**455d Development and Application of Mayer Sampling Methods for the Evaluation of Cluster Integrals**

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Mayer sampling refers to a collection of methods adapted from applications involving the calculation of free energies, and applied to the calculation of cluster integrals that appear in many theories of statistical mechanics. This paper describes our work to develop, evaluate, and apply a variety of techniques of this type. We first consider methods to generate arbitrary classes of clusters (perhaps numbering in the thousands) in a form suitable for calculation of integrals such as required to evaluate high-order virial coefficients. We then turn to examine the ability of different methods to evaluate the cluster integrals. Methods we consider include those based on simple free-energy perturbation, as well as staging approaches such as overlap and umbrella sampling, and other techniques such as parallel tempering. Finally, we consider issues related to the choice of a reference integral, and how this affects the quality of the result.

We present results for a wide array of systems and properties. These include simple spherical models such as Lennard-Jones (for which we attempt to obtain values up to eighth virial coefficient), models with electrostatics, alkanes, and mixtures. We examine the ability of the virial equation truncated at high order to describe the equation of state and locate the critical point. We also consider how cluster integrals used in other theoretical frameworks can characterize phase transitions.