Sharp Crossover Between the Mean-Field Critical Behavior and the Ising-Like Critical Behavior in Solutions of Polystyrene and Deuterocyclohexane

Yu. B. Melnichenko and G.D. Wignal
Solid State Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6393 USA

M.A. Anisimov, A.A. Povodyrev, and J.V. Sengers
Institute for Physical Science and Technology
and
Department of Chemical Engineering
University of Maryland
College Park, MD 20742 USA

It has been established experimentally that ordinary fluids and fluid mixtures as well as polymer blends exhibit a smooth monotonic crossover from the mean-field (classical) behavior far away from the critical point to the 3-d Ising model criticality in asymptotic proximity to the critical point of phase demixing. However, the crossover from the mean-field to the asymptotic critical behavior in solutions of long-chain polymers in low-molecular-weight solvents is less well understood. There are good reasons to believe [Anisimov *et al*., *Phys. Rev. Lett*. **75**, 3146 (1995); **76**, 4095 (1996)] that this type of crossover should be qualitatively different from that being observed in ordinary near-critical fluids and polymer blends, due to long-range correlations between segments of polymer chains in solutions providing a supplementary characteristic length in addition to the correlation length of the critical fluctuations. In this work we present experimental data on the temperature dependence of the susceptibility χ and the correlation length ξ in solutions of polystyrene ($5\times10^4 \leq M_W \leq 5\times10^5$ g/mol) in deuterocyclohexane at the critical concentration of the polymer. The data are obtained by small-angle neutron scattering over a temperature range between the Θ temperature and the critical temperature of phase demixing T^c. Indeed, we find that the critical exponents for both χ and ξ exhibit a sharp crossover from the mean-field values in the θ region to the Ising model values as $T \Rightarrow T^c$. Variation of the susceptibility with temperature for all studied solutions is well described by a crossover function which includes two crossover parameters reflecting existence of two characteristic lengths in the system.