The Importance of Compressed Liquid Density in Unambiguously Characterizing Molecular Interactions

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The compressed liquid density was studied using step potential models to improve understanding of what is necessary for a potential model to achieve an accurate description. In general, four isochores were for each compound. Properties for spherical molecules and n-alkanes through dodecane were available to high reduced pressures and temperatures from the NIST Webbook. Comparisons were based on compressibility factor (Z = PV/RT), temperature, and liquid density. Deviations are summarized in terms of the difference between temperatures needed to achieve the experimental Z at the specified density. The compressibility factor approaches zero near saturation, so the temperature intercept of the isochore precisely characterizes the saturation condition as well as compressed density. Accurate densities are an important preliminary to accurate prediction of transport properties. The Lennard-Jones equation of state (LJEOS) Kolafa and Nezbeda is applied as a basis for comparison for spherical molecules. LAMMPS simulations of the TraPPE-UA were compared for n-alkanes. An investigation using the square-well model exhibited remarkable sensitivity to the square-well diameter when applied in this manner. An optimal well-width of 1.7 led to much smaller deviations than the commonly assumed value of 1.5. On the other hand, the LJEOS yielded accurate correlations for spherical molecules without modification. For n-alkanes, however, the TraPPE model (also based on the LJ model) was not as accurate as the step potential model. The greatest reduction in error derives from details of the attractive range of the potential model, rather than the repulsive shoulder. The accuracy and utility of thermodynamic perturbation theory are assessed in addressing this problem. In conclusion, accurate compressed liquid densities probe details of the potential model with surprising sensitivity.