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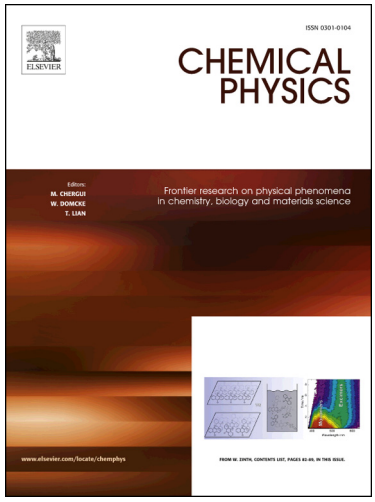

Crossover Equation of State of a Multi-Component Fluid Mixture in The Vicinity of Liquid-Vapor Critical Points

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ACCEPTED MANUSCRIPT

CROSSOVER EQUATION OF STATE OF A MULTI-COMPONENT FLUID MIXTURE IN THE VICINITY OF LIQUID-VAPOR CRITICAL POINTS

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Absrtact

The crossover equation of state (EOS) of a multi-component mixture valid in a broad vicinity of a liquid-vapor critical point is proposed. The form of the EOS does not depend on the mixture composition permitting one to apply the approach for mixtures with unknown compositions. The developed EOS was used for the description of a complex mixture to verify the approach. The model accurately describes the data for dew-bubble curve, temperature dependencies of the pressure $P(T)$ along isochores, near-critical behavior of the derivative $\left(\partial P/\partial T\right)_{\rho,x}$, and the heat capacity $C_{\rho,x}$. In addition, the critical parameters of the mixture were determined at the processing of the experimental data. Thus, the proposed EOS enables accurate description of thermodynamic properties of liquid mixture in a wide neighborhood of a liquid-vapor critical point.

Keywords: scaling theory; mixture critical point; crossover linear model; thermodynamic properties; equation of state.

1. Introduction

Critical fluids are widely used in various branches of modern industry. Therefore the description of thermodynamic properties of fluids and fluid mixtures is an important problem with numerous applications. If the required description accuracy is at the level of several percent, namely, 2-3% for the pressure and the temperature, and 5% for the density (it is usually enough for engineering applications), the ordinary cubic equation of state (EOS) [1, 2] can be employed. To reach a higher accuracy it is necessary to use multiparameter EOS [3-5]. Until recently such EOS had no alternative for an accurate description of multicomponent mixtures. Unfortunately, these equations cannot be used in a close vicinity of the critical point where both cubic and multiparameter EOS are incorrect.

Thermodynamic properties of the fluid system in the vicinity of critical point are strongly influenced by the anomalously large fluctuations of mixture density and component concentrations. Near the critical point the characteristic size of these fluctuations, the so-called correlation length, increases and exceeds the interaction radius of the molecules. As a result, the singular behavior of thermodynamic properties in a close vicinity of the critical point turns out to be universal. The universality of critical phenomena is commonly described in textbooks and reviews mainly for one-

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