Criticality, Coexistence, and Screening in Electrolytes: High-Resolution Simulations

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Recently devised finite-size extrapolation techniques [1,2] ó utilizing special loci in the temperature-density, (T, ρ), plane, specifically of isothermal maxima of $Q_L(T; \rho)$, the ratio of the squared mean-square density fluctuation to the mean fourth density-fluctuation moment, combined with high-resolution grand canonical fine-discretization Monte Carlo simulations of the hard-core 1:1 electrolyte (or restricted primitive model) in periodic cubes of edge length L, have convincingly demonstrated that, as long anticipated, the critical behavior is of short-range Ising character [3]. Extending the technique to examine the *minima* of $Q_L(T; \rho)$ below T_c, yields precise, ± 1-2 % estimates of the coexistence curve up to ~1 part in 10^3 of T_c [4]. Strong evidence of pressure mixing in the scaling fields [2, 5, 6], which implies a significant Yang-Yang anomaly [6, 7], is also uncovered [4].

To understand the associated screening behavior, over the (T, ρ) plane, we have studied the fluctuations of charge in families of subdomains. In the thermodynamic limit these fluctuations obey an area law that serves to define the Lebowitz screening length, $\xi_L(T; \rho)$ [8]. Elucidation of the finite-size effects allows reliable extrapolation to infinite systems; agreement with the exact low-density expansions [8] is found when T^* exceeds 0.4, but only for ρ^* less than 0.006 (in standard reduced units). For moderate densities (up to ρ^* about 0.1) the Lebowitz length lies above the Debye length ξ_D, which varies as $(T/\rho)^{1/2}$; but generalized DH theory [9] overestimates ξ_L. On the critical isochore we find that $\xi_L(T)$ remains finite when T approaches T_c; however, its variation is consistent with a weak, entropy-type singularity and, hence, a divergent T derivative.

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