

Recent Advances in the Calculation and Application of Virial Coefficients and Cluster Integrals

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Cluster integrals appear in many theoretical treatments in statistical mechanics. These are integrals over the configurations of relatively few molecules (typically fewer than 10), with an integrand that depends upon the intermolecular potential. The values of the integrals then appear as coefficients in models for the system defined by the potential. These approaches are appealing because they provide a rigorous connection between molecular and bulk behavior. The virial equation of state (VEOS) is a well-known example of such a treatment. Numerical evaluation of cluster integrals can be computationally intensive, both because the integrals are highly multidimensional, and often very many cluster integrals must be summed to obtain a model coefficient. Mayer-sampling Monte Carlo (MSMC) applies ideas from free-energy calculations to this task, and it has proven versatile and effective. In this presentation we survey some of the recent developments in MSMC methods and applications. These include: (1) flexible molecules, for which additional terms appear to account for effects of intramolecular conformations on the properties (with application to alkanes and to methanol); (2) associating fluids, which are not well described by the conventional VEOS, but which can be approached using the developments due to Wertheim (with application to water); (3) quantum effects, where we compare the performance of semiclassical treatments to rigorous methods based on path integrals (with application to helium-4).