

# Relation between dihedral angles and phase diagrams: Effects of multilayered adsorption

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Dihedral angles in silicates-fluid systems and the systems of metals-liquid alloys exhibit systematic change with temperature, pressure, and liquid composition. Takei & Shimizu (2003) employed a lattice-liquid statistical thermodynamic model to formulate the change of dihedral angles. In the model, the liquid phase is treated as a regular solution and adsorption is assumed to occur at the first liquid layer. Experimental data on the equilibrium dihedral angle in binary eutectic systems of metals and organic materials under atmospheric pressure, and that of the forsterite-H<sub>2</sub>O system under high pressure, were well explained by strong compositional dependence of solid-liquid interfacial tension (equivalent with the solid-liquid interfacial energy per a unit area). However, complicated behavior observed in the quartz-H<sub>2</sub>O system (Holness, 1993) was not fully understood by the monolayer lattice-liquid model.

Here we propose a simple thermodynamic method to estimate solid-liquid interfacial energy in eutectic and monotectic systems, based on the thermodynamic theory developed by Cahn and Hilliard (1958). A continuum model is used for the case of multilayered adsorption, and a discrete model is used for the case of monolayer adsorption. Change of interfacial energy and the amount of adsorption along a liquidus curve are calculated from a few bulk thermodynamic properties, i.e., melting temperature of a pure solid, entropy of fusion, and the interaction parameter of the liquid phase.

The model predicts that, in eutectic systems where non-ideality of the liquid is small, interfacial adsorption occurs within a few atomic layers, hence the discrete monolayer model rather than the continuum solution model applies. The solid-liquid interfacial energy is primary controlled by the bulk liquid composition and not sensitive to temperature. Consequently, interfacial energy and dihedral angle monotonously decrease with increasing concentration of the solid-component in the bulk liquid phase.

In monotectic systems where non-ideal atomic interaction in the liquid phase is strong, the contribution of interfacial entropy becomes significant. At the neighborhood of the immiscibility gap, multilayered adsorption occurs and thus interfacial energy is better described by the continuum model. The interfacial energy is significantly reduced around the two-liquid region.

The pressure and temperature dependence of dihedral angles in the quartz-H<sub>2</sub>O system is semi-quantitatively explained by the occurrence of multilayered adsorption.

## References:

Takei, Y. and Shimizu, I., 2003, The effects of liquid composition, temperature, and pressure on the equilibrium dihedral angles of binary solid-liquid systems inferred from a lattice-like model, *Phys. Earth Planet. Inter.*, 139, 225-242.