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An accurate direct technique for parametrizing cubic equations of state Part III. Application of a crossover treatment

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Abstract

This work presents an extension of a generalized van der Waals-type equation of state by including a crossover treatment to consider the fluctuations in the critical region. The original cubic equation depends on simple parameters of pure fluids, and it is able to reproduce vapor pressures and densities over a wide range of conditions, once the appropriate parametrization techniques are used. The equation is forced to reproduce the critical point by explicitly including this point into the fitting procedure. However, as all mean field theories, the equation does not take into account the fluctuations appearing as the critical region is approached. Hence, the non-analytical asymptotic behavior in the vicinity of the critical point is not well reproduced, leading to some inaccuracies in liquid and/or gas phase equilibria density calculations. To overcome this limitation we have applied a specific crossover treatment, based on White's work [J. White, Fluid Phase Equilib. 75 (1992) 53–64; L.W. Salvino, J.A. White, J. Chem. Phys. 96 (1992) 4559–4568] from the renormalization group (RG) theory [K. Wilson, Phys. Rev. B4 (1971) 3174–3205]. This treatment is done by incorporating the scaling laws valid asymptotically close to the critical point. In addition to accurate density estimations far from and close to the critical point, the extended equation is also able to reproduce the universal critical exponents describing the approach to the critical point. The extended equation has been applied to two chemical families: the *n*-alkanes and 1-alkanols, as well as to other compounds of industrial interest, including carbon dioxide, ethylene, toluene, xenon and water, providing excellent agreement with experimental data.

Keywords: Cubic equation of state; Soft-SAFT; Crossover; Critical region; *n*-Alkanes; 1-Alkanols; Carbon dioxide; Water

1. Introduction

Much effort has been devoted during the last years to the study of the critical region of pure fluids and their mixtures. The increasing number of industrial applications near the critical conditions has encouraged researchers to seek for an accurate description of the thermodynamic behavior of pure fluids and their mixtures in the vicinity of the critical point. However, the complex molecular behavior of any compound at these conditions makes it a difficult task. It is well known that near the critical region, density and concentration fluctuations caused by long-range correlations among all the molecules lead to singularities of the pure compound properties (and mixtures) at the critical point. The value of some properties changes very rapidly with a small modification of the operation conditions. From the mathematical point of view, the approach to the critical point leads to a non-analytic asymptotic behavior different that the one observed far away from the critical region. Most equations of state (EoSs) cannot reproduce this change of behavior because they are based in mean-field theories that do not take into account the inherent fluctuations in the critical region. Even the most refined molecular-based EoSs fail in the representation of the near-critical properties, unless a specific treatment is included.

In order to overcome this limitation, some efforts have been devoted to this task in the recent years. For instance, molecular-based EoSs parameters have been rescaled to the critical region, achieving good estimations in this region [1–4], although the

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new set of parameters was no longer valid for calculations far from the critical region, where some deviations were observed. An alternative approach is to include critical experimental data into the fitting of cubic EoSs in order to assure a correct description of the critical point, even though this deteriorates liquid density estimations far from the critical point [5,6]. The two previous papers of this series dealt with the improvement of van der Waals models [5,6] providing a direct parameterization scheme for specializing cubic EoS to the prediction of vapor–liquid equilibrium and vapor pressures. A generalized method applicable to a four-parameter cubic equation of state has been developed for this purpose. The required input data are the critical properties (temperature, pressure and volume) together with the boiling temperature, the local geometry of the vapor pressure curve and the volume of the liquid phase at a reference point. As shown in ref. [6] the method, applied to a large database of pure fluids, was able to predict accurate vapor pressures and reasonably accurate liquid volumes from the reference point up to the critical range. However, as it is stated in both papers, although good results can be achieved, the fluctuations inherent to the critical region were ignored, and some deviations in the liquid phase occurred as the shape of the curve was not well reproduced in the whole region. A proposed solution was the introduction of a τ factor that modified the critical compressibility factor but improved the shape of the liquid density curve [6]. While the τ factor gave an overall better shape of the curve, the inherent fluctuations near the critical region were still ignored and the equation was not able to capture the non-analytic asymptotic approach to the critical point.

In fact, the rigorous estimation of vapor liquid equilibria far from and close to the critical region requires a specific treatment taking into account the long-range fluctuations as one approaches the critical point. This effect can be incorporated by the application of a treatment based on the renormalization group (RG) theory [7]. Based on that work, some authors have developed different treatments to couple the RG theory to several EoSs, being able to reproduce the whole phase envelope [7–24]. These treatments are usually called *crossover* theories as they describe the crossover behavior from classical to non-analytical as the critical region is approached. The accuracy of these so-called crossover equations lays on the accuracy of the equation to which the non-classical behavior is coupled to since the equation reduces to the original equation far from the critical point.

One of the main advantages of adding a crossover term to correct the non-analytical behavior is that the methodology for critical region calculations can be implemented to any EoS model. The coupling between a classical EoS and a renormalization group method permits to obtain good results close to and far from the critical region using a unique set of parameters. Accurate phase equilibria descriptions have been obtained coupling this approach to the Statistical Associating Fluid Theory (SAFT) EoS [7–11], to the soft-SAFT EoS [12,13], to an EoS for chain fluids called EOSCF [14,15], to the mean sphere approximation (MSA) [16], to the first-order mean sphere approximation applied to SAFT (FMSA-SAFT) [17,18] and also to the SRK EoS [19,20]. Although there are other available approaches for calculating the fluctuations near the critical region [21–24], White's approach [8,9] was chosen in this work because of its mathematical simplicity (compared to the hierarchical reference theory of Parola et al. [21,22]) and the fact that fewer parameters are needed, and they are transferable within chemical families (as compared to the crossover-Landau method applied by Kiselev et al. [23,24]).

The objective of this work was to apply the crossover treatment proposed by White [8] and improved by Prausnitz and co-workers [14,15], into a van der Waals-type equation of state, in a similar manner as done by Cai and Prausnitz [19] for the Soave–Redlich–Kwong equation, to further improve the approach presented in previous works [5,6]. The purpose was to combine the simplicity of a cubic EoS with a specific treatment to consider the fluctuations in the critical region. In some previous works [12,13], the accuracy of the methodology was tested for a molecular-based EoS, the soft-SAFT EoS; this information has been used here to compare the performance of both equations in order to check the effect of the crossover treatment in each case.

The rest of the paper is organized as follows. In Section 2, a summary of the van der Waals equation model is presented, along with the crossover methodology and its implementation into the equation. Results are presented and discussed in Section 3, where the modified equation is applied to the calculation of several non-associating and associating compounds. A comparison with the soft-SAFT molecular-based EoS [25] with the same crossover treatment is done in some cases. The last section summarizes the main findings, giving some concluding remarks.

2. Methodology

We have considered a crossover approach applied to the following classical four-parameter van der Waals-type [25], described in detail in references [5,6]:

$$P = \frac{RT}{\tilde{v} - b} - \frac{a}{(\tilde{v} + c_1 b)(\tilde{v} + c_2 b)} \tag{1}$$

where a and b are the cohesion and repulsion parameters, respectively, $\tilde{v}$ is the molar volume, T is the temperature, R is the gas constant and P is the pressure. c_1 and c_2 are the additional parameters that permit the specialization of the EoS in Eq. (1) to predict the liquid phase density data [6]. In addition, a and b are given by:

$$a = \Omega_\mathrm{a} \frac{(RT_\mathrm{c})^2}{P_\mathrm{c}} \alpha(T) \tag{2a}$$

$$b = \Omega_\mathrm{b} \frac{RT_\mathrm{c}}{P_\mathrm{c}} \tag{2b}$$

Ω_a, Ω_b are the numerical constants that can be calculated from Eq. (1) by applying the critical point conditions ($P_\mathrm{V} = P_\mathrm{2V} = 0$), thus yielding an exact description of the critical temperature and pressure in the classical approach of the EoS (with no crossover term). α, in turn, corresponds to the thermal cohesion function. The correlation of Stryjek and Vera [26] has been selected in