

Scaling Fields and the Nature of Order Parameter in Asymmetric Near-Critical Liquid Mixtures

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Application of the principle of critical-point universality to various phase transitions in fluid mixtures, also known as “isomorphism hypothesis”, is based on analytic relations between theoretical scaling fields (“ordering” and “thermal”) and physical fields, such as chemical potentials and temperature [1]. As a result, the universal Ising-model order parameter appears to be a combination of physical density-like variables, such as molar density, molar concentration, and molar entropy. Fisher and coworkers [2] recently suggested that the two theoretical scaling fields in fluids include also a contribution from pressure. We have examined experimental consequences of this formulation (“complete scaling”) with regard to the asymmetry of liquid-liquid coexistence in binary mixtures. We have clarified a controversial issue regarding the proper definition of the order parameter in binary fluids. While the properly constructed universal Ising-model-like order parameter in fluids as a function of the “thermal” field is completely symmetric with respect to the change of its sign, the molar concentrations of the coexisting phases as a function of temperature exhibit asymmetry with respect to the critical concentration. We have shown that the liquid-liquid asymmetry in binary solutions originates from two different sources: one is associated with a correlation between entropy and concentration and generates a $(T-T_c)^{1-\alpha}$ term (T_c is the critical temperature, $\alpha = 0.11$), whereas the second source is a lower-order, and thus more significant, $(T-T_c)^{2\beta}$ term ($\beta = 0.326$). A microscopic interpretation of the origin of the $(T-T_c)^{2\beta}$ term deserves a careful study; however, by analyzing the coexisting curves of liquid solutions of nitrobenzene in various hydrocarbons (from *n*-pentane to *n*-hexadecane), we have observed that, while the $(T-T_c)^{1-\alpha}$ term is almost independent on the solvent/solute molecular-volume ratio, the amplitude of the $(T-T_c)^{2\beta}$ term is strongly correlated with this ratio and with the values of the critical molar fraction.

[1] Anisimov *et al.*, *Phys. Rev. E*, **51**, 1199 (1995).

[2] Fisher *et al.* *Phys. Rev. Lett.* **85**, 696 (2000); *Phys. Rev. E* **67**, 061506 (2003).