Calculating and Measuring Thermodynamic Properties in the Critical Region

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The knowledge of the thermodynamic properties in the vicinity of critical points is very important in Chemical Engineering, particularly in the field of supercritical fluid extraction. It is well known (van Konynenburg and Scott [1]) that the critical temperature and pressure of a mixture is different from those of the pure components, and that different types of phase diagrams can be observed depending on the nature of the chemical species. There are several experimental techniques for the determination of critical points for both pure components and mixtures. For example, we can cite the "dynamic-synthetic" method, for which the critical point is determined by observing the critical opalescence phenomenon in a view cell. We can also determine the critical properties by applying the asymptotic scaling laws to experimental densities. Despite recent progress in the field of equations of state, the use of Cubic Equations of State (EoS) such as Redlich-Kwong EoS remains common in the industry. It has already been proved that such classical EoS based on a mean field theory cannot accurately describe the thermodynamic properties in the critical region. Moreover, it is well known that in this area the representation of thermodynamic properties must rely on scale invariance. In this work, we propose a new Landau-Crossover treatment for pure fluids [2,3]. This approach needs only two additional parameters and is applied to a generalized form of cubic EoS. Comparison is done between the new Landau-Crossover treatment and White's recursive procedure [4, 5 ,6]. We also have applied the new crossover approach to test mixtures and a good description of the experimental data is obtained.

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