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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

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

\[
\Delta U_{SE} = \left( \frac{U_{\text{surface}} - U_{\text{bulk}}}{A} \right)
\]
Growth Morphology

- Quasi-kinetic
- Uses the attachment energy
  - $U_{\text{att}}$ defined as the energy per molecule released when a new slice of depth $d_{\text{hkl}}$ 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: Al(OH)$_3$
Calculated Gibbsite Morphology

Size of (200) and (110) faces underestimated

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


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))
    • $\Delta H \text{ immersion} = -0.535 \text{ J/m}^2$ (Coll. Surf. A, 80, 261 (1993))
  – Calculated:
    • $0.711 \text{ J/m}^2$ (Raiteri & Gale, 2010)
    • $0.261 \text{ J/m}^2$ (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


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


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