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Generalized thermodynamics of solid surfaces applied to size effects on equilibrium ROBERT CAMMARATA, Johns Hopkins University — In his thermodynamics of liquid interfaces, Gibbs introduced the "dividing surface" and rigorously derived the general conditions for equilibrium, and showed how the size of phases can affect the equilibrium state. However, the case of systems with solid surfaces, he imposed certain restrictions, such as considering only single component solids, which limited the applicability of his approach. In the case of finite size and multicomponent solids, difficulties arise when defining the chemical potentials for the interface, which leads to difficulties in defining the surface energy. It will be shown how these difficulties can be overcome by using the concept of "surface availability," analogous to the availability used in bulk thermodynamics. A generalized surface thermodynamics can be formulated consistent with Gibbs' analysis for liquid surfaces but that can be used for general multicomponent solid systems. Also, employing the surface availability allows one to dispense with the dividing surface construction and treat the interfacial region as a separate inhomogeneous phase. Applications to nanoscale materials will be discussed.

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