Assessment of Thermodynamic Models Using Brown's Characteristic Curves

Simon Stephan[1, S, C]

[1]*RPTU Kaiserslautern, Kaiserslautern, Germany*
simon.stephan@rptu.de

For several applications, thermodynamic properties of fluids need to be modeled at high pressure and temperature, e.g., in rocket propulsion systems, tribology, geology, and astronomy. For such applications, usually equation of state (EOS) models are used. However, in parts, no experiments for determining thermophysical property data are feasible today at extreme conditions and no experimental data is available for the parametrization and validation of EOS at such conditions. For the assessment of the thermodynamic consistency of EOS models, Brown's characteristic curves can be used. E.H. Brown postulated – for simple fluids – four characteristic curves that define lines on the thermodynamic surface where special thermodynamic conditions hold [1]. There is one first-order curve (called Zeno curve) and three second-order characteristic curves (called Amagat, Boyle, and Charles curves). These curves are located within a large pressure and temperature range. For a given simple fluid, Brown postulated certain thermodynamic features for these curves [1,2], which can be used for qualitatively testing the consistency of an EOS. While the characteristic curves and their features were derived for simple spherical molecules [1], they are today also applied for more complex substances. In this work, molecular simulation is used for the assessment of the applicability of Brown's curves to complex molecules. Therefore, the influence of different molecular architecture and interaction features on Brown's curves is investigated. The method proposed in a recent work of our group [2] was used for determining Brown's curves from a given force field. Additionally, for the first time, the molecular simulation data is used as pseudo-reference data for a quantitative assessment of various EOS models. Both model fluids (the classical Lennard-Jones fluid [3], Mie fluids [4], Stockmayer fluids, and two-center Lennard-Jones plus dipole and plus quadrupole fluids – 2CLJD and 2CLJQ) as well as real substance fluids (e.g., alkanes, alcohols, and aromatic components [5]) were studied by molecular simulation and EOS. Different types of EOS were studied such as molecular-based EOS and empirical multi-parameter EOS. The results provide a wealth of insights in the thermodynamic consistency of different model types at large pressure and temperature. Important differences are observed for different EOS showing that especially molecular-based EOS are often in excellent agreement with the molecular simulation reference data for the characteristic curves. Also, interesting insights are obtained on the influence of different molecular properties on the characteristic curves, e.g., the Mie potential exponents and the dipole and quadrupole moment. In all studied cases, i.e., also for complex molecules, the obtained characteristic curves conform with Brown's postulates, which is an important finding regarding the applicability of Brown's criteria to an arbitrary molecular fluid. This study moreover yields novel insights into the applicability of the corresponding states principle at high pressure and temperature.

References

1. Brown, Bulletin de l'Institut International du Froid Annexe 1960–1 (1960) 169-178.
2. Urschel & Stephan, J. Chem. Theory Comp. 19, 5 (2023) 1537.
3. Stephan & Deiters, Int. J. Thermophys. 41 (2020) 147.
4. Stephan & Urschel, J. Mol. Liqu. 383 (2023) 122088.
5. Staubach & Stephan, in 'International Research Training Group Conference on Physical Modeling for Virtual Manufacturing Systems and Processes', Springer, Berlin (2023) 170-188.