Fundamental Reverse van der Waals Equation of State

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It is now almost one and a half centuries since the van der Waals equation of state (vdW EoS) was published. The vdW EoS was the first model to describe the liquid–vapor phase transition, unifying both states at a critical point.

Another significant 19th-century development was the Dieterici EoS, the first model to introduce an exponential term to improve performance in the critical region. Together, the vdW EoS and the Dieterici EoS can be considered the base for today's EoS of wide industrial application. While the vdW EoS is the origin of all cubic EoS, the Dieterici EoS, with its exponential term, can be considered the precursor of the Benedict–Webb–Rubin EoS and the subsequent multiparameter empirical reference EoS.

A common difficulty with multiparameter reference EoS is their unphysical behavior in the vapor–liquid two-phase region, particularly the appearance of spurious minima and maxima, sometimes exceeding the critical pressure by orders of magnitude. These make it difficult, sometimes even impossible, to apply the Gibbs global stability analysis, i.e., to construct a global support tangent plane between the equilibrium phases. The unphysical behavior not only impairs the calculation of vapor pressure curves, but also precludes the prediction of surface tensions or properties of metastable fluids. Moreover, it creates serious problems when such EoS are extended to mixtures.

In this work, we modify the original vdW EoS, which results in a semi-cubic EoS with respect to its volume dependence. The key modification is the replacement of the hard-sphere parameter (covolume) with a soft-sphere expression. This simple modification greatly improves the accuracy of the vdW model while preserving key thermodynamic properties, such as a stable, single van der Waals loop. The mathematical structure of the modified vdW EoS is close to that of the original EoS. Still, its constants can be empirically parameterized to a degree of accuracy competitive with multiparameter reference EoS. On the other hand, advanced statistical concepts, such as those applied in the Statistical Associating Fluid Theory (SAFT), can also be implemented, resulting in a statistical mechanics-based perturbation of the original vdW EoS. In both cases, the "Reverse van der Waals EoS" (named so because it was obtained by differentiating a Helmholtz energy model instead of integrating the EoS to obtain the Helmholtz energy) can deliver a performance comparable to empirical models, such as the multiparameter reference EOS, or statistical models, such as the SAFT models.

In addition, one-fluid mixing rules are proposed, which allow for a good representation of selected mixtures of industrial interest, including some light and heavy compounds as well as liquid–vapor equilibria involving dense liquids.