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Generalized Surface Thermodynamics of Solids with Application to Nucleation[1] ROBERT CAMMARATA, Johns Hopkins University — J.W. Gibbs formulated a general thermodynamics for surfaces in multicomponent fluid systems. For the case of solid-fluid surfaces, he restricted attention to single component solids. Attempts to generalize Gibbs' results for surfaces between multicomponent solids and fluids are problematic owing to the difficulty that the surface chemical potentials in the solid are generally not well defined, and therefore any expressions involving these chemical potentials will also not be well defined. A formulation of a general surface thermodynamics that can take into account capillary effects in systems involving interfaces between multicomponent solids and fluids while avoiding the aforementioned difficulties will be discussed that utilizes the concept of thermodynamic availability. It will be shown how this approach allows Gibbs-Thomson effects for finite size solids, an adsorption equation for a solid surface, and the thermodynamics of nucleation during solidification to be treated in a straightforward manner that avoids all references to ill defined surface quantities. In particular, a derivation will be presented that is the first to properly generalize Gibbs' analysis for the reversible work of nucleation to the case of solidification.

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