MatCalc
Engineering

MatCalc approach for the modelling of the precipitate/matrix interfacial energy

(MatCalc 5.60.1003)

P. Warczok

Outline

- What is it all about?
- Why do we care?
- How do we estimate it?
  - Planar sharp interface
  - Curvature correction
  - Diffusive interface

What is it all about?

- Various contributions to Gibbs energy…

$$G = \sum_i N_i \mu_i + \sum_k A_k \gamma_k + \cdots$$

Chemical part

Interfacial part

- Interfaces considered
  - Precipitate/matrix interface
  - Grain boundary
  - Subgrain boundary

G – Gibbs energy

N_i - Number of moles of „*i*“-species

μ_i - Chemical potential of „*i*“-species

A_k - Area of „*k*“-interface

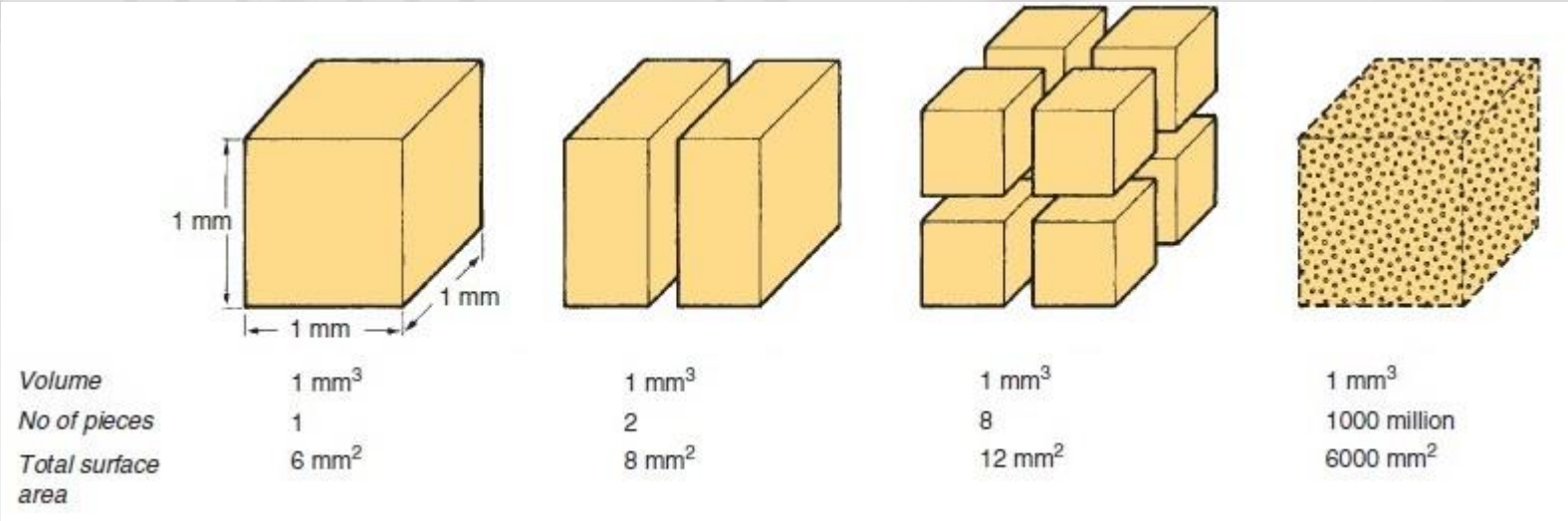
γ_k - Interfacial energy of „*k*“-interface

What is it all about?

- Various contributions to Gibbs energy…

$$G = \sum_i N_i \mu_i + \sum_k A_k \gamma_k + \cdots$$

- Interfacial contribution dependent on the dispersion…



Volume	1 mm^3	1 mm^3	1 mm^3	1 mm^3
No of pieces	1	2	8	1000 million
Total surface area	6 mm^2	8 mm^2	12 mm^2	6000 mm^2

What is it all about?

- Various contributions to Gibbs energy…

$$G = \sum_i N_i \mu_i + \sum_k A_k \gamma_k + \cdots$$

- Various derivatives…

$$\gamma = \left(\frac{\partial U}{\partial A}\right)_{S,V,N_i,N_j\ldots} = \left(\frac{\partial H}{\partial A}\right)_{S,p,N_i,N_j\ldots} = \left(\frac{\partial F}{\partial A}\right)_{T,V,N_i,N_j\ldots} = \left(\frac{\partial G}{\partial A}\right)_{T,p,N_i,N_j\ldots}$$

U – Internal energy

H – Enthalpy

F – Free energy

S – Entropy

p – pressure

V – Volume

Why do we care?

MatCalc Engineering

- Classical Nucleation Theory

$$J \sim exp\left(-\frac{G^*}{RT}\right)$$

$$G^* = \frac{16\pi\gamma^3}{3\left[\frac{\Delta G_{chem} + \Delta G_{el}}{v^\alpha}\right]^2}$$

J – Nucleation rate

R – Gas constant

T – Temperature

G^*- Critical nucleation energy

ΔG_{chem} - Chemical contribution of nucleation Gibbs energy

ΔG_{el} - Mechanical contribution of nucleation Gibbs energy

v^α - Molar volume of the matrix

Why do we care?

MatCalc Engineering

- Coarsening (Ostwald ripening)

$$\left(\bar{r}(t)\right)^3 = \left(\bar{r}(t_0)\right)^3 + K_{LSW}t$$

$$K_{LSW} = \frac{8c_B^{\alpha}D_B^{\alpha}v^{\beta}}{9\left(c_B^{\beta} - c_B^{\alpha}\right)RT}\gamma$$

t – time

$\bar{r}(t)$ – Mean radius at time t

D_B^{α} - Diffusion coefficient of solute in the matrix

c_B^{α} - Solute concentration in the matrix

c_B^{α} - Solute concentration in the precipitate

v^{β} - Molar volume of precipitate phase

How do we estimate it?

- Becker concept

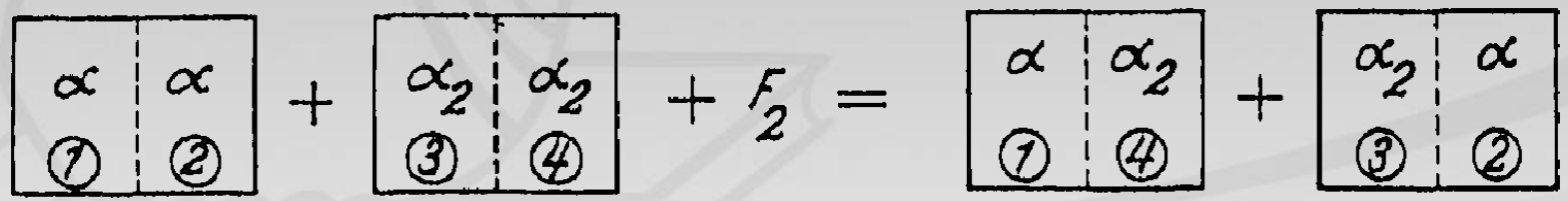


Abb. 6. Schema zur Berechnung der Oberflächenenergie

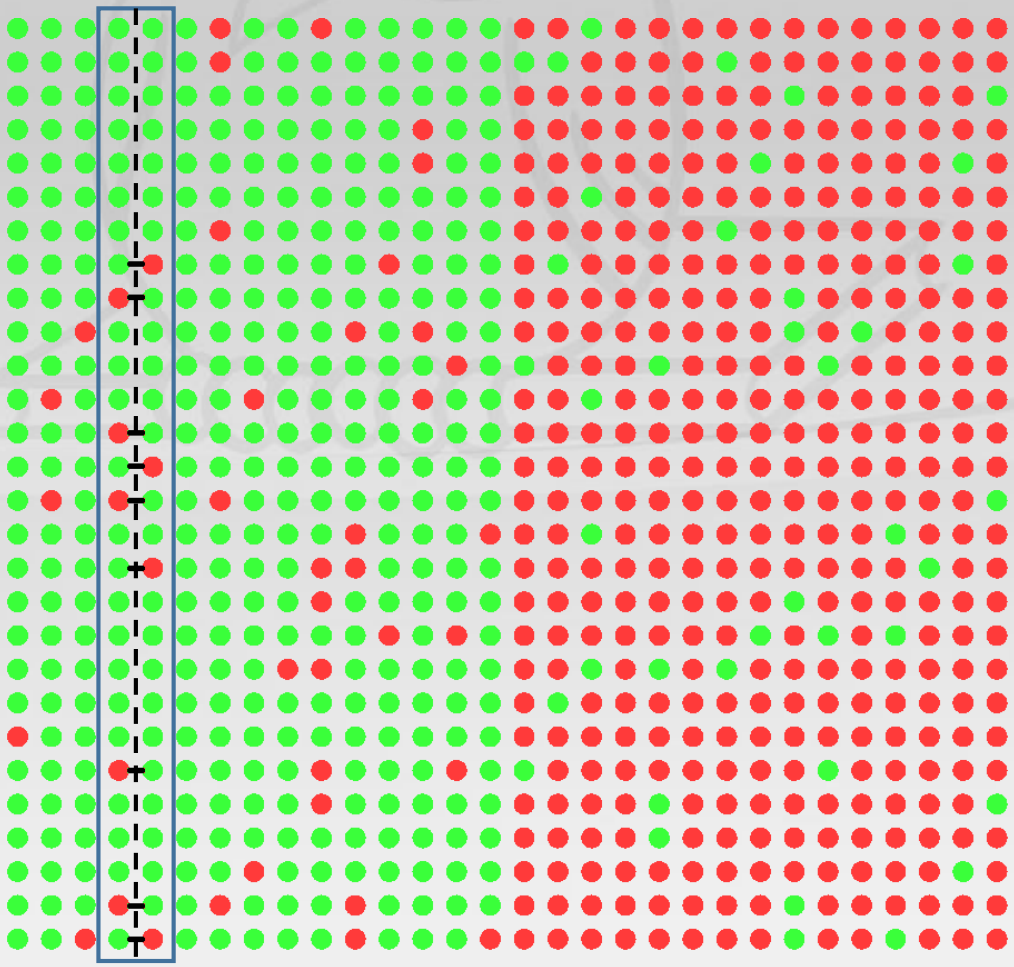
$$\gamma = \frac{F_2}{(A_{1-4} + A_{3-2})}$$

Becker R., Ann. Physik 32 (1938) 128-140

How do we estimate it?

MatCalc Engineering

- Source of energy – chemical bonds



$$E_{\alpha 1} = n_s z_s \varepsilon_{\alpha 1}$$

$$\varepsilon_{\alpha 1} = \frac{\sum_i \sum_{j \geq i} n_{ij} \varepsilon_{ij}}{n_s z_s}$$

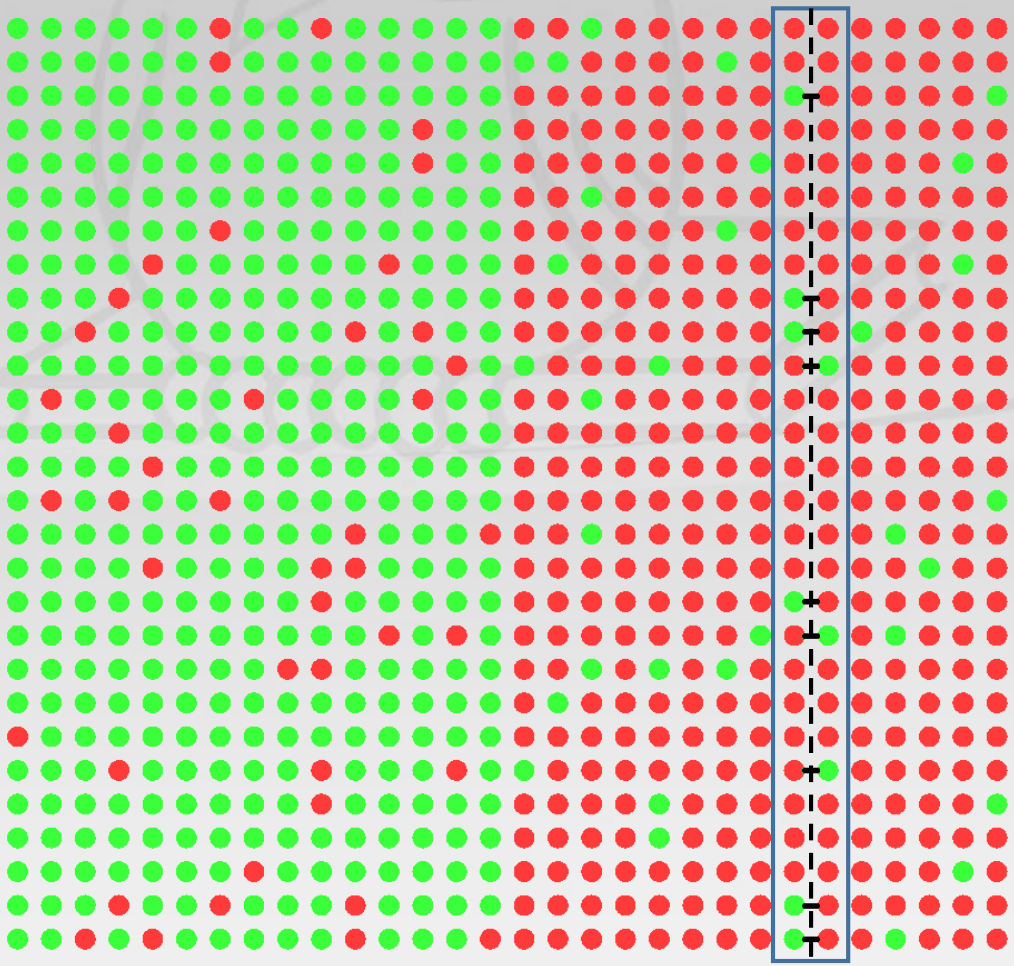
n_s - Number of atoms per interface area

z_s - Number of bonds between the nearest neighbors „broken“ by the interface

How do we estimate it?

MatCalc Engineering

- Source of energy – chemical bonds



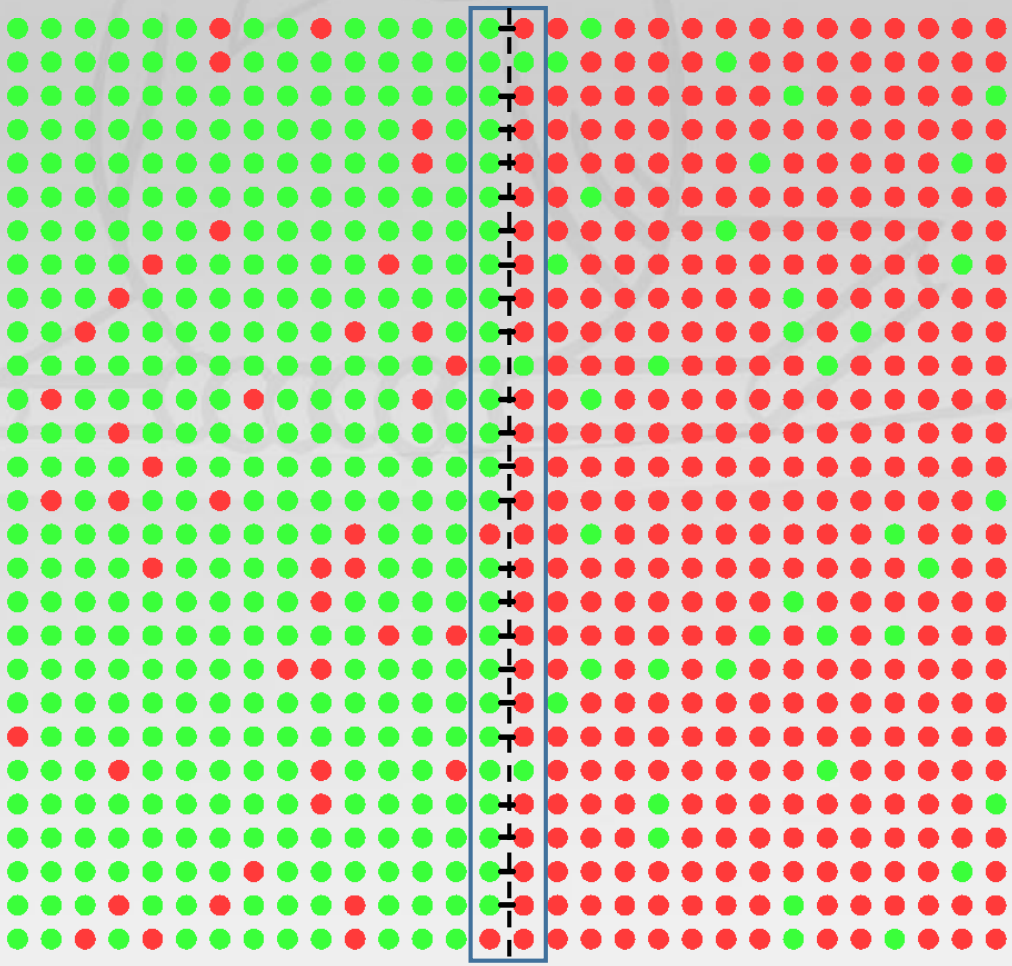
$$E_{\alpha 2} = n_s z_s \varepsilon_{\alpha 2}$$

$$\varepsilon_{\alpha 2} = \frac{\sum_i \sum_{j \geq i} n_{ij} \varepsilon_{ij}}{n_s z_s}$$

How do we estimate it?

MatCalc Engineering

- Source of energy – chemical bonds



$$E_{\alpha 1/\alpha 2} = n_s z_s \varepsilon_{\alpha 1/\alpha 2}$$

$$\varepsilon_{\alpha 1/\alpha 2} = \frac{\sum_i \sum_{j \geq i} n_{ij} \varepsilon_{ij}}{n_s z_s}$$

How do we estimate it?

MatCalc Engineering

- Becker concept

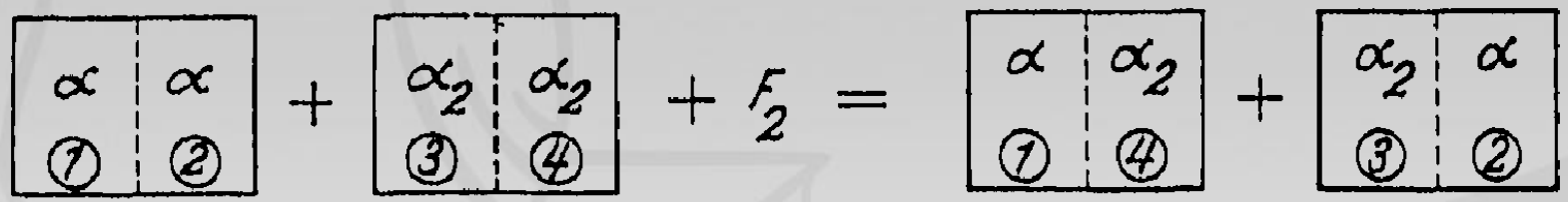


Abb. 6. Schema zur Berechnung der Oberflächenenergie

$$\gamma = \frac{F_2}{(A_{1-4} + A_{3-2})} = n_s z_s \left(2\varepsilon_{\alpha 1/\alpha 2} - \varepsilon_{\alpha 1} - \varepsilon_{\alpha 2}\right) = n_s z_s \varepsilon^*$$

$$\varepsilon^* = 2\varepsilon_{\alpha 1/\alpha 2} - \varepsilon_{\alpha 1} - \varepsilon_{\alpha 2}$$

How do we estimate it?

MatCalc Engineering

- Using Turnbull concept

$$H_{\alpha 1} = N_{\alpha 1}\varepsilon_{\alpha 1} \qquad H_{\alpha 2} = N_{\alpha 2}\varepsilon_{\alpha 2}$$

$$H_{\alpha 1/\alpha 2} = \left(N_{\alpha 1} - N_{\alpha 1/\alpha 2}\right)\varepsilon_{\alpha 1} + N_{\alpha 1/\alpha 2}\varepsilon_{\alpha 1/\alpha 2}$$

$$H_{\alpha 1/\alpha 2} = \left(N_{\alpha 2} - N_{\alpha 1/\alpha 2}\right)\varepsilon_{\alpha 2} + N_{\alpha 1/\alpha 2}\varepsilon_{\alpha 1/\alpha 2}$$

N_i - Number of bonds in phase „*i*“

$N_{i/j}$ - Number of bonds on the interface between phase „*i*“ and „*j*“

Turnbull D., Impur. Imperf. 32 (1955) 121-143

How do we estimate it?

MatCalc Engineering

- Using Turnbull concept

$$\Delta H_{sol} = 2H_{\alpha 1/\alpha 2} - H_{\alpha 1} - H_{\alpha 2} = N_{\alpha 1/\alpha 2}\left(2\varepsilon_{\alpha 1/\alpha 2} - \varepsilon_{\alpha 1} - \varepsilon_{\alpha 2}\right) = n_L z_L \varepsilon^*$$

$$\varepsilon^* = 2\varepsilon_{\alpha 1/\alpha 2} - \varepsilon_{\alpha 1} - \varepsilon_{\alpha 2}$$

$$N_{\alpha 1/\alpha 2} = n_L z_L$$

n_L - Number of solute atoms

z_L - Number of nearest neighbors

How do we estimate it?

MatCalc Engineering

- Planar sharp interface. Nearest neighbor broken bond (NNBB) model
  - n_S, z_S - dependent on the interface orientation
  - z_L - dependent on the matrix crystal structure
  - $n_L = N_A$
  - ΔH_{sol} taken as $\left(\partial H_{matrix,eq} / \partial f_{prec,eq}\right)$

$$\gamma_{NNBB} = \frac{n_S z_S}{n_L z_L} \Delta H_{sol} = \frac{n_S z_S}{z_L N_A} \left(\frac{\partial H_{matrix,eq}}{\partial f_{prec,eq}} \right)_{f_{prec,eq}=0}$$

How do we estimate it?

MatCalc Engineering

- Planar sharp interface. Generalized broken bond (GBB) model

Reaching beyond
the nearest neighbors…

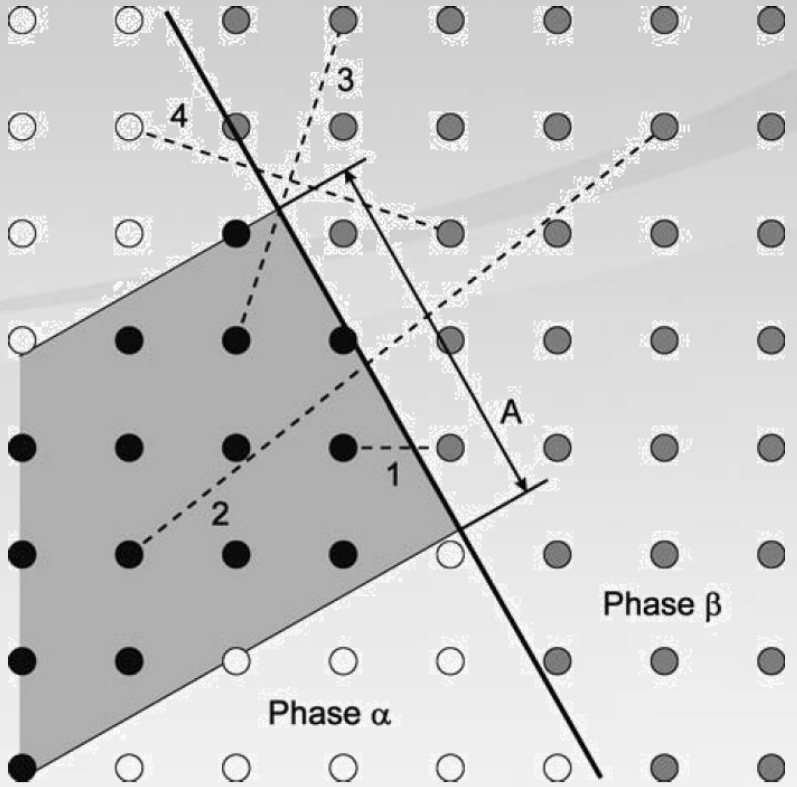


Fig. 1—Broken bonds across a randomly oriented interface.

How do we estimate it?

MatCalc Engineering

- Planar sharp interface. Generalized broken bond (GBB) model
  - $n_S = (N_A/V_M)^{2/3}$
  - $z_S/z_L \approx 0.329$

Table III. Minimum, Maximum, and Mean Values of $z_{S,\text{eff}}/z_{L,\text{eff}}$ for 100 Nearest-Neighbor Shells and r^{-6} Dependence of Interaction Potential

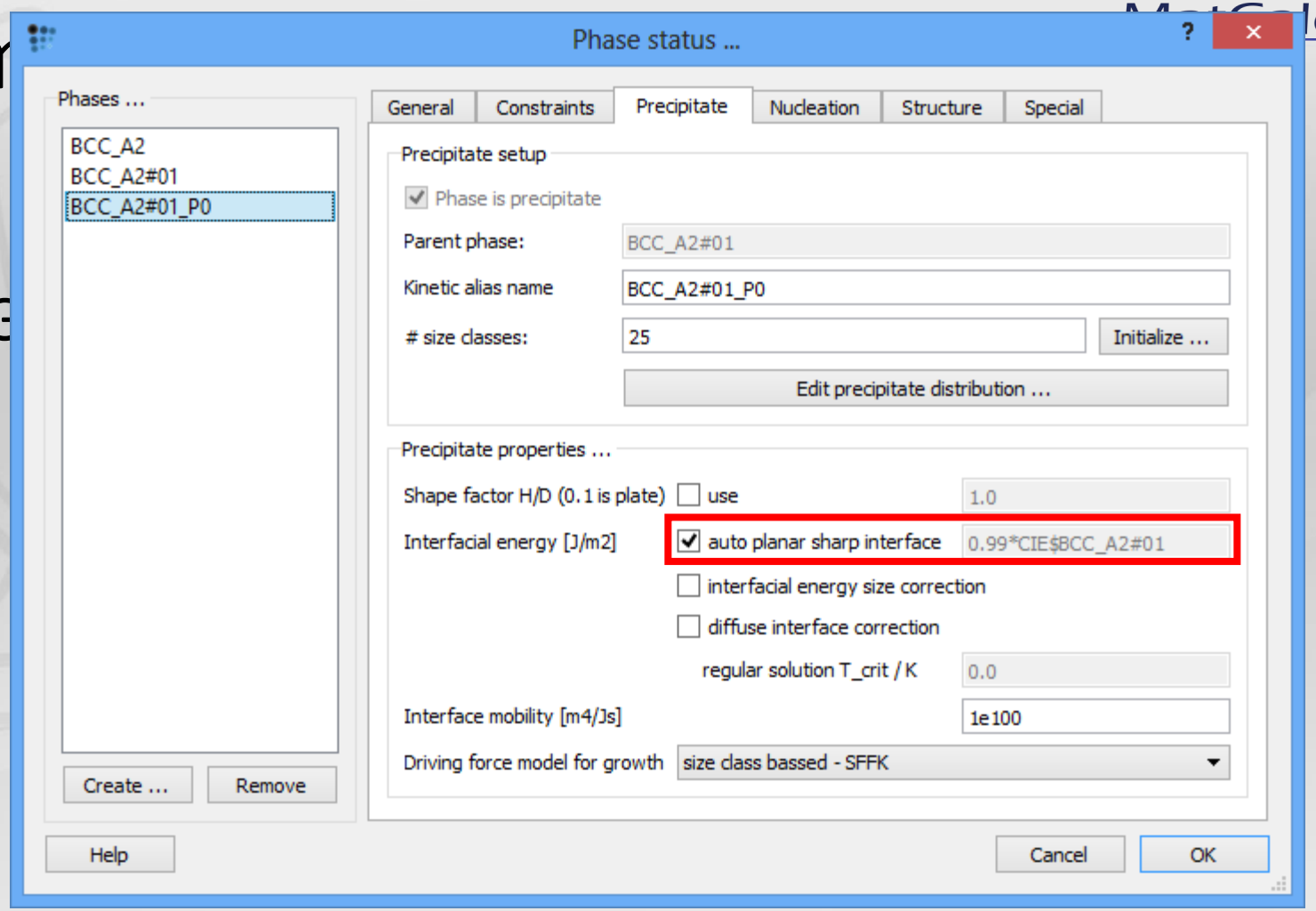
Structure	Minimum	Maximum	Mean	Anisotropy
Fcc	0.2871 [1,1,1]	0.3398 [10,5,1]	0.3291	18.4 pct
Bcc	0.2905 [1,1,0]	0.3415 [10,2,1]	0.3280	17.6 pct

$$\gamma_{GBB,pl,sh} = \frac{n_S z_S}{z_L N_A}\left(\frac{\partial H_{matrix,eq}}{\partial f_{prec,eq}}\right) = 0.329(N_A V_M^2)^{-\frac{1}{3}}\left(\frac{\partial H_{matrix,eq}}{\partial f_{prec,eq}}\right)$$

Sonderegger B. Kozeschnik E., Metall. Mater. Trans A. 40A (2009) 499-510

How do we estim

- Planar sharp interface. G
  - $n_S = (N_A/V_M)^{2/3}$
  - $z_S/z_L \approx 0.329$



$$\gamma_{GBB,pl,sh} = 0.329(N_A V_M^2)^{-\frac{1}{3}} \left(\frac{\partial H_{matrix,eq}}{\partial f_{prec,eq}} \right)$$

How do we estim

- Planar sharp interface. G
  - $n_S = (N_A/V_M)^{2/3}$
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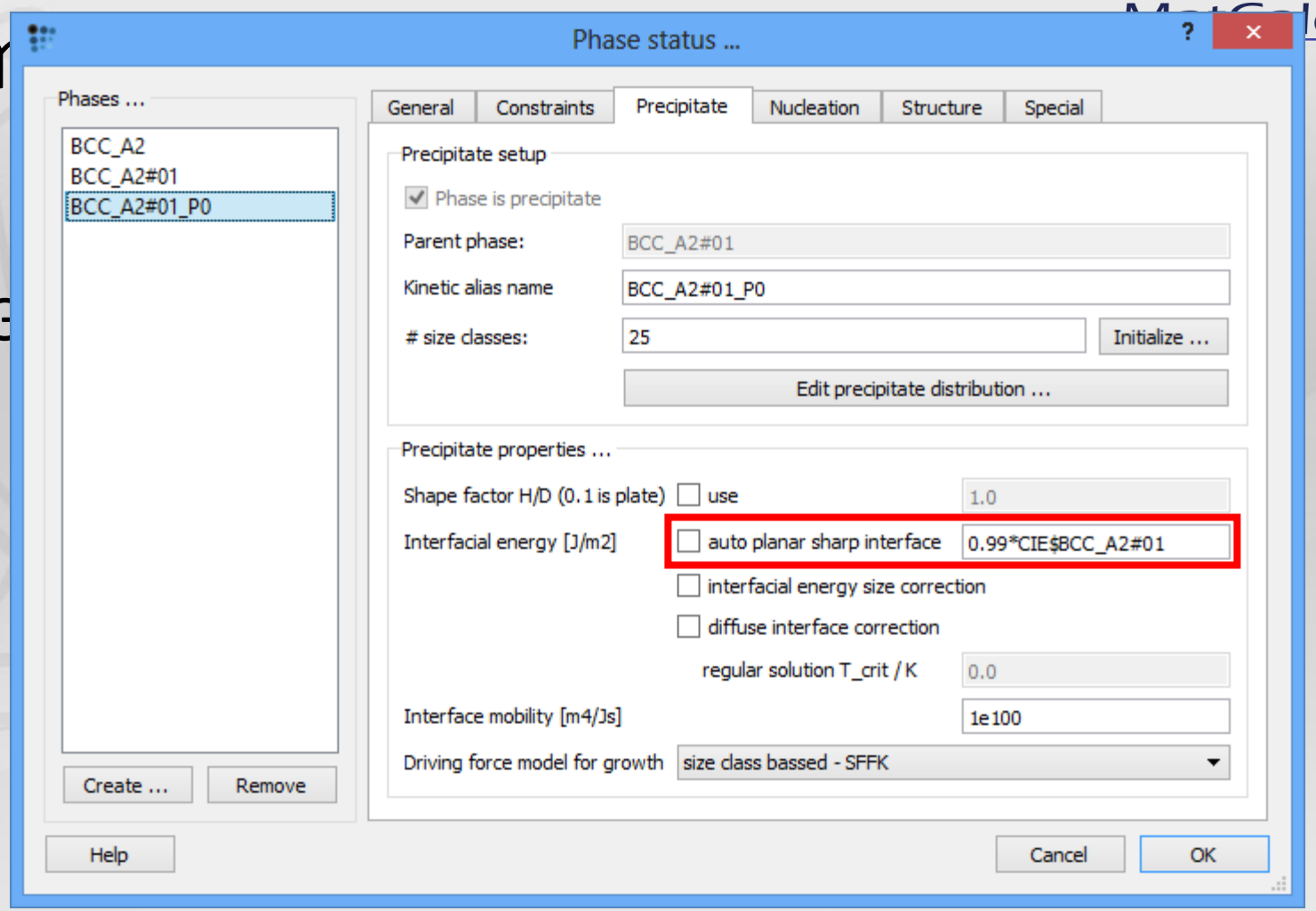
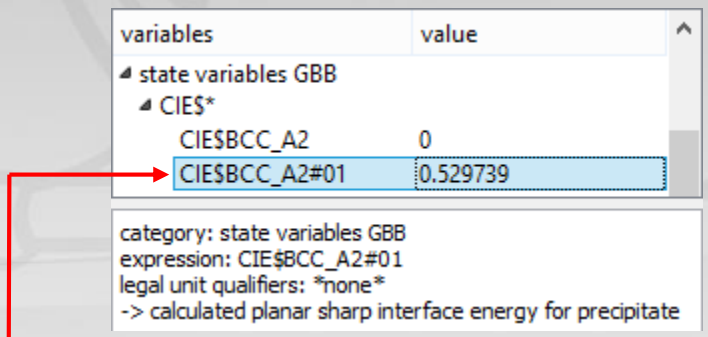


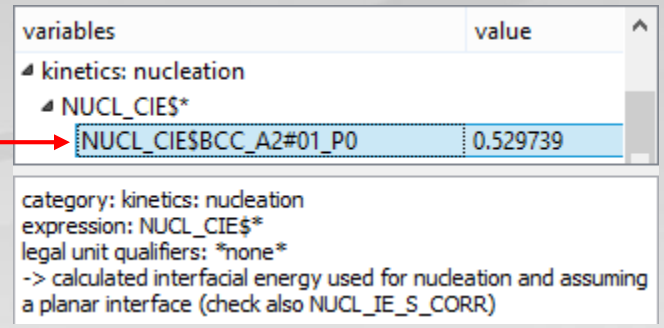
$\gamma_{GBB,pl,sh}$ - user defined...

How do we estimate it?

MatCalc Engineering

- Planar sharp interface. Generalized broken bond (GBB) model
  - $n_S = (N_A/V_M)^{2/3}$
  - $z_S/z_L \approx 0.329$





$$\gamma_{GBB,pl,sh} = 0.329(N_A V_M^2)^{-\frac{1}{3}} \left(\frac{\partial H_{matrix,eq}}{\partial f_{prec,eq}} \right)$$

How do we estimate it?

MatCalc Engineering

- Spherical correction factor $\alpha(r)$

Moving from planar to spherical interface…

Recounting the broken bonds…

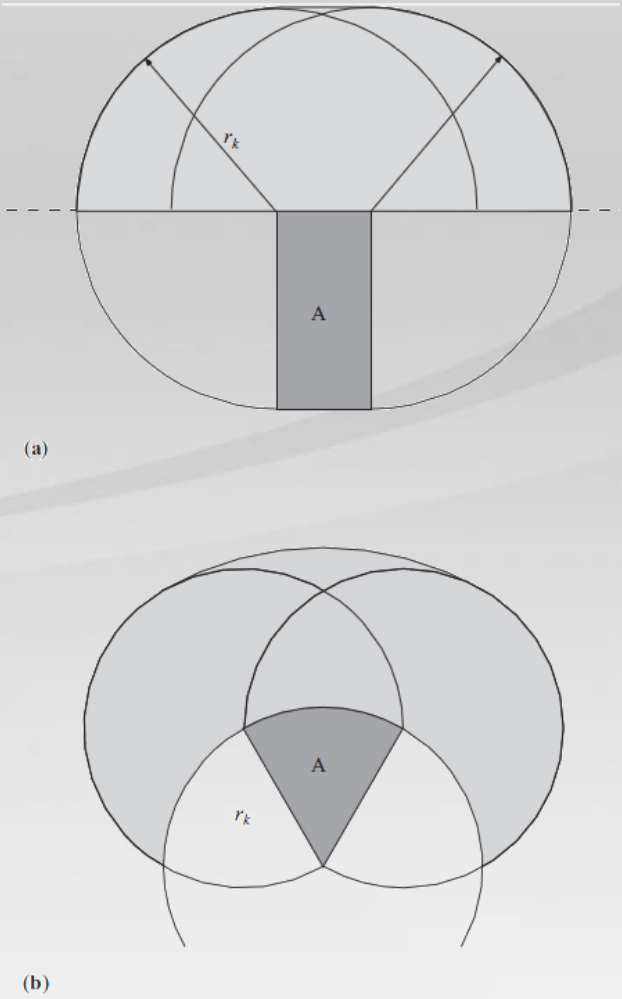


Figure 4.11. Sketch of model for bond counting with (a) planar interface and (b) curved interface. See text for explanation.

Sonderegger B. Kozeschnik E., Scr. Mater. 60 (2009) 635-638

How do we estimate it?

MatCalc Engineering

- Spherical correction factor $\alpha(r)$

$$\gamma_{GBB,sph} = \gamma_{GBB,pl}\alpha(r)$$

$$\alpha(r) = 1 - \frac{6}{11}\left(\frac{r_1}{r}\right) + \left[0.8921 + 0.045ln\left(\frac{10r}{3r_1}\right)\right]\left(\frac{r_1}{r}\right)^2$$

r_1 - Nearest neighbor distance ($2.48*10^{-10}$ m)

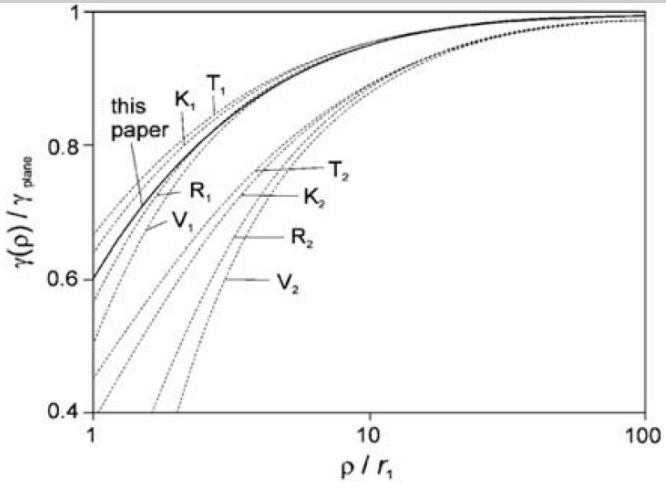


Figure 4. Comparison of present size-correction function $\alpha(\rho)$, Eq. (27), with results of Tolman [2] (T), Kashchiev [3] (K), Rasmussen [8] (R) and Vogelsberger et al. [9] (V). Subscripts 1 for $\delta_0 = 0.25$; subscripts 2 for $\delta_0 = 0.6$.

How do we estimate it?

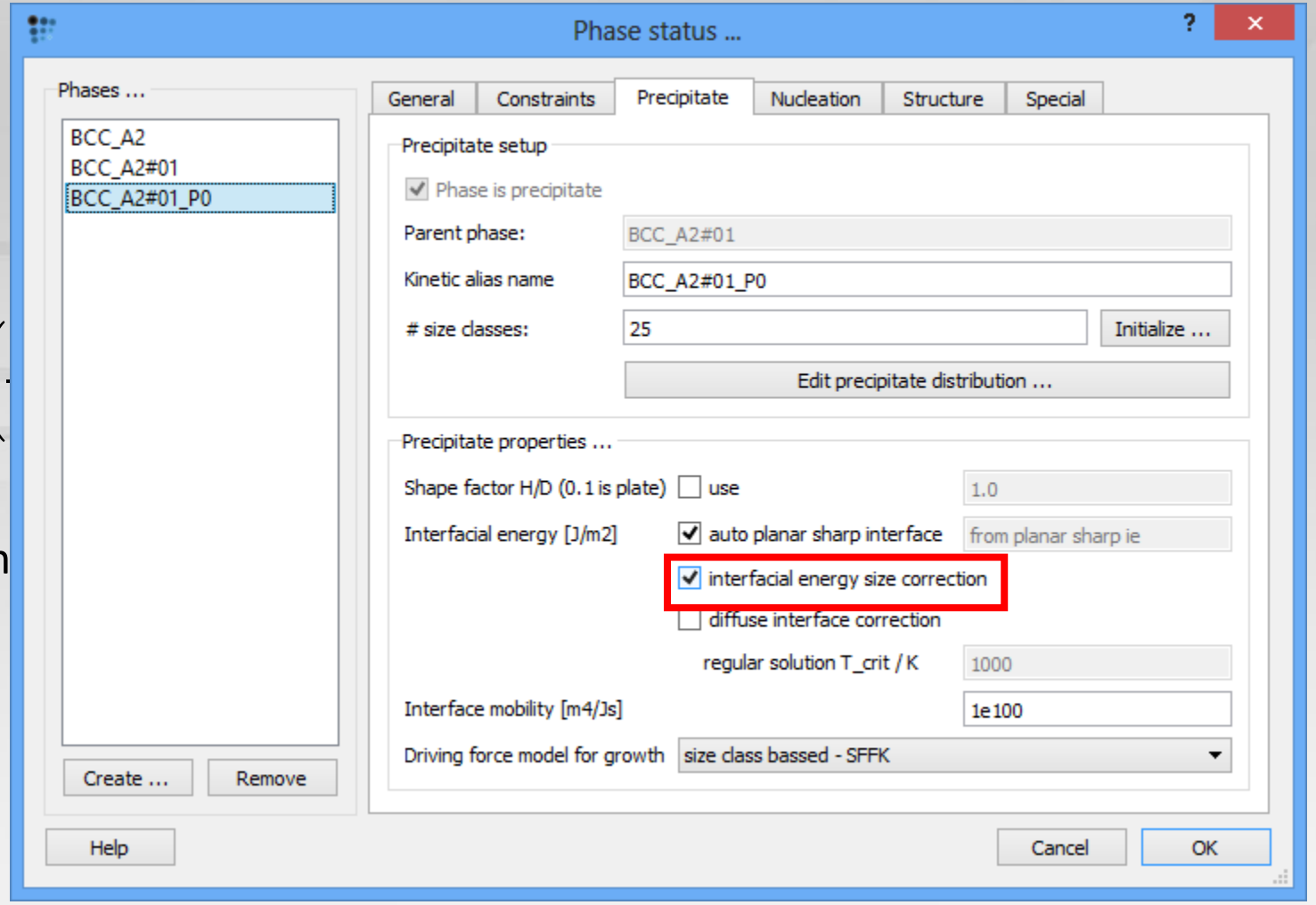
MatCalc Engineering

- Spherical correction factor

$$\gamma_{GBB,sph} = \gamma_{GBB,pl}\alpha(r)$$

$$\alpha(r) = 1 - \frac{6}{11}\left(\frac{r_1}{r}\right) + \left[0.8921 + 0.045ln\left(\right.\right.$$

r_1 - Nearest neighbor distance ($2.48*10^{-10}$ m

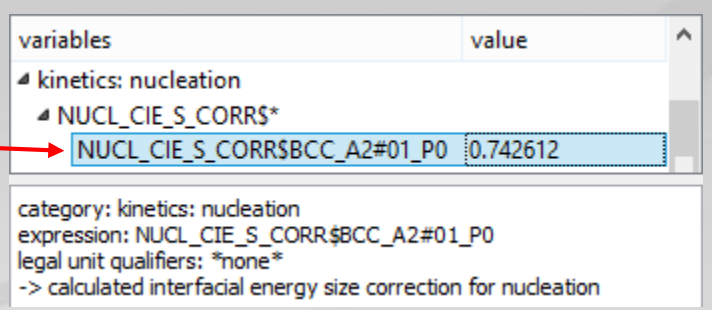


How do we estimate it?

MatCalc Engineering

- Spherical correction factor $\alpha(r)$

$$\gamma_{GBB,sph} = \gamma_{GBB,pl}\alpha(r)$$



$$\alpha(r) = 1 - \frac{6}{11}\left(\frac{r_1}{r}\right) + \left[0.8921 + 0.045ln\left(\frac{10r}{3r_1}\right)\right]\left(\frac{r_1}{r}\right)^2$$

r_1 - Nearest neighbor distance ($2.48*10^{-10}$ m)

How do we estimate it?

MatCalc Engineering

- Diffuse interface correction factor

Moving from sharp to diffuse interface…

Recounting the broken bonds again…

η – Solute fraction

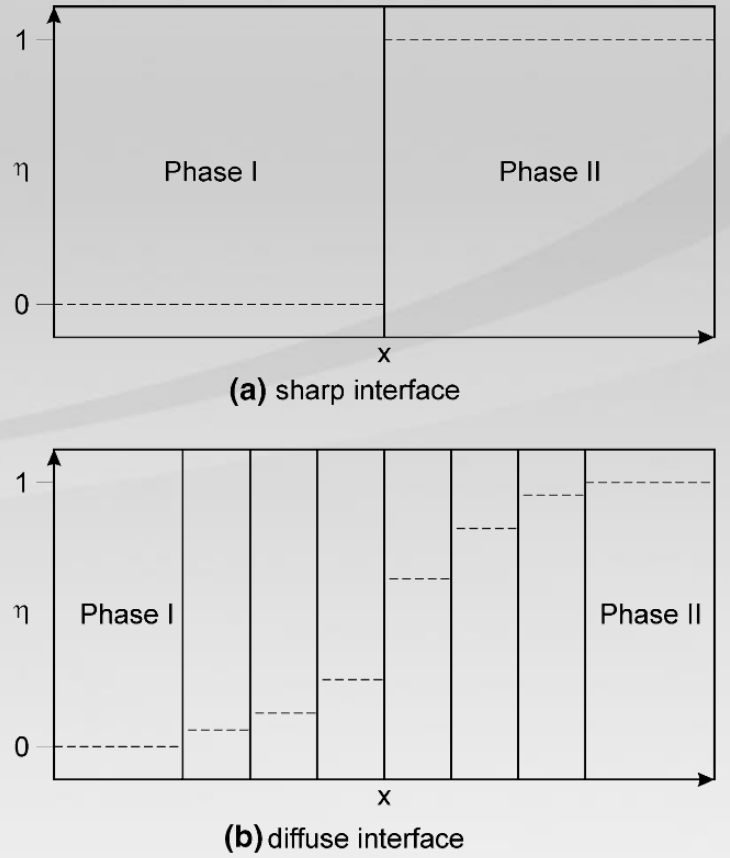
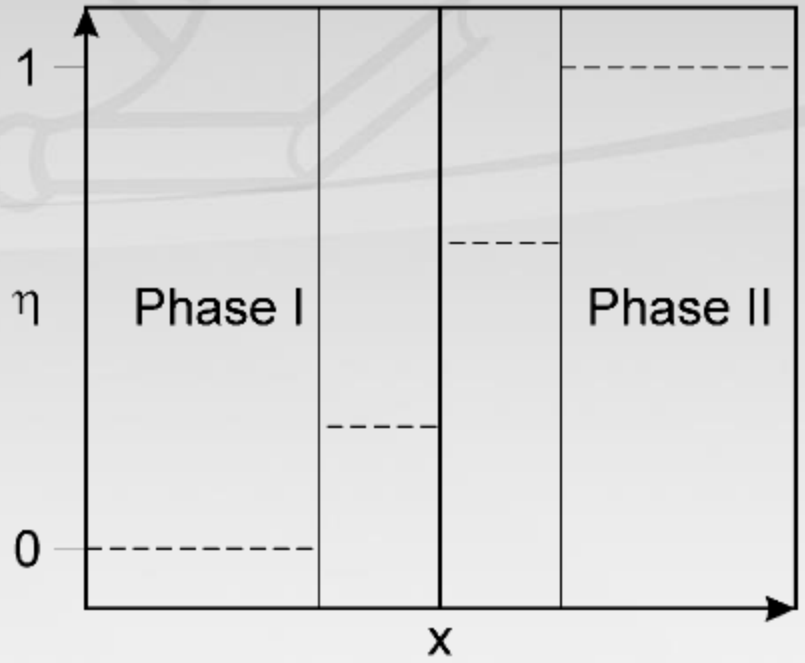


Fig. 1—Schematic concentration profiles of sharp and diffuse interfaces.

Sonderegger B. Kozeschnik E., Metall. Mater. Trans A. 41A (2009) 3262-3269

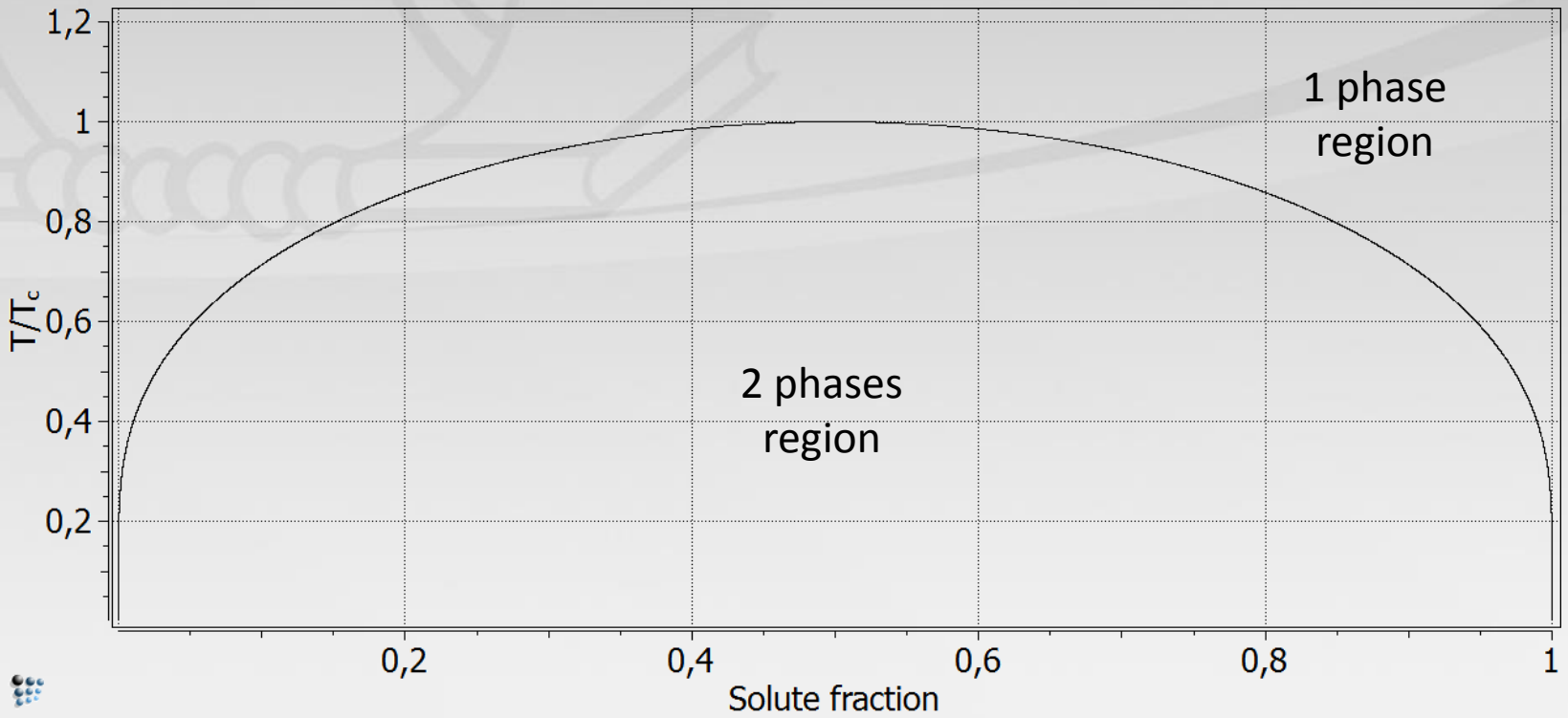
How do we estimate it?

- Diffuse interface correction factor. MatCalc application
  - Two intermediate layers (one on each side of the interface)



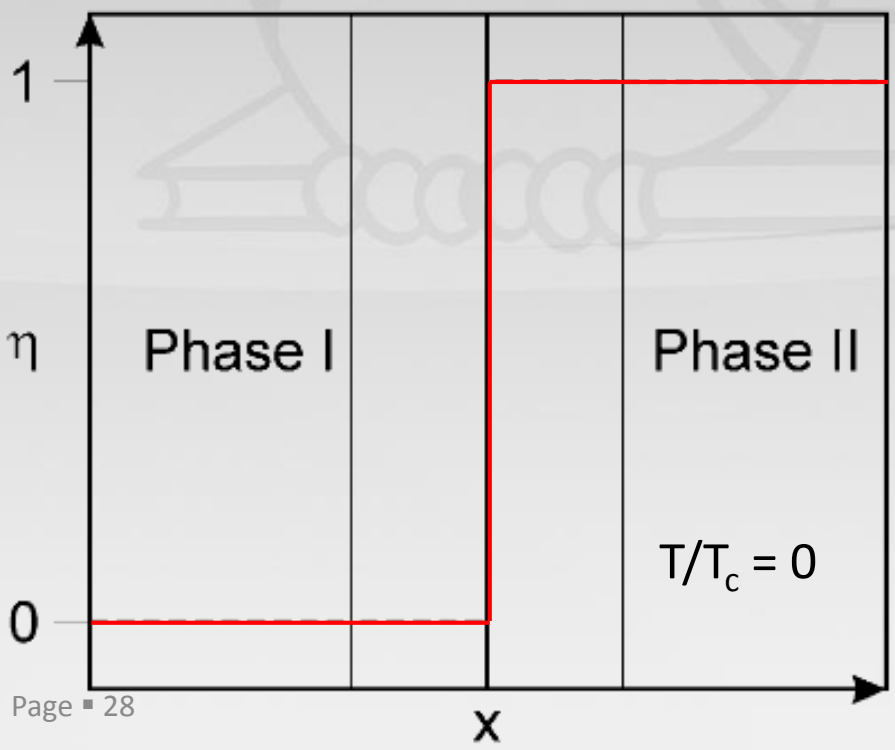
How do we estimate it?

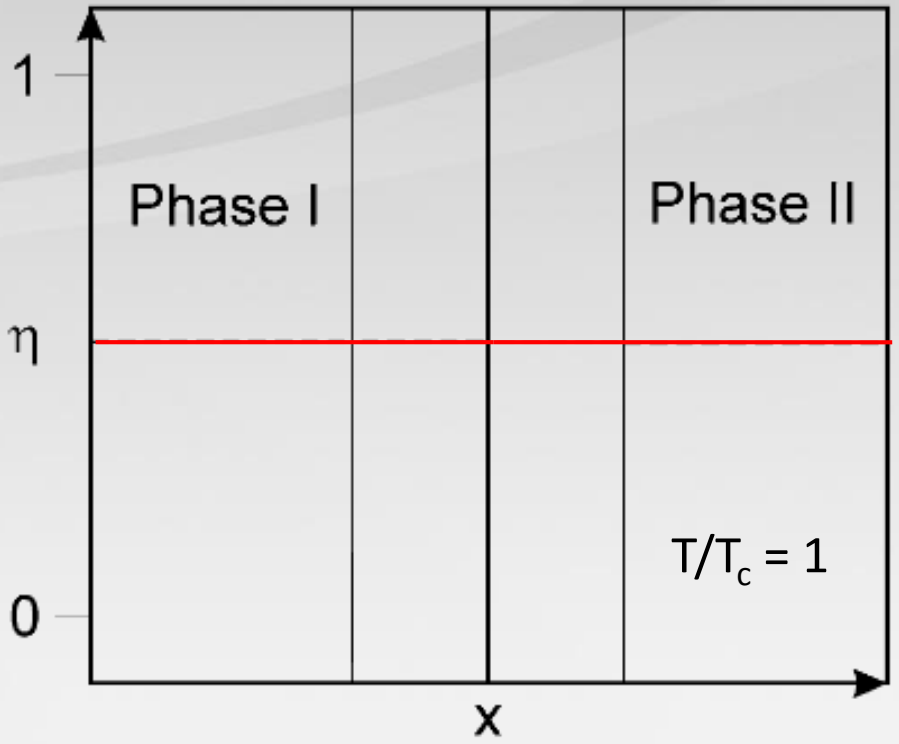
- Diffuse interface correction factor
  - Concept of critical temperature of regular solution



How do we estimate it?

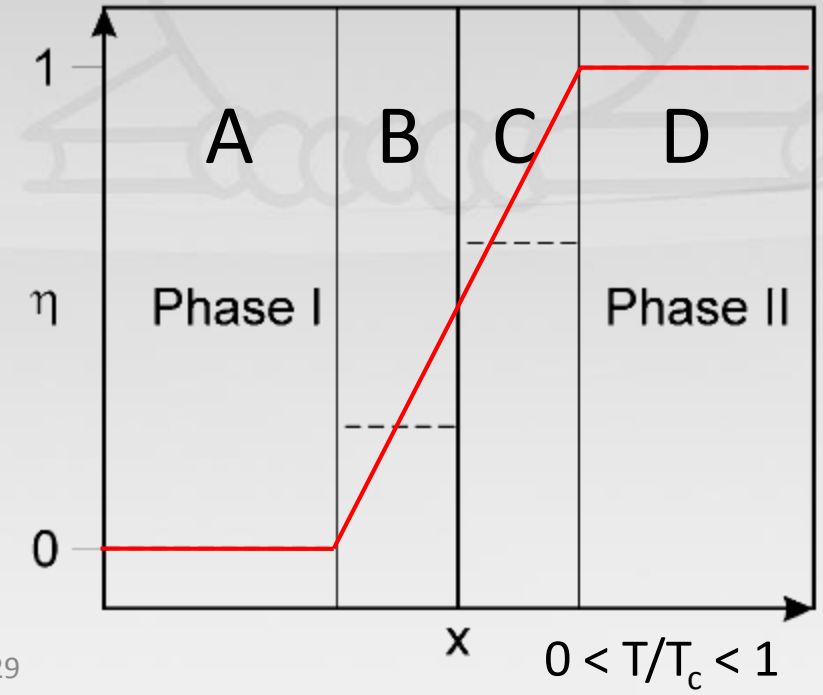
- Diffuse interface correction factor. MatCalc application
  - Minimization of Gibbs energy of the system





How do we estimate it?

- Diffuse interface correction factor. MatCalc application
  - Evaluation of interfacial energy (broken bond counting…)



$$\gamma_{GBB,diff} = \gamma_{AB} + \gamma_{AC} + \gamma_{AD} + \gamma_{BC} + \gamma_{BD} + \gamma_{CD}$$

How do we estimate it?

- Diffuse interface correction factor. MatCalc application
  - Numerical solution

$$K = \left(\frac{T}{T_c}\right)$$

$$\gamma_{GBB,diff} = \gamma_{GBB,sh}\beta(K)$$

$$\beta(K) = \begin{cases} 8.4729K^6 - 26.691K^5 + 32.717K^4 - \\ -17.674K^3 + 2.2673K^2 - 0.09K + \\ +1.00047632 \end{cases} \text{, for K} > 0.07$$

$$1 \qquad \text{, otherwise}$$

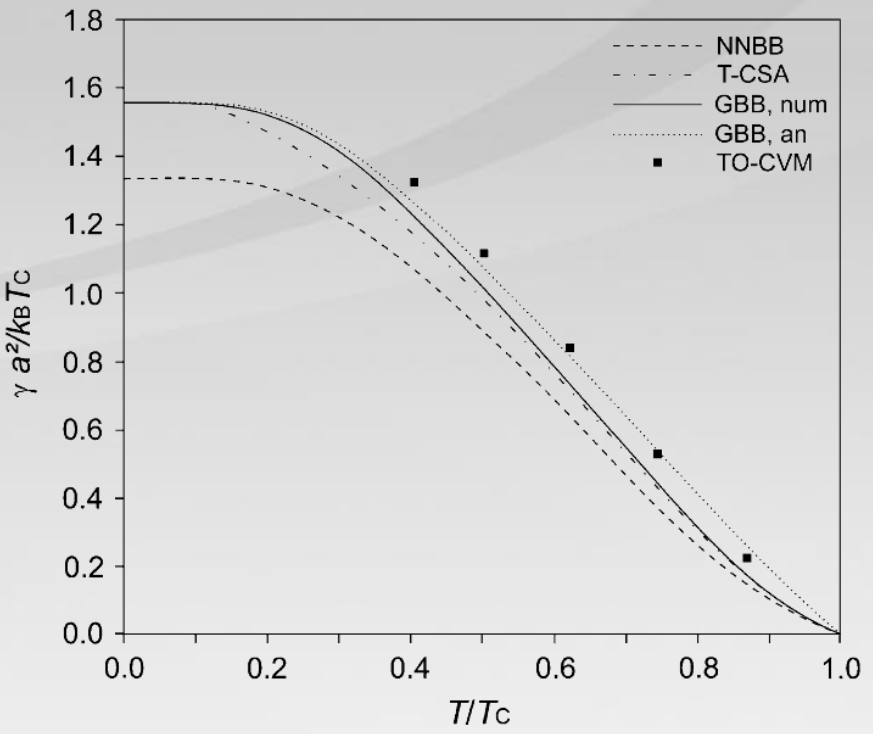


Fig. 3—Interfacial energy of an (100) interface in fcc systems. NNBB model (Ref. 4), T-CSA,[13] TO-CVM,[11] and analytical (GBB, an) and numerical GBB (GBB, num) approach.

How do we estimate it?

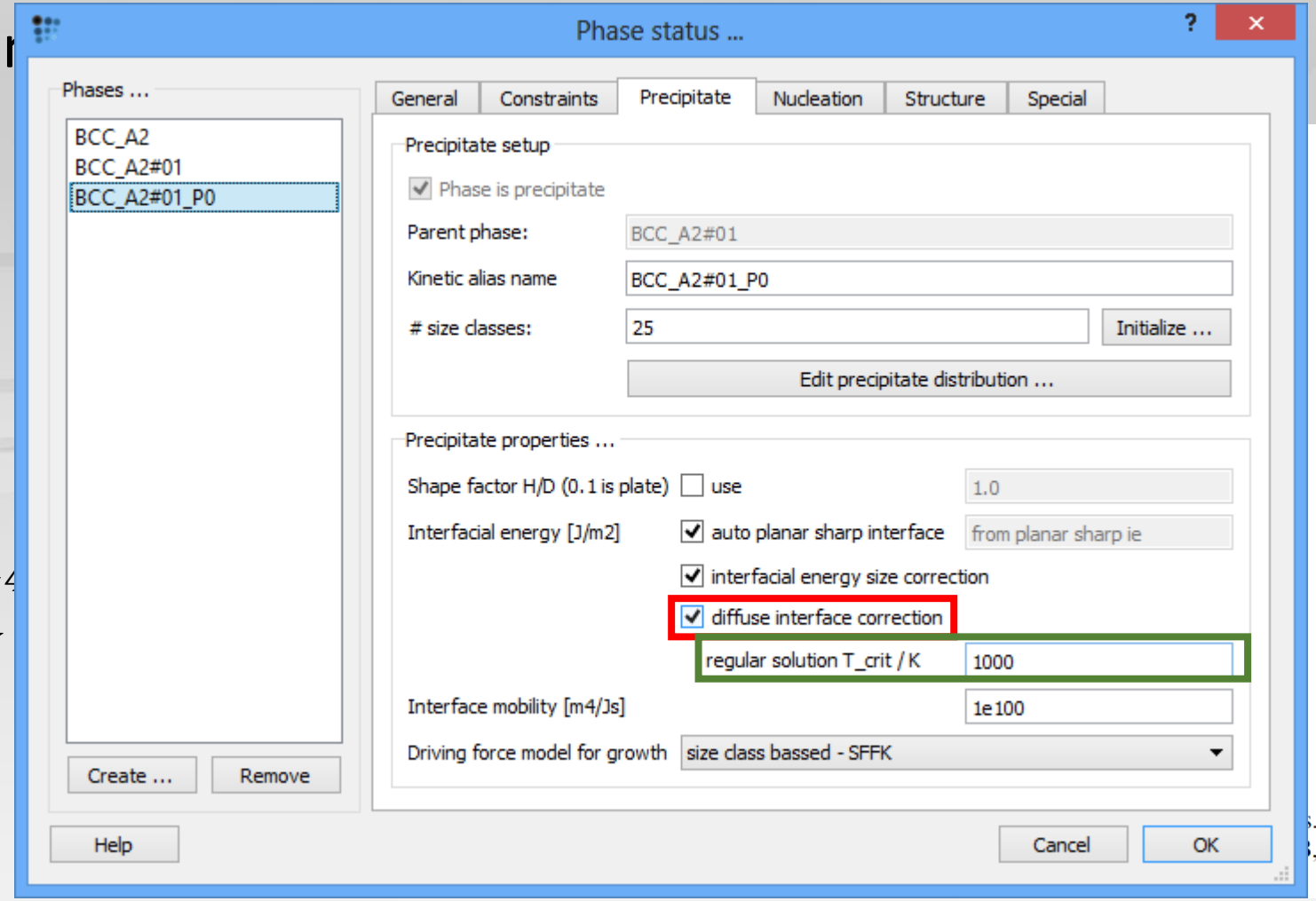
MatCalc Engineering

- Diffuse interface correction
  - Numerical solution

$$K = \left(\frac{T}{T_c}\right)$$

$$\gamma_{GBB,diff} = \gamma_{GBB,pln,sh}\,\beta(K)$$

$$\beta(K) = \begin{cases} 8.4729K^6 - 26.691K^5 + 32.717K^4 \\ -17.674K^3 + 2.2673K^2 - 0.09K \\ +1.00047632 \\ \\ 1 \end{cases}$$



How do we estimate it?

- Diffuse interface correction factor. MatCalc application
  - Numerical solution

$$K = \left(\frac{T}{T_c}\right)$$

$$\gamma_{GBB,diff} = \gamma_{GBB,pln,sh}\,\beta(K)$$

$$\beta(K) = \begin{cases} 8.4729K^6 - 26.691K^5 + 32.717K^4 - \\ -17.674K^3 + 2.2673K^2 - 0.09K + \\ +1.00047632 \end{cases} \text{, for K} > 0.07$$

$$1 \qquad \text{, otherwise}$$

variables	value
kinetics: precipitates	
CIE_DI_CORR$*	
CIE_DI_CORR$BCC_A2	1
CIE_DI_CORR$BCC_A2#01	1
CIE_DI_CORR$BCC_A2#01_P0	0.244428

category: kinetics: precipitates
expression: CIE_DI_CORR$BCC_A2#01
legal unit qualifiers: *none*
-> calculated diffuse interface energy correction (requires input of T_crit_reg_sol)

variables	value
kinetics: precipitates	
EIE$*	
EIE$BCC_A2#01_P0	0.129483

category: kinetics: precipitates
expression: EIE$BCC_A2#01_P0
legal unit qualifiers: *none*
-> effective interfacial energy of precipitate in matrix phase (CIE$@ minus gb, disl energy)

Examples

MatCalc Engineering

- MatCalc website
  - E10 (finding minimal nucleation barrier, binary system)
  - E11 (finding minimal nucleation barrier,)
  - P80 (application to Fe-Cu precipitation kinetic simulation)