

Thermodynamic Consistency Near the Liquid-Liquid Critical Point

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Near the liquid-liquid critical point of a binary mixture, thermodynamic response functions such as $C_{p,xc}$ and $\alpha_{p,xc}$ diverge to infinity following a power law characterized by the critical exponent α . As a consequence of $\alpha_{p,xc}$ behaviour, the density ρ_{xc} presents a small anomaly governed by the exponent $1-\alpha$. The thermodynamic consistency between $C_{p,xc}$ and ρ_{xc} has been questioned given the small value of the density anomaly [1]. Recent measurements [2] have proved that an adequate treatment of density data is the key factor in solving this problem. In this work, a detailed study of the determination of critical amplitudes of $C_{p,xc}$ and ρ_{xc} is presented. The systems under study are those conformed by 1-nitropropane and alkanes, for which $C_{p,xc}$ and ρ_{xc} have been measured using a Seratam Micro DSC-II differential scanning calorimeter and an Anton-Paar DMA-5000 vibrating tube densimeter, respectively. The relative importance of including correction to scaling terms in the critical contribution and/or quadratic terms in the regular contribution has been taken into account. Accordingly, both quantities were fitted in three different ways combining the terms above stated. To get final results, one of the fitting strategies has been chosen as the most adequate. The verification of the thermodynamic consistency has been carried out by checking the values of the slope of the critical line –as obtained from the critical amplitudes– against directly measured literature values [3].

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