Scaling in Fluid-Fluid Criticality: the Case of Weakly Compressible Binary Mixtures

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The thermodynamics of fluid-fluid (i.e., gas-liquid, liquid-liquid, or gas-gas) phase transitions in which there is a variable that develops a line of critical points, termed a nonordering field, is revised in the frame of the complete-scaling formulation of asymmetric criticality [1,2]. For the particular case of liquid-liquid demixing in weakly compressible binary mixtures, we show that pressure, which acts as a nonordering field, enters into the three scaling fields. Three specific results are discussed, namely, (i) the coexistence-curve diameter in the density–temperature plane exhibits a $-\Delta T^{2\beta}$ [with $\Delta T \equiv (T-T_c)/T_c$ and $\beta = 0.326$] contribution, (ii) two relevant mixing coefficients are related to each other through the difference between the molar volumes of the pure liquids and (iii) the proposed, extended scaling formulation sheds light on the issue of the appropriate composition variable in binary liquid mixtures. All these findings are tested against literature data at coexistence, either directly measured or determined in an indirect way from refractive-index measurements via the Lorentz-Lorenz relation.

[1] For pure fluids, for which it was originally devised, see M.E. Fisher and G. Orkoulas, Phys. Rev. Lett. **85** (2000) 696 and Y.C. Kim, M.E. Fisher, and G. Orkoulas, Phys. Rev. E **67** (2003) 061506.
[2] Generalization to binary-fluid criticality can be found in C.A. Cerdeiriña, M.A. Anisimov, and J. V. Sengers, Chem. Phys. Lett. **424** (2006) 414 and J.T. Wang, C.A. Cerdeiriña, M.A. Anisimov, and J.V. Sengers, Phys. Rev. E **77** (2008) 031127.