Development of Thermodynamic Equations of State by Means of New Fitting Techniques

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The development of thermodynamic equations of state in terms of the reduced Helmholtz energy is a challenging optimization problem. Since the problem is highly non-convex, classical approaches such as Newton's method fail to solve the task. Compliance with numerous boundary conditions makes it especially difficult to solve the optimization problem. One of these boundary conditions is that density exponents need to be integer values, while temperatures exponents can be floating-point numbers. Given this limitation, the optimization problem can be seen as a mixed integer non-linear problem. Structural optimization techniques such as proposed by Setzmann and Wagner (1989) or non-linear fitting techniques like the one proposed by Lemmon (2020) enable either the optimization of integer values for density exponents but no fit of floating-point numbers for temperature exponents or vice versa.

In this work, a local optimization algorithm is combined with a branch and bound algorithm to effectively adjust integer density exponents as well as floating-point numbers for all other parameters. This enables a more comprehensive investigation of the functional form for Helmholtz-energy equations of state as established many years now. Based on molecular simulation data, the new algorithm is applied to develop fundamental equations of state in terms of the Helmholtz energy for a series of spherical fluids. Special attention is paid to boundary conditions such as allowing only one van-der-Waals loop in the vapor-liquid two-phase region, and to the extrapolation behavior of the equation of state.

References

U. Setzmann, W. Wagner (1989), "A New Method for Optimizing the Structure of Thermodynamic Correlation Equations", Int. J. Thermophys. 10(6), 1103–1126 E.W. Lemmon (2020), "Non-Linear Fitting Algorithm for the Development of Fundamental Equations of State", personal communication