Application of a Renormalization-Group Treatment to the Statistical Associating Fluid Theory for Potentials of Variable Range (SAFT-VR)

Esther Forte C, S

Imperial College London, Department of Chemical Engineering, London, United Kingdom
e.forte07@imperial.ac.uk

Felix Llovell and Lourdes F. Vega

Institut de Ciència de Materials de Barcelona, Consejo Superior de Investigaciones Científicas, Bellaterra, Barcelona, Spain

J. P. Martin Trusler and Amparo Galindo

Imperial College London, Department of Chemical Engineering, London, United Kingdom

An accurate prediction of phase behavior at conditions far and close to criticality cannot be accomplished by mean-field based theories that do not incorporate long-range density fluctuations. A treatment based on renormalisation-group (RG) theory as developed by White and co-workers has proven very successful in improving the predictions of the critical region with different equations of state. The basis of the method is an iterative procedure to account for contributions to the free energy of density fluctuations of increasing wavelengths. Typically, this treatment involves two adjustable parameters: a cut-off wavelength $L$ for density fluctuations and an average gradient of the wavelet function $\Phi$. In this work, the SAFT-VR [1] equation of state is extended with a similar treatment [2] where $\Phi$ is evaluated based on the interpretation of White's latter developments so that only $L$ needs to be adjusted. The approach used here begins with an initial free energy incorporating only contributions from short-wavelength fluctuations, which are treated locally. The contribution from long-wavelength fluctuations is incorporated through an iterative procedure based on attractive interactions which incorporate the structure of the fluid following the ideas of perturbation theories and using a mapping that allows integration of the radial distribution function. Good agreement close and far from the critical region is obtained using a single fitted parameter $L$ that can be related to the range of the potential. In this way the thermodynamic properties of a square-well (SW) fluid are given by the same number of independent intermolecular model parameters as in the classical equation. Far from the critical region the approach provides the correct limiting behavior reducing to the classical equation (SAFT-VR). In the critical region the $\beta$ critical exponent is calculated and is found to take values close to the universal value. By determining $L$ for SW fluids of varying well width a unique equation of state is obtained for chain and associating systems without further adjustment of critical parameters. We use computer simulation data of the phase behavior of chain and associating SW fluids to test the accuracy of the new equation. The approach is further on successfully applied to model the phase behaviour and second derivative properties of a number of pure fluids, such as $n$-alkanes, carbon dioxide and water.