

Evaluation of Virial Coefficients and their Temperature Derivatives for Multibody Potential Models

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The most widely used molecular models are pairwise-additive and have been formulated to describe properties of condensed phases. As a result, they do not describe the true interactions between molecule pairs, but rather are effective potentials that attempt to include multibody interactions and other temperature- and density-dependent effects in the pairwise form. With improvements in simulation algorithms and computer speed, it is becoming increasingly viable to perform calculations using potentials that more accurately describe the true interactions between/among two, three, or more molecules. These include polarizable models such as GCPM, and explicit pair and three-body potentials fit to *ab initio* potential surfaces. A crucial test of any model that purports to describe true intermolecular interactions is its ability to reproduce experimental virial-coefficient data, which rigorously characterize interactions of two, three, etc. molecules. Wheatley recently introduced a very efficient recursive algorithm for evaluation of the integrand needed for virial coefficient calculations. Wheatley's derivation assumes a pairwise additive potential, but we show that it may be extended for application to multibody potentials, and moreover it provides a route for calculation of temperature derivatives. This allows calculation of high-order virial coefficients for such models. Coefficients determined this way can be compared to experimental data where available (which is typically no higher than the 3rd-order coefficient), thereby providing an assessment of the accuracy of the model. It can also be used to formulate equations of state that are fully predictive and accurate over much of the supercritical region, for both pure substances and mixtures; these models may also be used to compute critical properties. In this manner the usefulness of the accurate molecular model is greatly extended. We discuss these theoretical issues and demonstrate applications.