87b Cluster Integral Calculations Via Mayer-Sampling Molecular Simulation: Higher-Order Virial Coefficients, Thermodynamic Properties, and Molecular Clustering

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Mayer-Sampling molecular simulation is used to calculate higher-order (classical) virial coefficients for various water models (SPC, SPC/E, MSPC/E, TIP3P, and TIP4P) and the two-center Lennard-Jones plus point quadrupole (2CLJQ) fluid. For the 2CLJQ fluid, we have performed both a parametric study of the model parameters, as well as a specific study of carbon dioxide. Values of the second through sixth virial coefficients (B_2-B_6) have been determined for all of these models (water and 2CLJQ). Prior to this investigation, higher-order coefficients were not known for several of the model fluids considered.

The higher-order virial coefficients obtained are used in three distinct ways. First, critical properties (T_c, P_c, ρ_c) for each model fluid are calculated and compared using virial equations of state up to the sixth order. For each model fluid, critical properties are calculated from successive truncations of the virial equation of state at higher order terms. The equations truncated at B_3 (the third coefficient) predict the critical temperature better than the equations truncated at B_4. As a whole, including B_5 and B_6 in the virial expansion does not improve the prediction of critical properties.

Next, the sixth-order virial equation of state is used to calculate the pressure-volume-temperature behavior of the various model fluids under gas-phase and supercritical thermodynamic conditions. For each model fluid, thermodynamic properties are calculated from successive truncations of the virial equation of state at different orders. The virial equation of state with coefficients up to the sixth order (based on the TIP4P model) is capable of describing the thermodynamics of real water within 10% over a wide range of temperature (350-750 K) and pressure (up to 250 atm).

Lastly, the higher-order virial coefficients are used to determine the distribution of molecular clusters (monomers, dimers, trimers, etc.) of water and carbon dioxide at various gas-phase and supercritical thermodynamic state points. The cluster analysis indicates that water molecules tend to cluster in the gas phase more than other non-associating fluids, such as Lennard-Jones fluids (as expected). Also, the cluster compositions and average cluster sizes calculated from the cluster integral virial coefficients for gaseous and supercritical water are in quantitative agreement with the values determined from ab initio and conventional Monte Carlo simulations, respectively. The equilibrium cluster distributions for gaseous and supercritical carbon dioxide, based on the newly determined values of B_2-B_6, are an especially new contribution to the field.

The results from these investigations highlight the usefulness of cluster integrals for obtaining fundamental molecular-level properties and describing macroscopic behavior of pure component gas-phase environments.