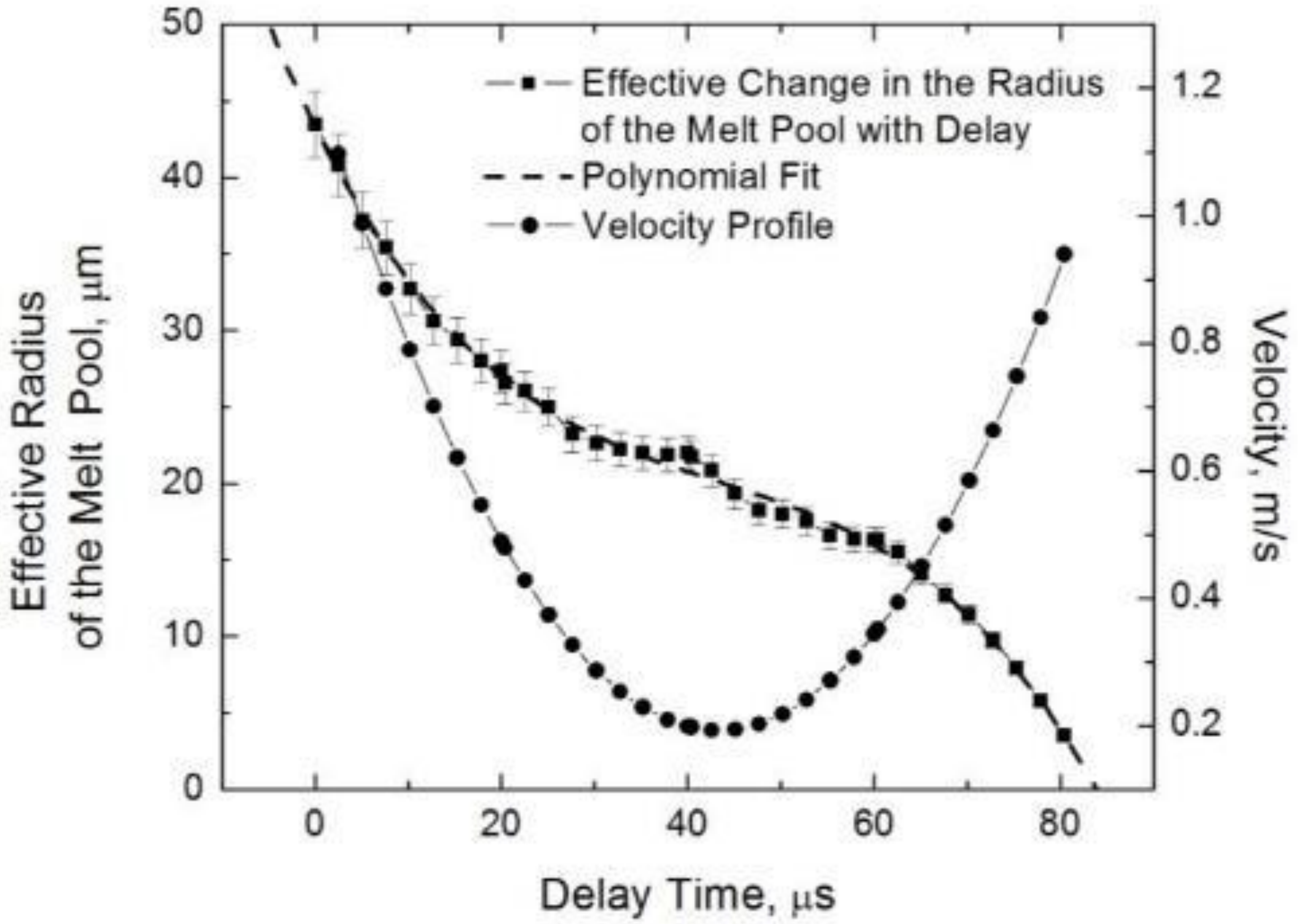
Al-16%Cu alloy films have a parabolic solidification velocity





Solidification velocities are controlled via an interplay between heat extraction, nucleation, and diffusion kinetics