Essential information to build up the diffusion genome

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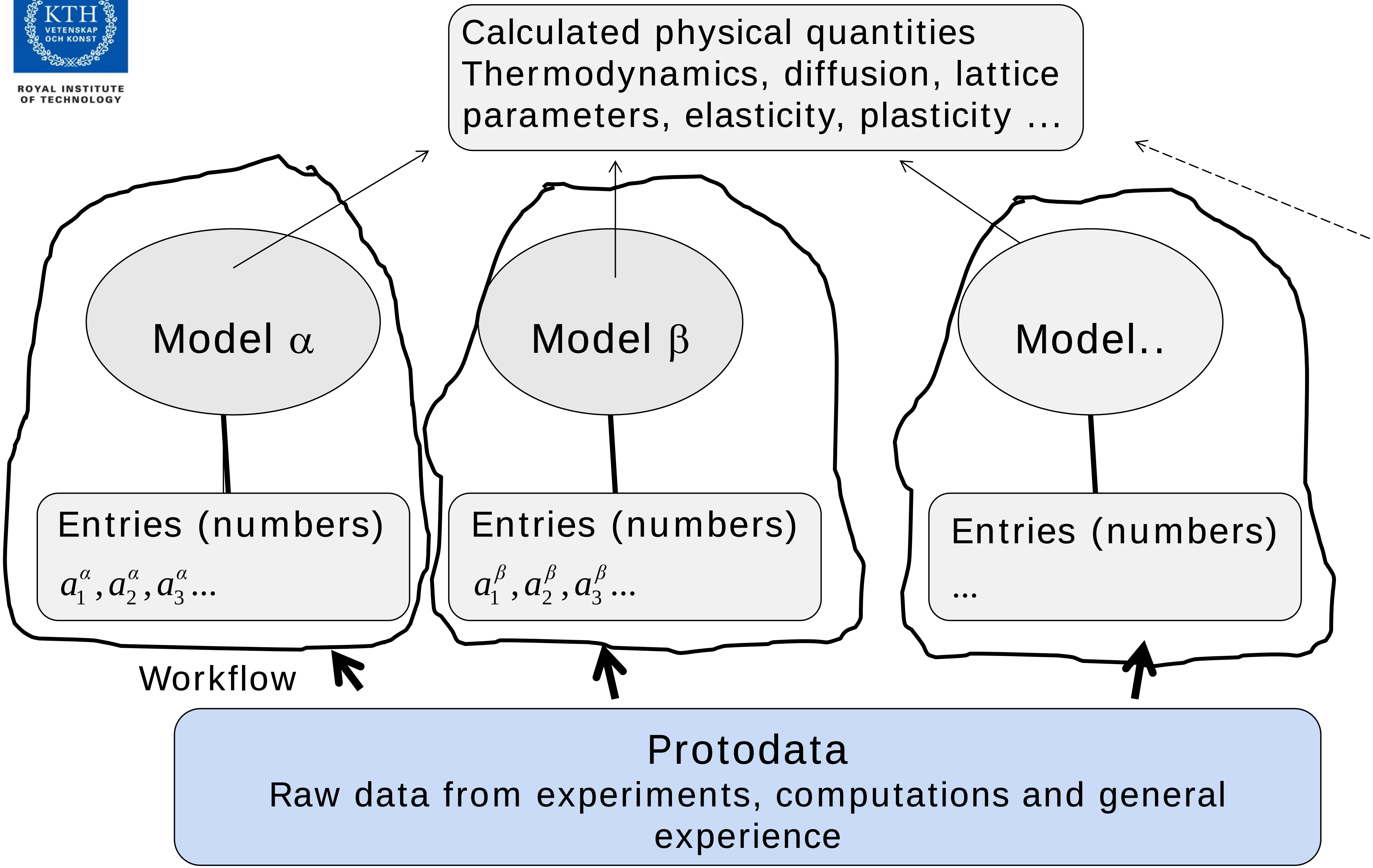
1. Advanced genome databases for diffusion – needs and present status

Materials Genome – an engineering approach to reduce the time for development and deployment of new materials. It is based on computations, experiments and data.

The diffusion genome should account for

- Multicomponent composition gradients in most important type of phases
- Thermal gradients
- Stress gradients
- Short-circuit diffusion, e.g. interfaces, grain boundaries etc
- Radiation
- ...

Advanced genome databases



Multicomponent composition gradients in most important type of phases

- Random-solution approximation (substitutional and interstitial)
  - Many databases are available , e.g. NIST Ni-base alloys, TCS (MOBFEX, MOBNIX,MOBALX)
  - There is a steady increase of assessments in literature
  - For liquids mostly estimates, some MD
- Ordered phases (sublattice approximation)
  - B2, $L1_2$ some assessments available.
- Carbides, nitrides
  - No systematic work – some estimates available
- Oxides
  - Some systematic work has been initiated at CEA and KTH.
  - Molten oxides?

Advanced genome databases available for physical effetcs including

- Thermal gradients
  - Not very much
- Stress gradients
  - Nothing?
- Short-circuit diffusion, e.g. interfaces e.g. grain boundaries etc
  - Simple estimates based on bulk properties although there are extensive compilations of experimental data available, see e.g. compilation by Kaur and Gust.
- Radiation
  - Nothing?
- …

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2. Diffusion couples in multicomponent systems – rationale for mobilities

Boltzmann-Matano:

$n-1$ independent concentration profiles may be integrated

$$\frac{1}{2t}\int_{c_k^1}^{c_k} x\,dc_k = -\sum_j^{n-1} D_{kj}^n \frac{\partial c_j}{\partial x}$$

Number of interdiffusion coefficients (number fixed-frame of reference)

D_{kj}^n is $(n-1)^2$

Number of components	Number of independent profiles (equations)	Number of interdiffusion coefficients	Number of diffusion couples
2	1	1	1
3	2	4	2
4	3	9	3
5	4	16	4
6	5	25	5

Only at the intersection between diffusion paths when D varies with composition!

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If we use the Onsager form:

$$J_k = -\sum_j^n L_{kj} \frac{\partial \mu_j}{\partial x}$$

(number fixed-frame of reference $L_{kj} \rightarrow L_{kj}^{"}$)

we have

$$\frac{1}{2t} \int_{c_k^1}^{c_k} x \, dc_k = -\sum_j^{n-1} L_{kj}^{"} \frac{\partial (\mu_j - \mu_n)}{\partial x}$$

$L_{kj}^{"}$ symmetric and has $(n\text{-}1)n/2$ components

Number of components	Number of independent profiles (equations)	Number of interdiffusion L-parameters	Number of diffusion couples
2	1	1	1 (1)
3	2	3	2 (2)
4	3	6	2 (3)
5	4	10	3 (4)
6	5	15	3 (5)

Mobilities

The L''_{kj} $\left((n\text{-}1)^2 \text{ parameters}\right)$ are functions of n mobilities.

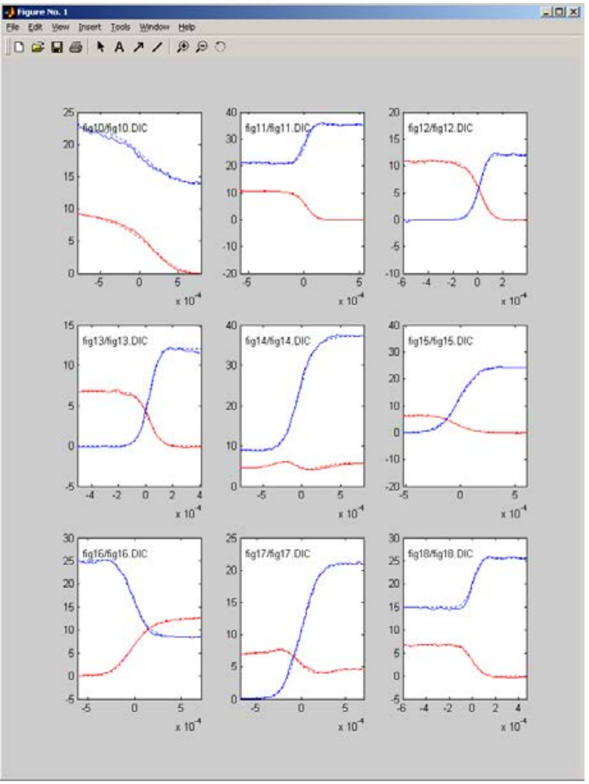
The $n-1$ concentration profiles and information on the Kirkendall shift can in principle be used to evaluate all mobilities from a single diffusion couple regardless the number of components. Example binary A - B with vacancy mechanism:

$$J_B = -\frac{y_{Va}}{V_m} x_B (1-x_B)\left(x_B M_A + (1-x_B) M_B\right)\frac{\partial(\mu_B - \mu_A)}{\partial x}$$

$$\frac{v}{V_m} = -\frac{y_{Va}}{V_m} x_B (1-x_B)\left(M_A - M_B\right)\frac{\partial(\mu_B - \mu_A)}{\partial x}$$

Using Manning's approach there will be extra terms when correlation is taken into account but they only depend on the mobilities.

Generalized Boltzmann-Matano



- Fit mobilities directly to measured concentration profiles and marker migration by a numerical calculation and a least-square fit between calculated and experimental profile.
- Smoothing procedures?

- Höglund et al. 2004
  - Simultaneous optimization of mobilities to concentration profiles in ternary system (Al-Cr-Ni)
  - Information from 9 different diffusion couples was used

3. Correlation effects

Manning's treatment (1961):

Tracer diffusivity

$$D_k^* = RT\ f_c M_k^{random}$$

$f_c \cong 0.83$ for fcc.

$f_c \cong 0.75$ for bcc.

Can as well be included in M_k.

Correlation effect in multicomponent systems

Manning's treatment (1970):

$$J_k = -\sum_j^n L_{kj} \frac{\partial \mu_j}{\partial z}$$

$$L_{kj} = \left(\delta_{kj} + \eta\, c_k M_k\right) c_j M_j$$

where

$$\eta = \frac{2}{\beta_0 \sum_i^n c_i M_i}$$

and $\beta_0 = 7.15$ in fcc and 5.33 in bcc.

$$J_{Va} = \frac{(\beta_0 + 2)}{\beta_0} \sum_k^n c_k M_k \frac{\partial \mu_k}{\partial z}$$

$\dfrac{(\beta_0 + 2)}{\beta_0}$ vacancy flux enhancement factor

1.28 for fcc and 1.37 for bcc.

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4. Temperature gradients

(Similar treatment for diffusion in electric fields.)

$$J_k = -\sum \frac{L_{kj}}{T} \nabla \mu_j - \frac{L_{kT}}{T^2} \nabla T$$

$$J_Q = -\sum \frac{L_{Tj}}{T} \nabla \mu_j - \frac{L_{TT}}{T^2} \nabla T$$

Onsager reciprocity laws:

$$L_{kj} = L_{jk}$$

$$L_{Tj} = L_{jT}$$

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Heat of transport Q_j^* :

$$J_k = -\sum \frac{L_{kj}}{T} \nabla \mu_j - \frac{L_{kT}}{T^2} \nabla T = -\sum \frac{L_{kj}}{T} \left(\nabla \mu_j + \frac{Q_j^*}{T^2} \nabla T \right)$$

i.e. $L_{kT} = \sum L_{kj} Q_j^*$

In lattice fixed frame of reference vacancy mechanism yields

$$L_{kk} = \frac{u_k y_{Va}}{V_s} M_{kVa}$$

$L_{kj} = 0$ when $i \neq j$

one has in the absence of a temperature gradient a heat flow:

$$J_Q = \sum J_j Q_j^*$$

$$Q_j^* = \left(\frac{\partial J_Q}{\partial J_j} \right)_{\nabla T = 0}$$

Thermal migration – a Kirkendall effect or a cross effect?

- Pure component A in lattice-fixed frame:

$$J_A = -\frac{u_A y_{Va}}{V_s} M_{AVa} \frac{Q_A^*}{T^2} \nabla T$$

Kirkendall (marker) velocity:

$$v_K = -\sum V_S J_k$$

5. Stress gradients

Substitutional diffusion with vacancy mechanism

$$d(F-\sigma_{ij}\Omega_{ij}) = -SdT - \Omega_{ij}d\sigma_{ij} + \sum \mu_k dN_k$$

Ω_{ij} = strain volume ($d\Omega_{ij} = d\varepsilon_{ij}V$)

Exchange of B atom with vacancy

$$d(F-\sigma_{ij}\Omega_{ij}) = -SdT - \Omega_{ij}d\sigma_{ij} + (\mu_B - \mu_{Va})dN_B$$

From Maxwell relation

$$\frac{\partial\,(\mu_B - \mu_{Va})}{\partial\,\sigma_{ij}} = -\frac{\partial\,\Omega_{ij}}{\partial\,N_B} = -\Omega_{ijB}$$

Ω_{ijB} = Partial molar strain volume (strain of transport)

$$\nabla(\mu_B - \mu_{Va}) = \nabla(\mu_B - \mu_{Va})^{chem} - \Omega_{ijB}\nabla\sigma_{ij}$$

Special case: Pressure induced diffusion.

$$\nabla(\mu_B - \mu_{Va}) = \nabla(\mu_B - \mu_{Va})^{chem} + V_B\nabla P$$

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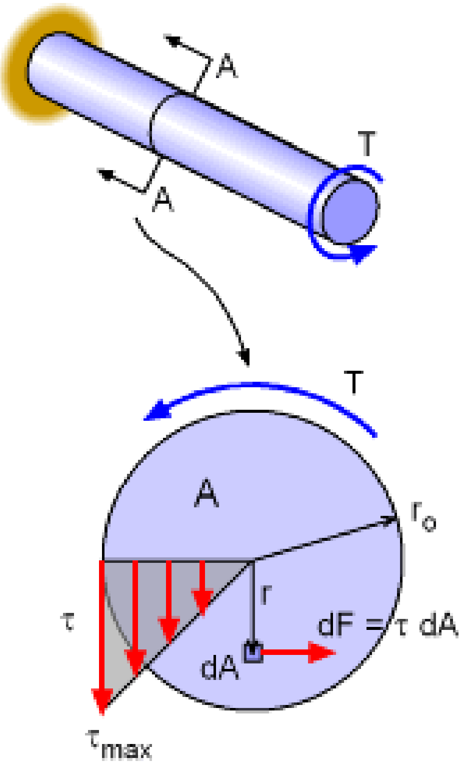
Substitutional diffusion with vacancy mechanism

$$J_B = -\frac{u_B y_{Va}}{V_s} M_{BVa} \left[\nabla(\mu_B - \mu_{Va})^{chem} - \Omega_{ijB} \nabla \sigma_{ij} \right]$$

Special case: Pressure induced diffusion.

$$J_B = -\frac{u_B y_{Va}}{V_s} M_{BVa} \left[\nabla(\mu_B - \mu_{Va})^{chem} + V_B \nabla P \right]$$

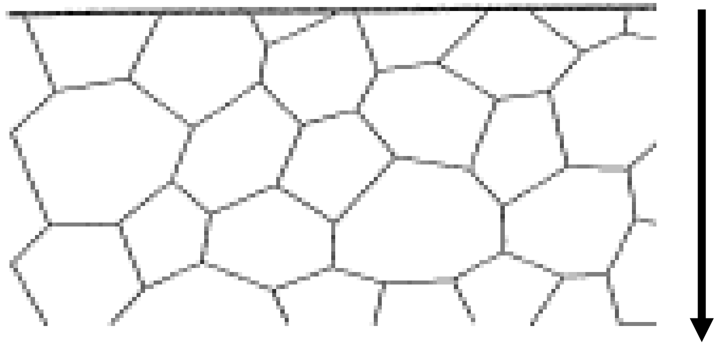


6. Short-circuit diffusion

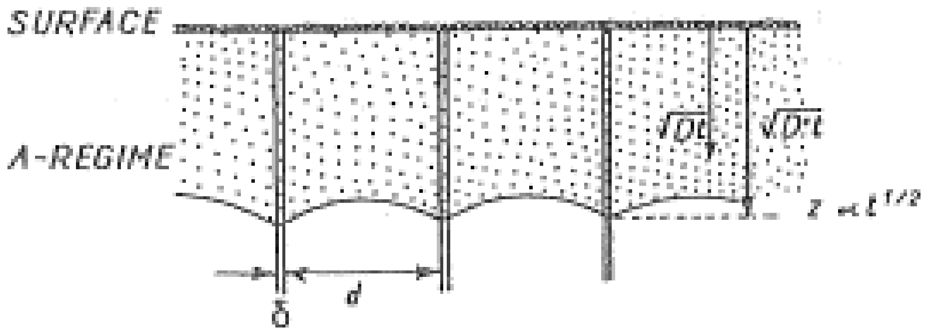
GB diffusion Type A, B or C kinetics (Harrison 1961)

$$\text{Type A}: \sqrt{Dt} >> d:$$

Surface



$$\sqrt{Dt} >> d:$$



Hart equation:

$$D_{app} \cong (1-3\delta/d)D^{vol} + 3\,\delta\,D^{gb}/d$$

Implemented in DICTRA

Since $D^{gb} >> D^{vol}$ and $Q^{gb} < Q^{vol}$

(Rule of thumb: $Q^{gb} \cong Q^{vol} / 2$)

grain boundary diffusion becomes important when temperature is low enough!

$D^{app} > D^{vol}$

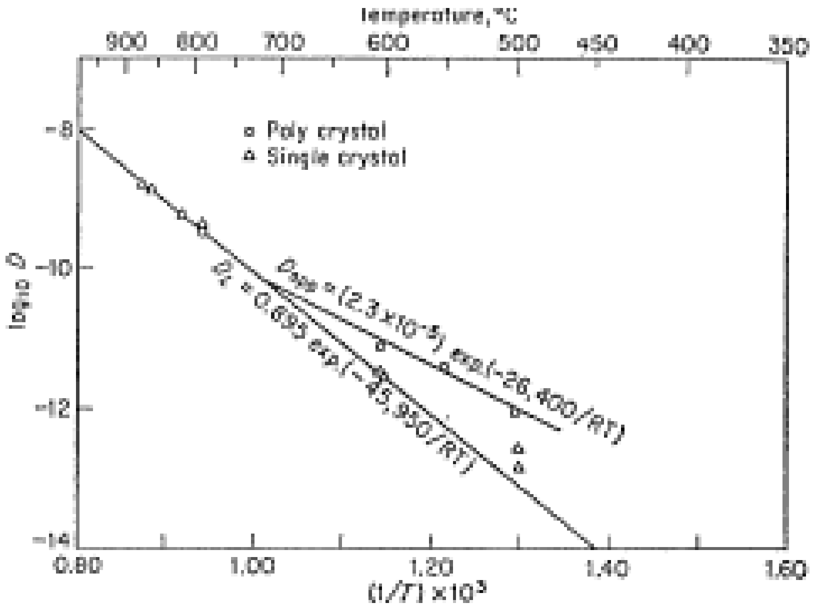


Fig. 6-1 — Values of D_T for silver in silver single-crystals and polycrystalline samples. [D. Turnbull, in *Atom Movements*, ASM, Cleveland, (1951) p.129.]

Type B and C

- Analytical solutions of 2D diffusion problem (Fisher model etc).
- Included automatically in phase-field simulations if GB diffusion is well described.

Evaluation of experimental data concerning type A and B only gives δD^{gb} or $s\delta D^{gb}$.

Experiments in regime type C allow determination of D^{gb}. Difficult measurements!

Remark: Diffusion along grain boundaries considered. What about diffusion across the boundaries?

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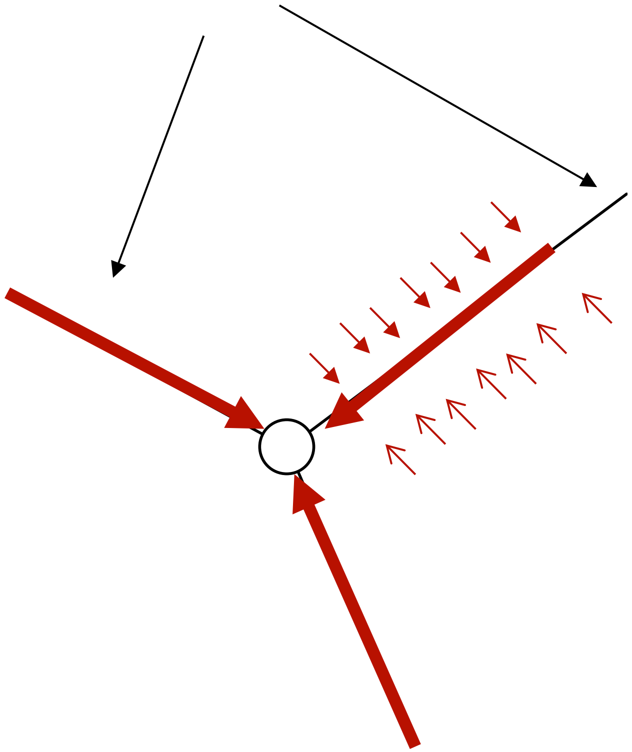
Grain boundaries

Precipitate growing at low T. Volume and GB diffusion coupled in series.

Volume diffusion very slow at low T but volume diffusion to a grain boundary may still be rate controlling.



Precipitate growth can occur at low temperatures at grain boundaries.

Modelling interfacial properties in general

- The structure of the two phases on each side
- The relative crystallographic orientation of the two lattices as well as the orientation of the interface, 5 degrees of freedom)
- The composition of the material
- Segregation of elements to the interface

$$\varphi = f(\alpha, \beta, \theta_1, \theta_2, \theta_3, n_x, n_y, n_z, c_1^i, ...c_{n-1}^i ...)$$

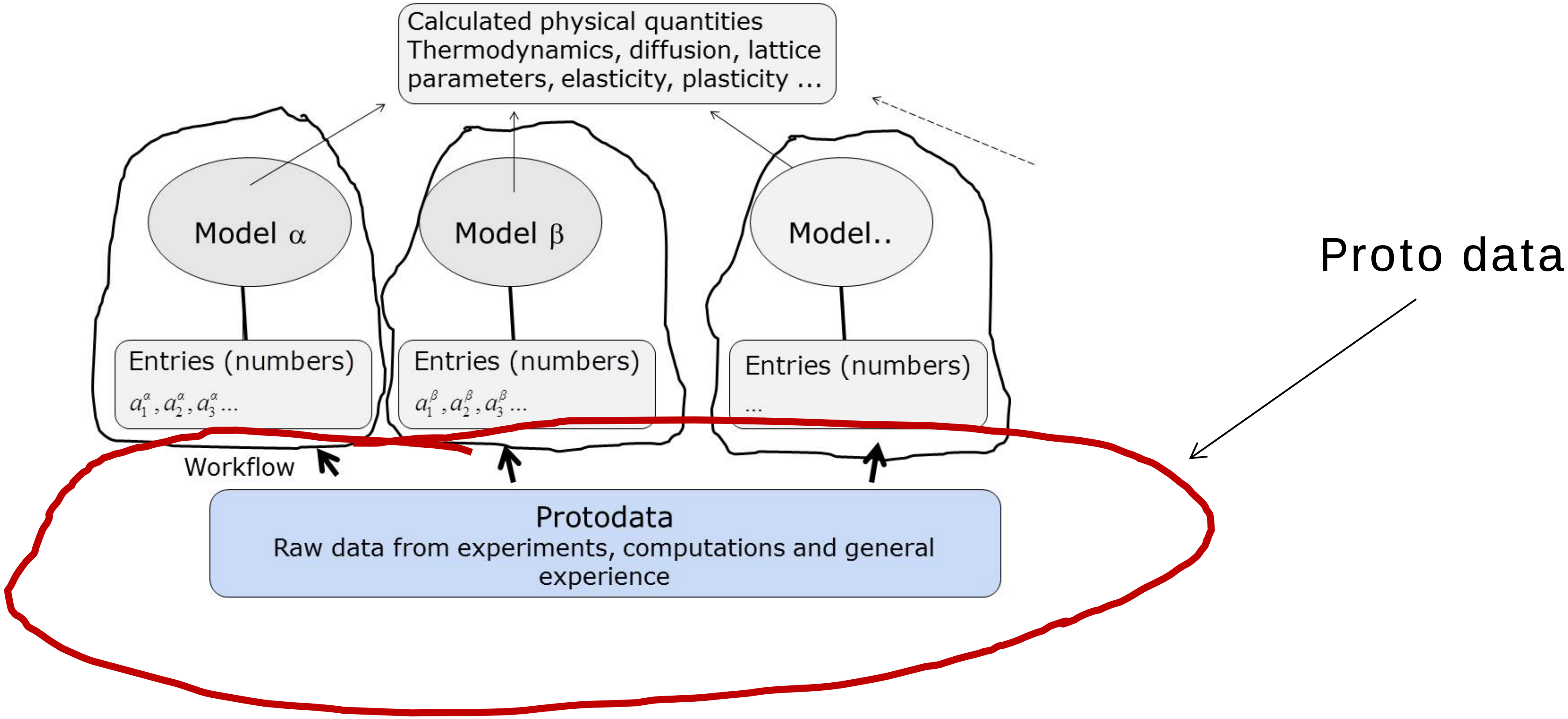
$\theta_1, \theta_2, \theta_3$ Euler angles of relative orientation

$|\overline{n}| = 1,$ Normal vector of interface

The most important interfacial properties are

- Interfacial energy
- Interfacial mobility
- Interfacial diffusion (transverse and longitudinal)

7. Protodata: raw data from experiments, computations and general experience



Proto data

- Experiments
  - Diffusion couples, multiples etc
    - Concentration profiles give data on interdiffusion
    - With marker migration also data on intrinsic diffusion → mobilities
  - Temperature gradients
  - Stress gradients
  - Tracer diffusion in homogeneous alloys
    - Tracer diffusivities give directly mobilities (including correlation correction)
  - Phase transformation rates
    - Give rather indirectly estimates of order of magnitudes of mobilities

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- Calculations
  - DFT
    - Elastic constants - stresses
    - Activation barriers – temperature dependence and frequency factors
  - MD (DFT or with potentials based on DFT)
    - Tracer diffusivities
  - Empirical correlations

For volume diffusion in fcc metals:

$Q \cong 18.4 R T_m$

$D_0 \cong 10^{-4} m^2 s^{-1}$

$\delta D^{gb} \approx 10^{-18} m^3 s^{-1}$

For $\delta \approx 10^{-9} m \Rightarrow D^{gb} \approx 10^{-9} m^2 s^{-1}$ i.e. same order of magnitude as for liquid metals at their melting point.

$Q^{gb} / Q^{vol} \approx 0.5$

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8. The need of ”lattice” mobilities

- Experimental information from different type of experiments and other sources are used to fit the mobilities.
- Mobilities in general are concentration and temperature dependent, e.g. substitutional alloy

$$RTM_k = v\delta^2 f_c\, y_{Va} \exp(\Delta S_k^* / R) \exp(-\Delta H_k^* / RT)$$

$$RT \ln(RTM_k) = RT \ln(v\delta^2 f_c) + RT \ln y_{Va} + \Delta S_k^* T - \Delta H_k^*$$

$$RT \ln(RTM_k) = \Phi_k = \sum_i x_i\, {}^o\Phi_{ki} + \sum_i \sum_{j>i} x_i x_j \;\; \Phi_{kij}$$

Example: Binary substitutional A B:

$$-RT \ln(RTM_k) = (1-x_B)\left(\Delta^\circ H_A^* + \Delta^\circ G_{VaA} - T\left[R \ln(v_A \delta_A{}^2 f_{cA}) + \Delta^\circ S_A^*\right]\right) +$$

$$x_B\left(\Delta^\circ H_B^* + \Delta^\circ G_{VaB} - T\left[R \ln(v_B \delta_B{}^2 f_{cB}) + \Delta S_B^* T\right]\right) + \text{higer order terms}$$

Lattice mobilities

- The need to establish a common set of lattice ”mobilities”. Similar to the set of lattice stabilities in conventional Calphad.
  - E.g. the mobility of Fe in pure Fe in the most important crystal structures.
  - Mobilities are needed also in crystal structures which are not stable for the element, e.g. pure Cr in fcc structure.

Mobility databases from diffusion couples

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Calculated Interdiffusion coefficients
Simulation of multicomponent diffusion couples

Model for diffusion

Model for Gibbs energy

Mobilities evaluated solely from diffusion couples are strictly speaking only valid combined with a specific thermodynamic database.

Entries (numbers)

${}^{0}\Phi^{\alpha}_{ki}, \Phi^{\alpha}_{kij} \ldots$

Entries (numbers)

${}^{\circ}G^{\alpha}_{k}, L^{\alpha}_{jk} \ldots$

Workflow

Protodata

Raw data from experiments, computations and general experience

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9. Conclusive remarks

- In an advanced genome database for diffusion
  - Diffusion model and accompanying thermodynamic model
  - Mobilities (easy to include Manning correlations) and accompanying thermodynamic parameters
  - Heat of transport (charge of transport for electric fields)
  - Strain volumes
- Lattice mobilities