Virial Equation of State Using Volume-Dependent Coefficients

Andrew Schultz[1, S] and David Kofke[1, C]

[1]*Chemical and Biological Engineering, University at Buffalo, SUNY, Buffalo, NY, U.S.A.*
kofke@buffalo.edu

The conventional development of the virial equation of state (VEOS) invokes the thermodynamic limit, and consequently the virial coefficients, which are integrals involving only a few molecules (typically fewer than ten in practice), are independent of volume. On the one hand, at conditions where the series is converged this allows the VEOS to describe behavior in the thermodynamic limit, while treating just a few molecules. On the other hand, the absence of volume effects renders the VEOS unable to describe, in principle, condensation and condensed phases. Attempts exist in the literature to examine this issue, but they are largely based on conjectures about the volume dependence of the coefficients. In this presentation we address the question with correct volume-dependent coefficients that we have computed for some simple models.

We discuss how the VEOS is modified when applied using volume-dependent coefficients. We first examine the development when expressed as a series in the activity, where convergence is poor even in the absence of a phase transition. Considering the one-dimensional hard-rod model, we examine steps in the development of the activity VEOS that introduce inaccuracy that leads it to form a divergent series. We discuss the role of volume dependence of the virial coefficients, and present expressions and calculations for volume-dependent coefficients for the model, up to order n = 200. We examine alternative methods for computing properties from the activity-series coefficients. We then turn to the Lennard-Jones model in three dimensions, and compute values of volume-dependent coefficients and apply them to estimate the equation of state. We examine the series behavior in comparison to small-system simulations to ascertain the source of observed inaccuracies, considering also complications resulting from propagation of stochastic error in the computed coefficients. Finally, we consider ways to approximate higher-order coefficients, and their volume dependence, aiming to achieve the capability to calculate behavior in the thermodynamic limit.