

Something New in Thermodynamics: Excess Properties and Density Fluctuations from Free Energy Perturbation Theories for Polar, Polarizable, and Associating Molecules

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Free energy perturbation theories are dominant models for engineering calculations of fluid properties and phase behavior. These theories are less often used to calculate excess properties such as activity coefficients due to the numerical iterations involved. Using general thermodynamic relationships, we discover simple relations for the excess chemical potential and for density fluctuations from free energy perturbation theory. Excess properties based on molecular size and shape as well as multiple polar functional groups, polarizability, and multiple association sites are shown to be in good agreement with experiment. Density fluctuations due to system size effects are shown to be in good agreement with molecular simulation results. Limitations of the approach are also discussed. Results of the study are general excess property models with realistic molecular interactions that can be validated versus molecular simulation results. Further, implications of the approach for coarse graining of molecular models and extensions to meso-scale modeling of self-assembling systems are discussed.