Fluctuation Solution Theory: Some of the Old and Some of the New

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Fluctuation Solution Theory (FST), first formulated by Kirkwood and Buff (1951) to relate integrals of the molecular total correlation function (TCFI) to derivative thermodynamic properties, has been applied to a variety of systems over the years. Some of the more successful early uses were to model the TCFI and the complementary direct correlation function integrals (DCFI) in corresponding states forms to describe properties of dense fluids, especially for liquids containing dissolved gases. Later, the extensions to near-critical systems intersected with, and were further stimulated by, the work of Anneke Levelt Sengers, ultimately leading to correlations for properties of geologic fluids at extreme conditions. We are currently continuing this approach for PvT properties and gas solubilities in ionic liquid systems. In recent years, computer simulations of the microscopic correlation functions have become reliable enough for integration to yield accurate predictions of thermodynamic properties. The presentation will highlight how FST should become an even more useful alternative molecular theory through the combination of macroscopic and microscopic analysis and development.