Gibbs and Helmholtz Local Basis Function Representations for Fluids, Solids, and Binary Phases

J. Michael Brown[1, S, C], Baptiste Journaux[1], Olivier Bollengier[2] and Steven D. Vance[3]

[1]*Earth and Space Sciences, University of Washington, Seattle, WA, U.S.A.*
[2]*Laboratory of Planetology and Geosciences, Nantes University, Nantes, France*
[3]*Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, U.S.A.*
jmbrown5@uw.edu

A collection of methods and numerical tools provides a path from measurements of thermodynamic properties to Gibbs or Helmholtz representations that are computationally efficient and accurate over a wide range of pressures and temperatures [1]. Parameters of the representation are values of energy within discrete intervals of the representation. Tensor b splines that are adequately differentiable in up to three dimensions (pressure or volume, temperature, and concentration) provide local and orthonormal basis functions to interpolate between the energy parameters. The parameters are determined through linear and non-linear collocation of the measurements. Since measurements (particularly at higher pressures) are sparse and have non-uniform distributions, a collection of regularization methods and limiting behavior constraints are required to obtain successful representations. Examples using these methods include determinations of the equations of state of multiple phases of water ices [2-3], oxides, hydrates, water [4], and aqueous solutions of water with NaCl or ammonia. The domains of representations encompass supercooled solutions to 2000 K for pressures extending to 10 GPa and beyond in the case of high-pressure ice phases. Key insights allowing construction into extended ranges of pressure and temperature include the increasingly "simple" behavior for apparent molal properties, the asymptotic high-pressure behavior of the pressure derivative of the bulk modulus, and simple gas behavior at higher temperature and lower pressures. Challenges remain in maintaining accurate predictions of partial molal properties of solutes as concentrations approach pure water.

References

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