338g Extrapolation of Molecular Simulation Data: Application to Supercritical Fluids

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Computer experiments make possible to measure transport and thermodynamic properties of model fluids. Typical techniques for such experiments are, e.g., the method of molecular dynamics or the Monte Carlo method. The resulting molecular simulation (MS) data are the raw material for analytical equations, which set a given transport or thermodynamic property as a function of temperature, density and molecular-level characteristic parameters. Such parameters account for the intermolecular forces in the chosen model fluid. Analytical equations for thermodynamic and/or transport properties have been developed for model fluids such as the hard-spheres fluid, the square well fluid and the Lennard-Jones fluid. Analytical molecular-simulation-based equations (thermodynamic or transport equations of state [EOSs]) are fitted to reproduce the available molecular simulation data, typically without paying attention to the qualitative behavior outside the window of conditions of such data. However, the real-fluid molecular-simulation-based modeling of the dependency of properties on density and temperature, in wide ranges of conditions, often requires the computation of a model-fluid reference property value beyond the temperature/density conditions of the supporting molecular simulation data. In this work, we concentrate on the problem of extrapolating computer experiments results for the specific case of viscosity, and for the Lennard-Jones (LJ) model fluid. From studying the viscous behavior of both, the LJ fluid and a number of real fluids, we identify here general patterns for viscosity as a function of density and temperature. From such study, we propose an analytical LJ viscosity equation of state (EOS) which gives a proper qualitative behavior at any temperature/density condition, i.e., within and beyond the range of the supporting LJ MS data. We use such LJ viscosity EOS as a basis for modeling the viscosity of pure supercritical fluids, over a wide range of conditions, with correlation results within the experimental accuracy of real-fluid viscosities. These results correspond to the limit that the best Lennard-Jones theories can reach for viscosity.