METRO
MEtallurgical TRaining On-line

Mathematical modeling of micro-scale transport phenomena

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Education and Culture

Modelling of Nucleation

Rate of nucleation

$$\frac{dN}{dt} = f(T)N_s N_{cr}$$

where:

- N – density of activated nuclei
- N_s – number of molecules on the nucleus surface
- f – collision frequency of molecules with nuclei
- N_{cr} – volumetric concentration of critical size nuclei

Modelling of Nucleation

Collision frequency of molecules with nuclei

$$f(T) = f_0 \exp\left(-\frac{\Delta G_f}{kT} \right)$$

where:

f_0 - jump frequency of the molecules at the surface of a nucleus

k - Boltzmann constant

ΔG_f - activation energy for the movement to the nucleus

Modelling of Nucleation

Concentration of critical size nuclei

$$N_{cr} = (N_0 - N_{cr})\exp\left[-\frac{\Delta G^*}{kT}\right]$$

where:

N_0 - initial nucleant particle density

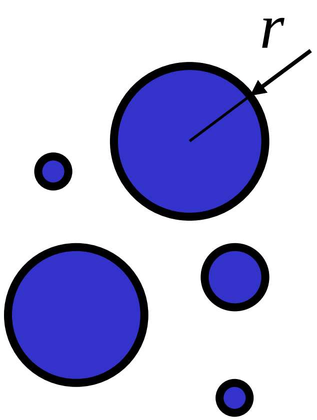
ΔG^* - the critical Gibbs free energy $\quad \Delta G^* = \frac{16}{3}\frac{\pi\gamma_{sl}^{\ 3}}{\Delta G_v^{\ 2}}$

ΔG_v - the Gibbs free energy of liquid/solid transformation per unit volume

Modelling of Nucleation

Rate of homogeneous nucleation

$$\frac{dN}{dt} = f^*(T) N_0 \exp\left[-\frac{\Delta G^*}{kT}\right]$$



where:

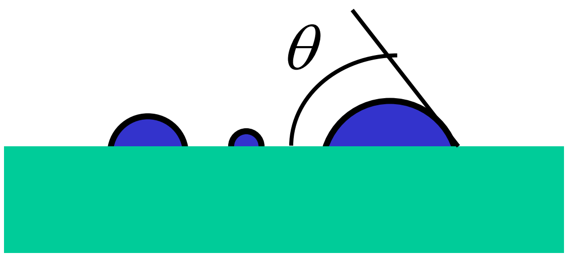
$$\Delta G^* = \frac{16}{3}\frac{\pi\gamma_{sl}^3}{\Delta G_v^2} = \frac{16\pi\gamma_{sl}^3}{3}\left[\frac{T_m V_m}{L_m (T - T_m)}\right]^2$$

V_m - molar volume

f^* - modified collision frequency, $f^* = f\, N_s$

Modelling of Nucleation

Rate of heterogeneous nucleation



$$\frac{dN}{dt} = f(T) N_0 \exp\left[-\frac{\Delta G^*}{kT}\right]$$

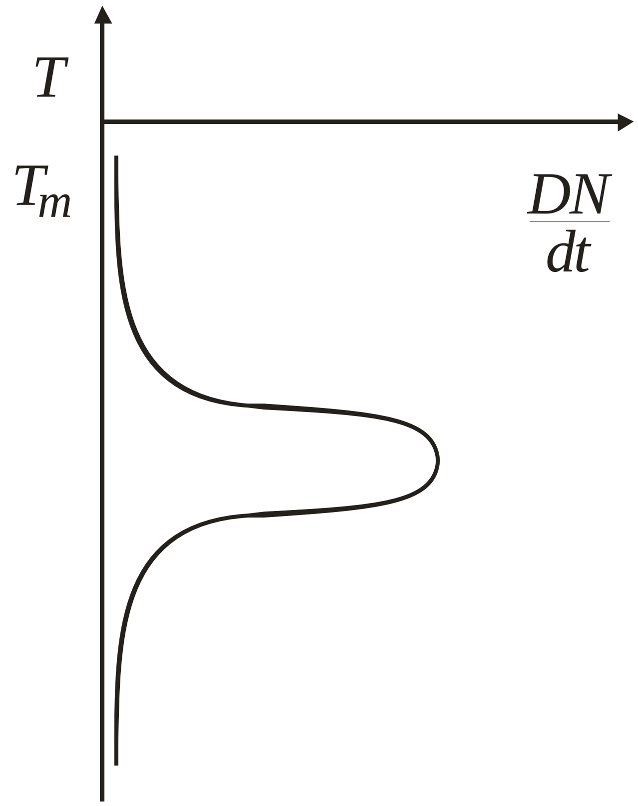
where: $$\Delta G^* = \frac{16}{3}\frac{\pi \gamma_{sl}^{3}}{\Delta G_v^{2}} = \frac{16\pi\gamma_{sl}^{3}}{3}\left[\frac{T_m V_m}{L_m (T - T_m)}\right]^2 F(\theta)$$

$$F(\theta) = (2 + \cos\theta)(1 - \cos\theta)^2 / 4$$

θ - wetting angle of the solid nucleus

Modelling of Nucleation

Nucleation rate as a fuction of temperature



Modelling of transport processes

- Processes leading to temperature and components distributions in alloys
  - Generation of heat at liquid/solid interface
  - Heat removal through the walls
  - Different solubilities of components in the phases
- Basic transport mechanisms of energy and components in alloys
  - diffusion
  - advection

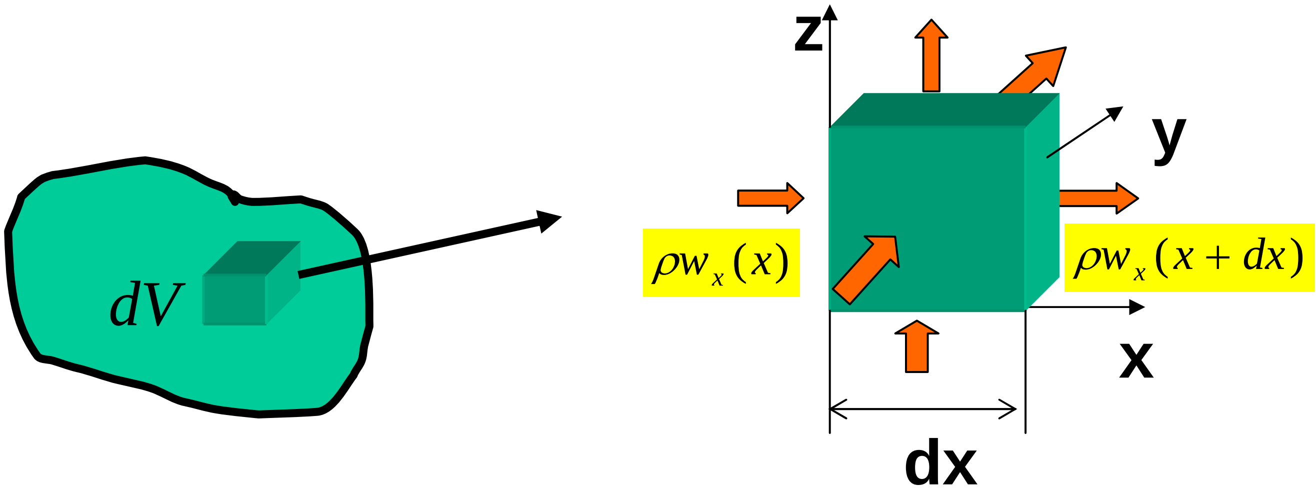
Modelling of transport processes

Basic relations needed for mathematical modelling of transport processes in solidification

- Balance equations for mass, momentum energy and components transfer inside the alloy
- Constitutive relations
- Balance equations for mass, momentum, energy and components transfer at the liquid/solid interface
- Boundary and initial conditions
- Thermodynamic relations between variables

Modelling of transport processes

Continuity equation in the liquid phase



$$\frac{\partial m}{\partial t} = [\rho w_x(x) - \rho w_x(x+dx)]dydz +$$
$$+[\rho w_y(y) - \rho w_x(y+dy)]dxdz + [\rho w_z(z) - \rho w_x(z+dz)]dxdy$$

where: m - mass, ρ - density, $\boldsymbol{w}$ - velocity

Modelling of transport processes

Continuity equation

$$[\rho w_x(x) - \rho w_x(x+dx)]dydz =$$

$$= \rho w_x\, dy\, dz - (\rho w_x + \frac{\partial \rho w_x}{\partial x} dx\,)dy\, dz = -\frac{\partial \rho w_x}{\partial x} dV$$

$$\frac{\partial \rho}{\partial t} dV = -(\frac{\partial \rho w_x}{\partial x} + \frac{\partial \rho w_y}{\partial y} + \frac{\partial \rho w_z}{\partial z})\, dV$$

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{w})$$

CONTINUITY EQUATION

Continuity equation

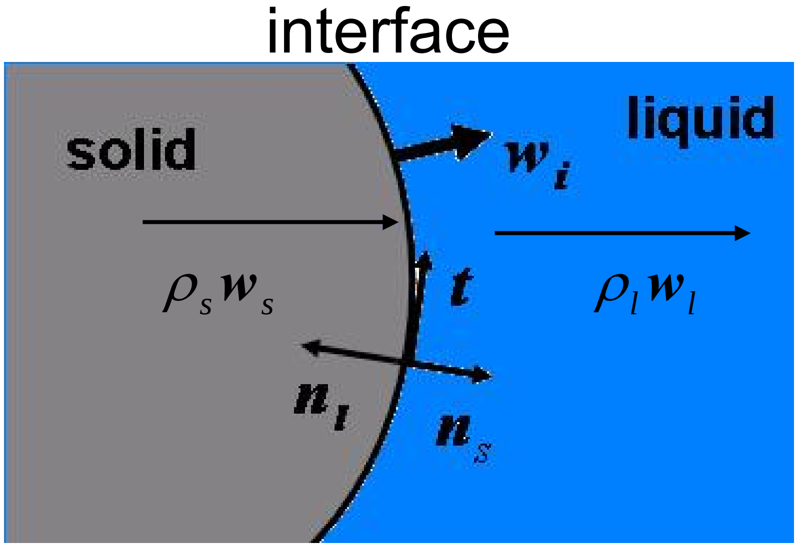
$$\frac{\partial \rho}{\partial t} + \boldsymbol{w} \cdot \nabla \rho = -\rho \nabla \cdot \boldsymbol{w}$$

advection term

Note: for incompressible liquid phase

$$\nabla \cdot \boldsymbol{w} = 0$$

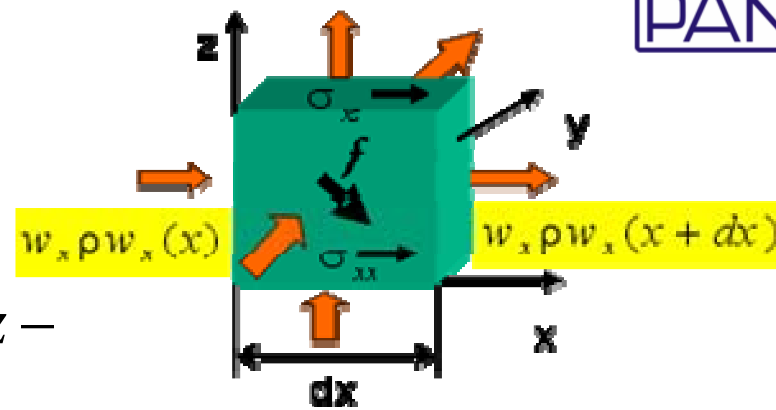
Mass balance for liquid / solid interface



$$\rho_s\left(\boldsymbol{w}_s-\boldsymbol{w}_i\right)\cdot\boldsymbol{n}_s+\rho_l\left(\boldsymbol{w}_l-\boldsymbol{w}_i\right)\cdot\boldsymbol{n}_s=0$$

Modelling of transport processes

Momentum equation



$$\frac{\partial P_x}{\partial t} = [w_x \rho w_x(x) - w_x \rho w_x(x+dx)]dydz -$$
$$-\left[\sigma_{xx}(x) - \sigma_{xx}(x+dx)\right]dydz + [w_x \rho w_y(y) - w_x \rho w_y(y+dy)]dxdz -$$
$$-\left[\sigma_{xy}(x) - \sigma_{xy}(x+dx)\right]dxdz + [w_x \rho w_z(z) - w_x \rho w_x(z+dz)]dxdy -$$
$$-\left[\sigma_{xz}(x) - \sigma_{xz}(x+dx)\right]dxdy + \rho dV f_x$$

where:

$P_x = \rho dV w_x$ - x-component of momentum of the elementary volume *dV*

$\sigma_{xx}, \sigma_{xy}, \sigma_{zx}$ - x-component of stress tensor

f_x - x-component of mass force acting on the elementary volume

Modelling of transport processes

Momentum equation

$$[w_x \rho w_x (x) - w_x \rho w_x (x + dx)] dydz =$$

$$= w_x \rho w_x \; dy \; dz - (w_x \rho w_x + \frac{\partial w_x \rho w_x}{\partial x} dx) \; dy \; dz = -\frac{\partial w_x \rho w_x}{\partial x} dV$$

$$[\sigma_{xx} (x) - \sigma_{xx} (x + dx)] dydz =$$

$$= \sigma_{xx} \; dy \; dz - (\sigma_{xx} + \frac{\partial \sigma_{xx}}{\partial x} dx \;) dy \; dz = -\frac{\partial \sigma_{xx}}{\partial x} dV$$

Modelling of transport processes

Momentum equation

$$\frac{\partial \rho w_x}{\partial t} dV = -\left(\frac{\partial w_x \rho w_x}{\partial x} + \frac{\partial w_x \rho w_y}{\partial y} + \frac{\partial w_x \rho w_z}{\partial z}\right) dV + \\ + \left(\frac{\partial \sigma_{xx}}{\partial x} + \frac{\partial \sigma_{xy}}{\partial y} + \frac{\partial \sigma_{xz}}{\partial z}\right) dV + \rho dV f_x$$

$$\frac{\partial \rho \boldsymbol{w}}{\partial t} = -\nabla \cdot (\boldsymbol{w} \rho \boldsymbol{w} - \boldsymbol{\sigma}) + \rho \boldsymbol{f}$$

MOMENTUM EQUATION

Momentum equation

$$\frac{\partial \rho \boldsymbol{w}}{\partial t} = -\nabla \cdot \left(\boldsymbol{w} \rho \boldsymbol{w} - \boldsymbol{\sigma} \right) + \rho \boldsymbol{f}$$

$$\frac{\partial \rho \boldsymbol{w}}{\partial t} + \boldsymbol{w} \cdot \nabla \rho \boldsymbol{w} = \nabla \cdot \boldsymbol{\sigma} + \rho \boldsymbol{f}$$

advection term   diffusion term

Modelling of transport processes

Constitutive relation for momentum

$$\boldsymbol{\sigma} = -p\boldsymbol{1} + 2\mu_l \boldsymbol{e}(\boldsymbol{w})$$

where:

p - pressure

μ_l - liquid viscosity

$\boldsymbol{e} = (\nabla \boldsymbol{w} + \nabla^T \boldsymbol{w})$ - deformation stress tensor

$\nabla^T \boldsymbol{w}$ - transversed gradient of velocity

Modelling of transport processes

Momentum equation in the liquid

$$\boldsymbol{\sigma} = -p\mathbf{1} + 2\mu_l \boldsymbol{e}(\boldsymbol{w})$$

$$\frac{\partial \rho \boldsymbol{w}}{\partial t} = -\nabla \cdot (\boldsymbol{w}\rho\boldsymbol{w} - \boldsymbol{\sigma}) + \rho\boldsymbol{f}$$

$$\frac{\partial \rho \mathbf{w}}{\partial t} + \nabla \cdot (\mathbf{w}\rho\mathbf{w}) = -\nabla p + \mu_l \nabla^2 \mathbf{w} + \rho\mathbf{f}$$

$$\rho\frac{\partial \boldsymbol{w}}{\partial t} + \rho\boldsymbol{w} \cdot \nabla(\boldsymbol{w}) = -\nabla p + \mu_l \nabla^2 \cdot \boldsymbol{w} + \rho\boldsymbol{f}$$

MOMENTUM EQUATION FOR THE LIQUID PHASE

Modelling of transport processes

Thermodynamic relations - density

$$\rho(T,[C_j]) = \rho_O(T_r,[C_j]_r)\left[1+\beta_T(T-T_r)+\sum_j \beta_{Cj}(C_j - C_{jr})\right]$$

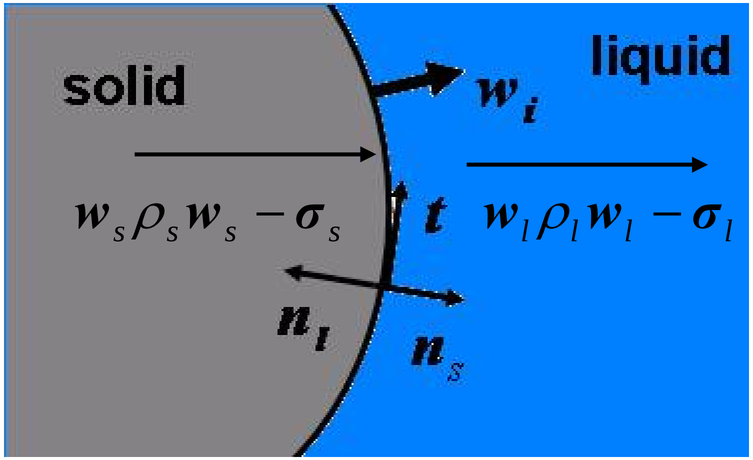
where: β_T – coefficient of thermal expansion

β_{Cj} – coefficient of species expansion

Terms in momentum equation for natural convection

$$-\nabla p + \rho f = (\rho - \rho_O) f = \beta_T(T-T_r)+\sum_j \beta_{Cj}(C_j - C_{jr})$$

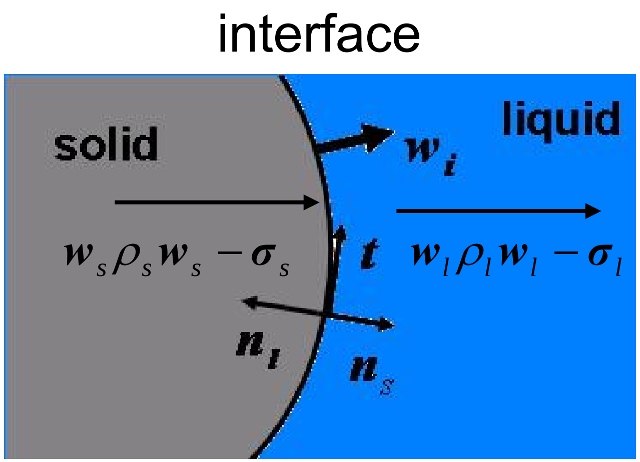
Momentum balance for liquid / solid interface



$$\left[\rho_s \boldsymbol{w}_s \left(\boldsymbol{w}_s - \boldsymbol{w}_i\right) - \boldsymbol{\sigma}_s\right] \cdot \boldsymbol{n}_s + \left[\rho_l \boldsymbol{w}_l \left(\boldsymbol{w}_l - \boldsymbol{w}_i\right) - \boldsymbol{\sigma}_l\right] \cdot \boldsymbol{n}_l = 2\kappa \gamma_{ls} \boldsymbol{n}_s - \nabla \gamma_{ls} \cdot \boldsymbol{t}$$

where: κ - interface curvature

Momentum balance for liquid / solid interface



From the mass balance at the interface

$$\rho_l \left(\boldsymbol{w}_l - \boldsymbol{w}_i\right) \cdot \boldsymbol{n}_l = -\rho_s \left(\boldsymbol{w}_s - \boldsymbol{w}_i\right) \cdot \boldsymbol{n}_s$$

$$\left(\boldsymbol{\sigma}_s - \boldsymbol{\sigma}_l\right) \cdot \boldsymbol{n}_s = \rho_s \left(\boldsymbol{w}_s - \boldsymbol{w}_l\right)\left(\boldsymbol{w}_s - \boldsymbol{w}_i\right) \cdot \boldsymbol{n}_l - 2\kappa\gamma_{ls} \boldsymbol{n}_s - \nabla \gamma_{ls} \cdot \boldsymbol{t}$$

where: $\boldsymbol{n}$ - unit vector perpendicular to the interface

$\boldsymbol{t}$ - unit vector tangential to the interface

Modelling of transport processes

Thermodynamic relations – surface tension

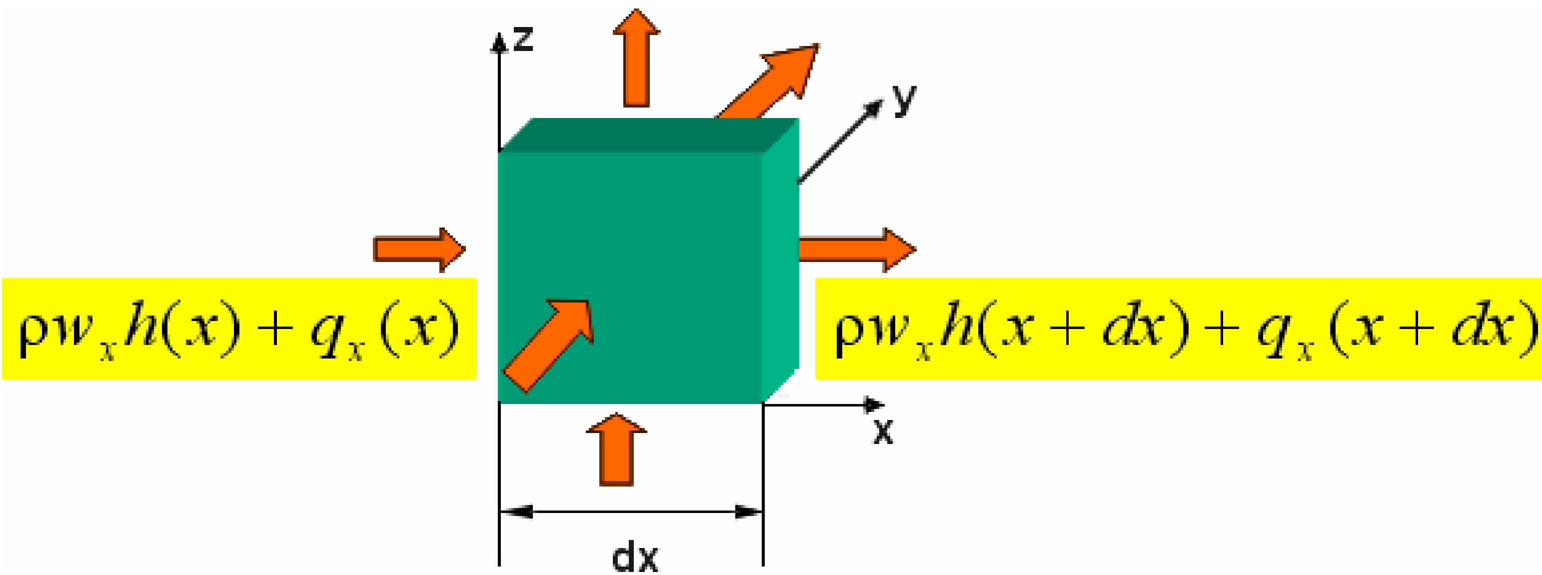
$$\gamma_{sl} = \gamma_{sl}(T,[C_j])$$

where: C_j - concentration of *j* component (mass fraction)

$$\nabla \gamma_{ls} \cdot \boldsymbol{t} = \frac{\partial \gamma_{sl}}{\partial T} \nabla T \cdot \boldsymbol{t} + \sum_j \frac{\partial \gamma_{sl}}{\partial C_j} \nabla C_j \cdot \boldsymbol{t}$$

Modelling of transport processes

Energy equation



where:

h - specific enthalpy

q - heat flux

Modelling of transport processes

Energy equation

$$\frac{\partial(\rho dVh)}{\partial t} = [\left(w_x \rho h(x) + q_x(x)\right) - \left(w_x \rho h(x+dx) + q_x(x+dx)\right)]dydz +$$
$$+[\left(w_y \rho h(y) + q_y(y)\right) - \left(w_y \rho h(y+dy) + q_x(y+dy)\right)]dxdz +$$
$$+[\left(w_z \rho h(z) + q_z(z)\right) - \left(w_z \rho h(z+dz) + q_z(z+dz)\right)]dxdy$$

$$[\left(w_x \rho h(x) + q_x(x)\right) - \left(w_x \rho h(x+dx) + q_x(x+dx)\right)]dydz =$$
$$= \left(w_x \rho h + q_x\right) dy\, dz - \left[\left(w_x \rho h + q_x\right) + \frac{\partial(w_x \rho h + q_x)}{\partial x} dx\right] dy\, dz =$$
$$= -\frac{\partial\left(w_x \rho h + q_x\right)}{\partial x} dV$$

Modelling of transport processes

Energy equation

$$\frac{\partial \rho h}{\partial t} dV = -\left[\frac{\partial (w_x \rho h + q_x)}{\partial x} + \frac{\partial (w_y \rho h + q_y)}{\partial y} + \frac{\partial (w_z \rho h + q_z)}{\partial z} \right] dV$$

$$\frac{\partial \rho h}{\partial t} = -\nabla \cdot (\boldsymbol{w} \rho h + \boldsymbol{q})$$

ENERGY EQUATION

$$\frac{\partial \rho h}{\partial t} + \boldsymbol{w} \cdot \nabla (\rho h) = -\nabla \cdot \boldsymbol{q}$$

advection term   diffusion term

Modelling of transport processes

Constitutive relation for heat flux

$$\boldsymbol{q} = -\lambda \nabla T$$

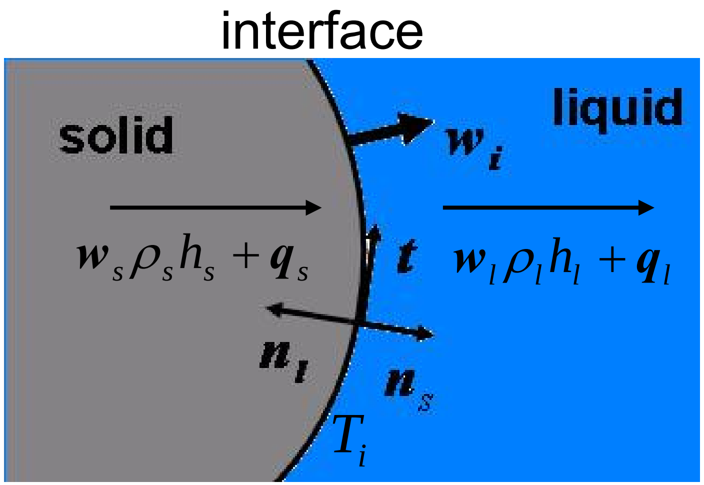
FOURIER LAW

where:

λ - thermal conductivity

Thermal conductivity of liquid and solid phases are differrent and depend on type of material, temperature, orientation, composition and microstructure of the solid phase

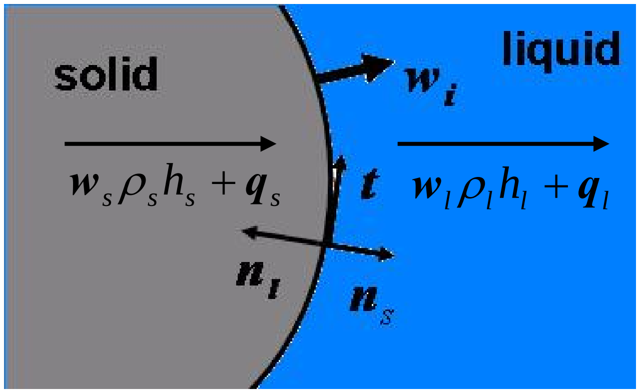
Energy balance for liquid / solid interface



$$\left[\rho_s h_s\left(\boldsymbol{w}_s - \boldsymbol{w}_i\right) + \boldsymbol{q}_s\right]\cdot \boldsymbol{n}_s + \left[\rho_l h_l\left(\boldsymbol{w}_l - \boldsymbol{w}_i\right) + \boldsymbol{q}_l\right]\cdot \boldsymbol{n}_l = 0$$

$$T_i = T_m + m_l(w_i)C_l - \frac{RT^2}{L_m}\frac{w_i}{w_s} - \frac{2\gamma_{ls}V_a T_m}{L_m}\kappa$$

Energy balance for liquid / solid interface



From the mass balance at the interface

$$\rho_l (\boldsymbol{w}_l - \boldsymbol{w}_i) \cdot \boldsymbol{n}_l = -\rho_s (\boldsymbol{w}_s - \boldsymbol{w}_i) \cdot \boldsymbol{n}_s$$

$$(\boldsymbol{q}_s - \boldsymbol{q}_l) \cdot \boldsymbol{n}_s = \rho_s (h_l - h_s)(\boldsymbol{w}_s - \boldsymbol{w}_i) \cdot \boldsymbol{n}_l$$

SPECIFIC ENTHALPY →

$$h = h(T, [C_j])$$

Modelling of transport processes

Thermodynamic relations - specific enthalpy

- <u>for the solid</u>

$$h_s(T,[C_j]) = h_r(T_r,0) + \sum_j \int_0^{C_j} h_{js}^*(T_r,[C_j])dC_j + \\ + \int_{T_r}^{T} c_s(T,[C_j])dT$$

where:

h_r - reference value of specific enthalpy

c_s - specific heat of the solid

h_{js}^* - partial enthalpy of the solid

Modelling of transport processes

Thermodynamic relations - specific enthalpy

- <u>for the solid</u>

$$h_l(T,[C_j]) = h_r(T_r,0) + \int_{T_r}^{T_m} c_s(T,0)\,dT + L_f + \\ + \sum_j \int_0^{C_j} h_{jl}^*(T,[C_j])\,dC_j + \int_{T_m}^{T} c_l(T,[C_j])\,dT$$

where: c_l - specific heat of the liquid

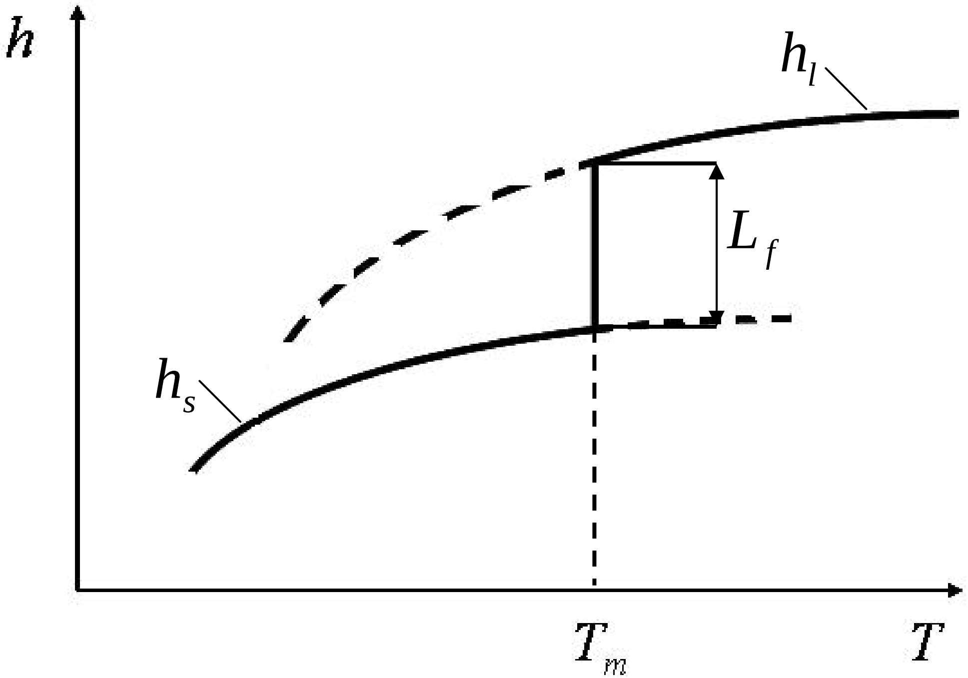
L_f - latent heat of solidification of pure solvent

h_{jl}^* - partial enthalpy of the liquid

Modelling of transport processes

Thermodynamic relations - specific enthalpy

For pure materials



Modelling of transport processes

Thermodynamic relations - specific enthalpy

For constant specific heats and negligible influence of concentration of components on the specific enthalpy (dilute systems)

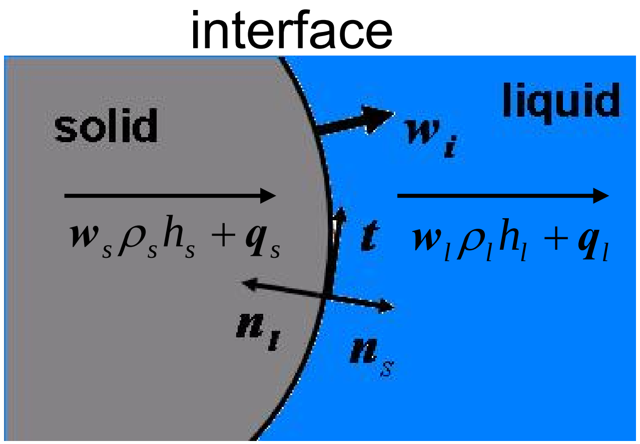
- for the solid

$$h_s(T,[C_j]) = h_r(T_r) + c_s(T - T_r)$$

- for the liquid

$$h_l(T,[C_j]) = h_r(T_r) + c_s(T_m - T_r) + L_f + c_l(T - T_m)$$

Energy balance for liquid / solid interface



For stationary solid phase, constant specific heats and negligible influence of concentration of components on the specific enthalpy (dilute systems)

$$\lambda_s \frac{\partial T_s}{\partial n_s} - \lambda_l \frac{\partial T_l}{\partial n_s} = \rho_s (h_l - h_s) w_{\mathbf{i}}$$

where:

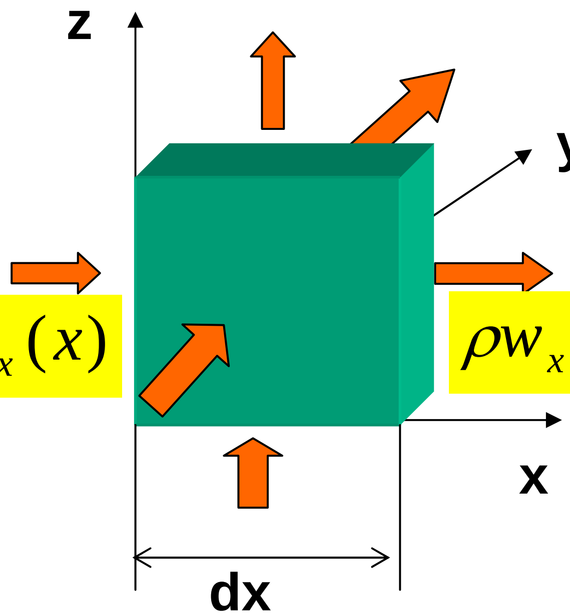
$$h_l - h_s = (c_s - c_l)(T_m - T_i) + L_f$$

T_i - interface temperature

Modelling of transport processes

Balance of alloy components

$$\rho w_x C_j(x) + j_{jx}(x)$$



$$\rho w_x C_j(x+dx) + j_{jx}(x+dx)$$

where:

C_j - concentration of *j* component (mass fraction)

j_{jx} - x-component of mass flux of *j* component

Modelling of transport processes

Balance of alloy components

$$\frac{\partial \rho C_j}{\partial t} = [\left(w_x \rho C_j(x) + j_{jx}(x)\right) - \left(w_x \rho C_j(x+dx) + j_{jx}(x+dx)\right)] dydz +$$
$$+ [\left(w_y \rho C_j(y) + j_{jy}(y)\right) - \left(w_y \rho C_j(y+dy) + j_{jx}(y+dy)\right)] dxdz +$$
$$+ [\left(w_z \rho C_j(z) + j_{jz}(z)\right) - \left(w_z \rho C_j(z+dz) + j_{jz}(z+dz)\right)] dxdy$$

$$[\left(w_x \rho C_j(x) + j_{jx}(x)\right) - \left(w_x \rho C_j(x+dx) + j_{jx}(x+dx)\right)] dydz =$$
$$= \left(w_x \rho C_j + j_{jx}\right) dy\, dz - \left[\left(w_x \rho C_j + j_{jx}\right) + \frac{\partial (w_x \rho C_j + j_{jx})}{\partial x} dx\right] dy\, dz =$$
$$= -\frac{\partial \left(w_x \rho C_j + j_{jx}\right)}{\partial x} dV$$

Modelling of transport processes

Balance of alloy components

$$\frac{\partial \rho C_j}{\partial t} dV = -\left[\frac{\partial (w_x \rho C_j + j_{jx})}{\partial x} + \frac{\partial (w_y \rho C_j + j_{jy})}{\partial y} + \frac{\partial (w_z \rho C_j + j_{jz})}{\partial z} \right] dV$$

$$\frac{\partial \rho C_j}{\partial t} = -\nabla \cdot (\boldsymbol{w} \rho C_j + \boldsymbol{j}_j)$$

COMPONENTS EQUATION

$$\frac{\partial \rho C_j}{\partial t} + \boldsymbol{w} \nabla (\rho C_j) = -\nabla \cdot \boldsymbol{j}_j$$

advection term — diffusion term

Modelling of transport processes

Constitutive relation for mass flux of *j* component

$$\boldsymbol{j}_j = -D_j \nabla C_j$$ ⬅ FICK LAW

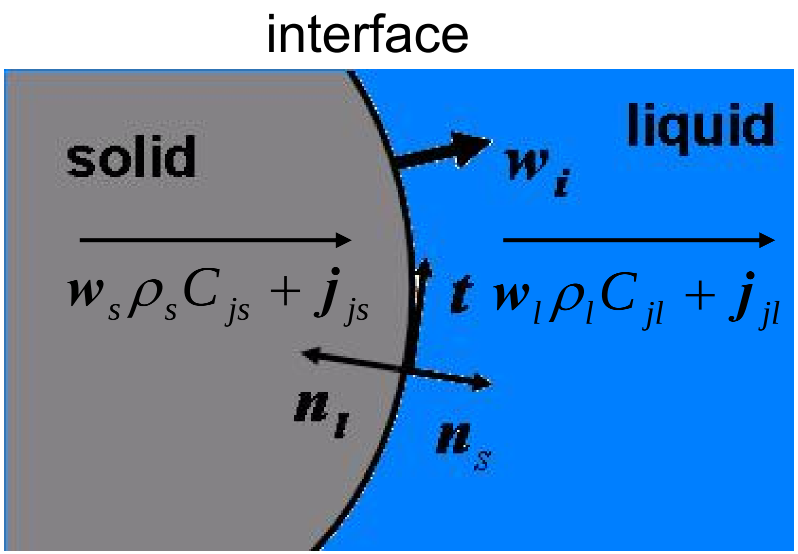
where:

D_j - diffusion coefficient of j component in the solvent

Diffusion coefficient of liquid and solid phases are significantly differrent and depend on type of material, temperature, orientation, composition and microstructure of the solid phase

Modelling of transport processes

Balance of *j* component
at liquid / solid interface

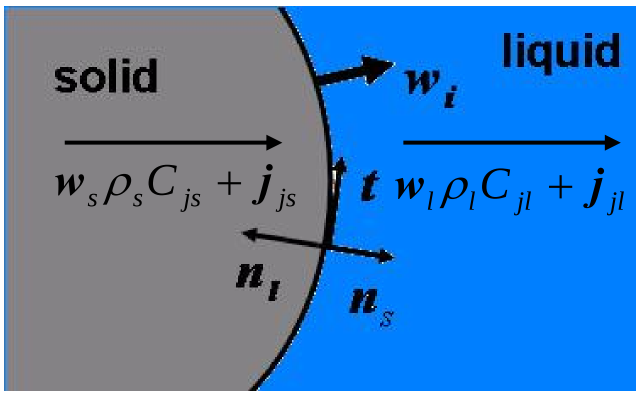


$$\left[\rho_s C_{js}\left(\boldsymbol{w}_s - \boldsymbol{w}_i\right) + \boldsymbol{j}_{js}\right]\cdot \boldsymbol{n}_s + \left[\rho_l C_{jl}\left(\boldsymbol{w}_l - \boldsymbol{w}_i\right) + \boldsymbol{j}_{jl}\right]\cdot \boldsymbol{n}_l = 0$$

Modelling of transport processes

Balance of *j* component at liquid / solid interface

interface



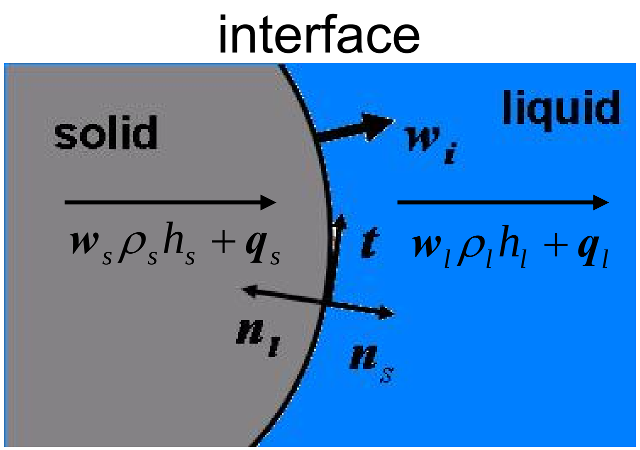
From the mass balance at the interface

$$\rho_l \left(\boldsymbol{w}_l - \boldsymbol{w}_i \right) \cdot \boldsymbol{n}_l = -\rho_s \left(\boldsymbol{w}_s - \boldsymbol{w}_i \right) \cdot \boldsymbol{n}_s$$

$$\left(\boldsymbol{j}_{js} - \boldsymbol{j}_{jl} \right) \cdot \boldsymbol{n}_s = \rho_s \left(C_{js} - C_{jl} \right) \left(\boldsymbol{w}_s - \boldsymbol{w}_i \right) \cdot \boldsymbol{n}_l$$

Modelling of transport processes

Balance of *j* component at liquid / solid interface



For stationary solid phase, binary system and the solute (dilute systems)

$$D_l \frac{\partial C_l}{\partial n_s} - D_s \frac{\partial C_s}{\partial n_s} = \rho_s \left(C_l - C_s \right) w_i$$

where:

$$C_l - C_s = (1 - \kappa_p) C_l$$

κ_p – partition coefficient

Modelling of transport processes

Mass transfer equation for *j* component at liquid free surface or at the liquid / mould interface

$$\frac{\partial \rho C_j^s}{\partial t} = -\nabla_s \cdot (\boldsymbol{w}\rho C_j^s + \boldsymbol{j}_j^s) + S_j$$

where:

C_j^s - surface concentration of *j* component (mass fraction of the component at the surface)

∇_s - divergence operator in surface coordinates

$\boldsymbol{j}_j^s$ - surface mass flux of *j* component

S_j - net exchange of *j* component due to adsorption

Modelling of transport processes

Mass transfer of *j* component at liquid free surface or at the liquid/mould interface

$$\boldsymbol{j}_j^s = -D_j^s \nabla_s C_j^s$$

$$S_j = \boldsymbol{j}_j \cdot \boldsymbol{n}_l = \beta_{sj} C_j (C_{j\infty}^s - C_j^s) - \alpha_{sj} C_j^s$$

adsorption — desorption

where:

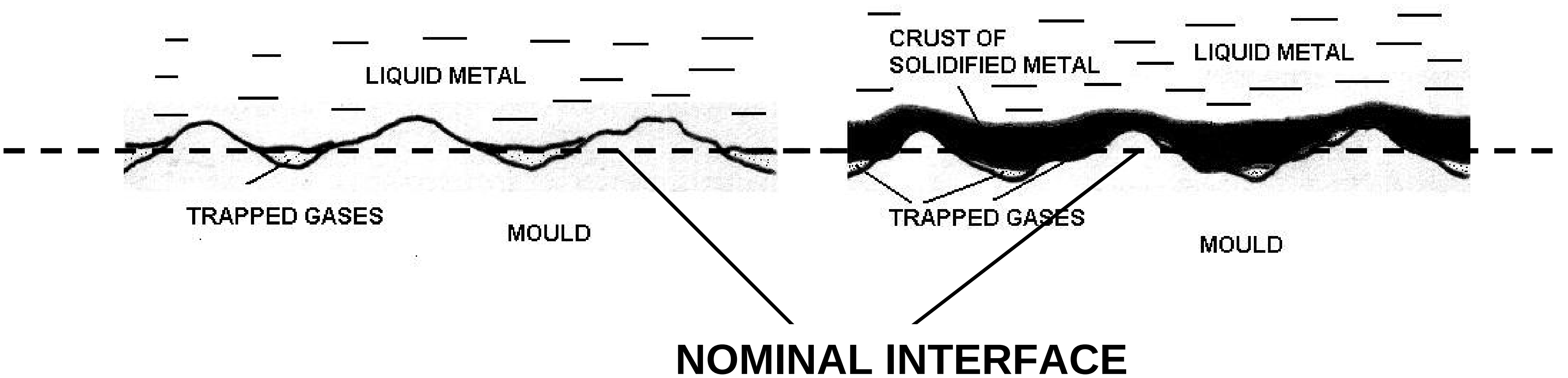
D_j^s - surface diffusion coefficient for *j* component

β_{sj}, α_{sj} - kinetic rates for adsorption and desorption

$C_{j\infty}^s$ - upper bound on *j* component concentration for monolayer adsorption

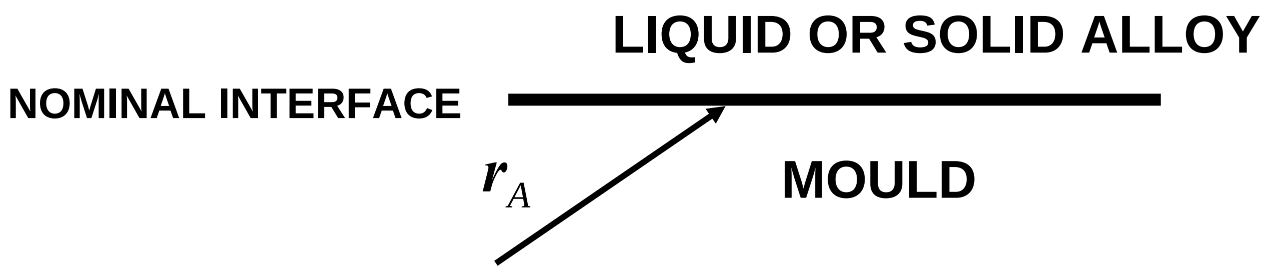
Modelling of transport processes

Heat transfer at liquid or solid / mould interface



Modelling of transport processes

Heat transfer at liquid or solid / mould interface



$$q_A(\boldsymbol{r}_A) = \boldsymbol{q} \cdot \boldsymbol{n}_l = \alpha_T(\boldsymbol{r}_A)(T - T_w)$$

where: α_T - local thermal conductance of the interface

T_w - temperature of the mould surface

Modelling of transport processes

Summary

Basic equations describing solidification phenomena in alloys contain:

- Nucleation models
- Models of transport phenomena of energy, alloy components and phase movement