Simple Quantum Corrections Improve the Accuracy of Cubic Equations of State for Mixtures That Contain Hydrogen, Helium, Neon and Deuterium

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The shortcomings of cubic equations of state (EoS) for describing fluids that exhibit quantum effects has for long been known. In his celebrated work that formed the basis for the SRK EoS [1], Soave pointed out that less accurate results were obtained for mixtures with hydrogen. Furthermore, the shape of the optimal α functions for helium and hydrogen in frequently used cubic equations of state do not decay monotonically as for other fluids [2]. This has been a long-standing problem which has resulted in poor predictions for mixtures that contain fluids that exhibit strong quantum effects, such as hydrogen and helium.

We present temperature-dependent quantum corrections for the covolume parameter of cubic EoS. These have been derived by mapping them onto the excluded volumes predicted by quantum-corrected Mie potentials. Subsequent regression of the Twu α function recovers a near classical behavior with a monotonic decay for most of the temperature range. The quantum corrections result in a significantly better accuracy, especially for caloric properties. While the average deviation of the isochoric heat capacity of liquid hydrogen at saturation exceeds 80% with the present state-of-the-art, the average deviation is 4% with quantum corrections. Average deviations for the saturation pressure are well below 1% for all four fluids. Using Péneloux volume shifts gives average errors in saturation densities that are below 2% for helium and about 1% for hydrogen, deuterium and neon.

The quantum-corrected cubic equation of state paves the way for technological applications of quantum fluids that require models with both high accuracy and computational speed. The quantum corrections have been released through the open source thermodynamic library, Themopack [3].

References

[1] G. Soave, Equilibrium constants from a modified Redlich-Kwong equation of state, Chem. Eng. Sci., 27 (6) (1972), pp. 1197-1203, 10.1016/0009-2509(72)80096-4

[2] Y. Le Guennec, S. Lasala, R. Privat, J.-N. Jaubert. A consistency test for a-functions of cubic equations of state. Fluid Phase Equilibria, 427 (2016), pp. 513-538, https://doi.org/10.1016/j.fluid.2017.04.015

[3] https://github.com/SINTEF/thermopack