

Singular behavior of second-order thermodynamic derivative properties in the near critical region

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Second order thermodynamic derivative properties are fascinating properties from both the fundamental and the applied point of view. Although they are directly obtained by derivation of a thermodynamic potential function, most of the classical equations of state fail in describing them, being a stringent test to any thermodynamic model. These are properties of clear practical interest, since their knowledge is needed to precisely design industrial processes.

We will present and discuss here the performance of a molecular-based equation on describing the behavior of these properties. For this purpose we use a modified version of the Statistical Associating Fluid Theory¹ (the so-called soft-SAFT equation²) combined with a renormalization term to take into account the long range density fluctuations appearing as one approaches the critical point. The combination of this new term with the original theory provides a crossover equation of state equally accurate far from and close to the critical region³. The procedure, based on Whites work⁴ from the renormalization group (RG) theory⁵, is implemented in terms of recursion relations where the density fluctuations are successively incorporated. The new equation is first used to calculate the influence of the chain length and the association effects on some thermal and volumetric second order thermodynamic derivative properties. This study allows to separate and quantify the influence of these parameters, providing some physical insights into the global behavior of these properties. We also have also checked the capabilities of the equation for providing the singular behavior these properties exhibit as a function of the density when the critical region is approached.

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