Accuracy of Kirkwood-Buff Integrals Derived from Experimental Thermophysical Data

Vladimir Diky [C, S] and Richard Messerly
Applied Chemicals and Materials Division, NIST, Boulder, CO, U.S.A.
diky@nist.gov

Kirkwood-Buff integrals (KBI) provide a way to relate thermodynamic properties of mixtures to molecular pair correlation functions. As direct calculation of KBI from molecular simulation is relatively straightforward, it is attractive to compare calculated KBI to the values derived from experimental data. Such derivations are generally not model-free, however, and so it is important to have adequate knowledge of the accuracy (uncertainty) and possible bias imposed by the models used for fitting the experimental data. Derivation of KBI from experimental data requires knowledge of the chemical potentials or activity coefficients of the components, their partial volumes, and the isothermal compressibility of the mixture. All three pieces can be obtained from a single empirical equation of state (EOS), but accurate EOS can be constructed for few mixtures at present. To serve the needs of KBI derivation, an infrastructure has been built in the NIST ThermoData Engine (TDE) software that allows combining models representing the three required experimental properties. Using these tools, uncertainties of obtained KBI were estimated in different ways: the built-in TDE covariance technique, Monte-Carlo simulation, Bayesian Markov Chain Monte Carlo, Bayesian model selection, and comparison between alternative models. Major contributions to the uncertainties have been revealed and the influence of correlation in parameters representing mutual interactions of the mixture components has been explored. These developments will enable future explorations of the utility of using KBI for benchmarking and parameterization of molecular simulations.