Monte Carlo Simulations of Criticality and Tricriticality: Finite-Size Scaling

C.J. O'Keeffe,[S] R. Ren, and G. Orkoulas[C]
Department of Chemical and Biomolecular Engineering, University of California, Los Angeles, UCLA, Los Angeles, CA, U.S.A.
makis@seas.ucla.edu

This work is focused on the determination of the coexistence curves and critical points of fluid models from simulations of systems of finite size. When the range of correlations and fluctuations exceeds the linear size of the simulated system, measured properties exhibit strong size effects. Finite-size theory, however, allows accurate property estimation via extrapolation to the thermodynamic limit according to standard scaling laws. Finite-size scaling theories were primarily developed for Ising or lattice-gas type systems, characterized by artificial "particle-hole" symmetries. Despite the apparent similarity in critical behavior, there are important differences between real fluids and lattice-gas type systems. Recently, we revised standard scaling/finite-size scaling theories to account for additional anomalies associated with off-lattice, asymmetric fluid models. In the framework of the revised theory, the critical point is determined from extrapolations of the maxima/minima of thermodynamic properties measured along specially constructed, asymptotically critical loci. We have tested our methodologies for the vapor-liquid transition of the hard-core square-well fluid. We have also developed a finite-size scaling technique for the case of higher-order critical points, specifically tricritical points. Tricritical points occur in a variety of systems, such as multi-component fluid mixtures, $^3He/^4He$ mixtures, and antiferromagnets and metamagnets. We present results for the phase behavior of a simple Ising "spin-1" (Blume-Capel) model. In addition, we have investigated order-disorder transitions of electrolyte systems on the simple-cubic lattice. The phase diagrams of these systems consist of a line of continuous transitions (the lambda-line) that becomes discontinuous, first-order, via a tricritical point. The lambda-line, the line of first-order transitions, and the tricritical point are determined using finite-size scaling techniques. Our general methodologies are applicable to any fluid model for which precise phase coexistence results are desired.