Critical-point and coexistence-curve properties for ionic and dipolar fluids

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Abstract

We have used grand canonical Monte Carlo simulations aided by histogram reweighting [1,2] and mixed-field finite-size scaling techniques [3] to investigate vapor-liquid transitions occurring in systems with long range forces such as the Restricted Primitive Model of ionic solutions (RPM) and dipolar soft-sphere fluids. By combining the results of several simulations performed at different temperatures and values of the imposed chemical potential, we obtain the thermodynamic properties of a system over a broad range conditions. Mixed-field finite size scaling theory allows us to map the near-critical density-and-energy distribution into its universal and scale invariant form. Accurate estimates of the critical point parameters can thus be obtained. Our present estimate for the critical point of the RPM using the Ewald sum for the summation of the electrostatic forces is $T^*=0.0490 \pm 0.0004$, and the critical density is $\rho^*=0.070 \pm 0.005$. These estimates compare reasonably well with the results of [4], which were obtained on a "hypersphere" and were $T^*=0.0487 \pm 0.0001$, and the critical density is $\rho^*=0.065 \pm 0.002$. We have also used histogram methods to confirm the absence of a liquid phase for the dipolar hard sphere system previously studied by van Leeuwen and Smit [5].

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