Review and Comparison of Equations of State for the Lennard-Jones Fluid

Simon Stephan [C, S] and Jens Staubach
Laboratory of Engineering Thermodynamics, TU Kaiserslautern, Kaiserslautern, Germany
simon.stephan@mv.uni-kl.de

Ulrich K. Deiters
Institute of Physical Chemistry, University of Cologne, Germany

Hans Hasse
Laboratory of Engineering Thermodynamics, TU Kaiserslautern, Kaiserslautern, Germany

The Lennard-Jones (LJ) fluid is of fundamental importance for the molecular modeling and simulation of fluids. It is frequently used as a starting base for the development of equations of state for complex fluids, e.g. in SAFT EOS. The present contribution reviews the state-of-the-art of equations of state (EOS) [1,2] available for the LJ fluid. Until now, no comprehensive evaluation of that important EOS type is available in the literature. 20 LJ EOS were used for the comparison, which comprise empirical EOS, semi-theoretical EOS, and theoretically-based EOS. It is shown that none of the presently available LJ EOS are satisfactory accurate in a sense that none of the LJ EOS meets the following two criteria: (1) it does not yield unphysical artifacts when used for extrapolations, and (2) it describes data from computer experiments within their statistical uncertainty in most fluid regions.

A systematic evaluation strategy was applied: Computer experiment data of the LJ fluid (35,000 data points) available in the literature were digitalized and systematically and critically assessed in a previous work of our group [3]. This data was used a reference. Both homogeneous state property data and vapor–liquid equilibrium data were considered. Thermal, caloric and entropic properties were considered. The fluid region was divided into characteristic sub-regions in the T–ρ space. Each property was studied in each region separately before the results were condensed to achieve an overall assessment. Four LJ EOS are found to yield an equally good and best performance. All data are made available in electronic form [1,2,3]. This makes the proposed test procedure fully transparent and readily reproducible and provides a benchmark for the development of new LJ EOS.

References

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[3] S. Stephan, M. Thol, J. Vrabec and H. Hasse: J. Chem. Inf. Model. 59 (2019) 4248−4265