Why Third Derivatives of Fluid Helmholtz Free Energies May Be Important

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Fits to fluid experimental data are a major resource for research. Typically, such fits are made to fluid experimental data containing derivatives of the Helmholtz free energy $a(T, \rho)$ up to second order. These fits are tested for quality by comparing with the input data. Harder to test for reliability is the accuracy of thermodynamic functions calculated from third derivatives of $a(T, \rho)$. Such functions include the density derivative of the isentropic compressibility identifying the BZT sound propagation anomaly in dense vapors with high heat capacity, and the thermodynamic curvature R from the geometry of thermodynamics. In my presentation I focus on R, a thermodynamic function providing key information about microscopic interactions. R is positive/negative for repulsive/attractive interactions. [R] indicates the volume of organized fluctuations at the mesoscopic size scale. I consider the following questions, all addressed by evaluating R from the fit $a(T, \rho)$. 1) To what extent do coexisting liquid and vapor phases have the same values of R? Do values not the same contribute to superheating? 2) Are positive values of R in the dense vapor phase connected with the BZT anomaly? Is the microscopic explanation of such positive R a gearing motion between neighboring molecules? Does this gearing motion explain why the asymptotic critical region in fluids is so contracted? 3) Do positive values of R in the liquid phase near the high pressure melting line indicate the formation of solid-like clusters of molecules? 4) In liquid water under ambient conditions, do positive values of R indicate solid- like mesoscopic formations responsible for the well-known water anomalies? Discussion of these questions requires reliable determinations of R, whose calculation employs third derivatives of the Helmholtz free energy.