“ Fundamentals of Thermodynamic Modelling of Materials ”

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PROFESSOR & TOPIC

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*Simulation of the
Thermodynamics of
surfaces and interfaces*

[04001]

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Simulation of the Thermodynamics of Surfaces and Interfaces

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Thermodynamics of the Solution Interface: Nucleation, Nanoparticles, Polymorphism and Morphology

Morphology

Alex Navrotsky, *PNAS*, **101**, 12096 (2004)

Surface Simulation

- Surface *in vacuo*
 - Lattice dynamics is generally best
- Solid-liquid interface
 - Molecular dynamics is appropriate
- Solid-solid interface
 - Can be most challenging case

Equilibrium Morphology

- Compute the surface energy

$$\Delta U_{SE} = \frac{(U_{surface} - U_{bulk})}{A}$$

Growth Morphology

- Quasi-kinetic
- Uses the attachment energy
 - U_{att} defined as the energy per molecule released when a new slice of depth d_{hkl} is attached to the crystal face.
 - Small attachment energy yields large faces

Surface Simulation Model

Two region
strategy

OR

Slab

Surface Types

Type 1

Type 2a

Type 2b

Morphology of Gibbsite: $\text{Al}(\text{OH})_3$

Calculated Gibbsite Morphology

Sodium Incorporation

Low levels of incorporation

High levels of incorporation
(Na⁺ only)

(10-14) Surface of Calcite

Imaginary mode
at $(1/2, 0)$ in BZ

Rohl et al, *Am. Miner.*,
88, 921 (2003)

Surface Thermodynamics

- Morphology only probes relative surface energy
- Calcite basal plane:
 - Experimental:
 - $0.347 \pm 0.045 \text{ J/m}^2$ (Int. J. Rock Mech., **5**, 253 (1968))
 - $1.4 \pm 0.4 \text{ J/m}^2$ (A. Navrotsky, Abstract GSA Meeting (2010))
 - ΔH immersion = -0.535 J/m^2 (Coll. Surf. A, **80**, 261 (1993))
 - Calculated:
 - 0.711 J/m^2 (Raiteri & Gale, 2010)
 - 0.261 J/m^2 (COSMIC Solvation, Gale & Rohl, 2007)

Grain Boundaries

Four region strategy:
2-1-1'-2'

General interfaces
possible for mismatch
< 5%

Barite (BaSO_4)

Surfaces of barite

(001)

(010)

(210)

See also:
Becker *et al*, *Am. J. Sci.*, **305**,
791 (2005)

The morphology of barite

Solvated surface energies:

(001) 241(18) mJm⁻²

(010) 193(15) mJm⁻²

(210) 194(15) mJm⁻²

A 100 ns in the life of a solvated (010) surface of barite

Reaction free energy for addition of barium to the surface

Clean surface
Sulphate

S. Piana *et al*, JACS, **128**, 13568 (2006)

Influence of aspartic acid on barite

S. Piana, F. Jones, JDG, *CrystEngComm*, 9, 1187 (2007)

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