Ionic Criticality:
Recent Progress, Open Questions

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Even for the simplest models of ionic fluids, charged hard spheres, many questions regarding the location and nature of phase separation and criticality remain unanswered. Recent progress achieved in collaboration [1] with Y.C. Kim, J.-N. Aqua, S. Banerjee, E, Luijten and A.Z. Panagiotopoulos will be sketched.

The critical temperatures and densities, $T_c(z)$ and $\rho_c(z)$, of multivalent z:1 (z = 1, 2, 3) equisized hard-sphere electrolyte models have been accurately determined. The universal Ising character of criticality, including for 1:1 *non*equisized systems, is well confirmed. Novel scaling algorithms determine the coexistence curve and its diameter to unprecedented precision. The RPM (1:1 equisized) diameter closely resembles that of liquid metals contrasting with the hard-core square-well (HCSW) result which matches insulating fluids. Yang-Yang ratios $R_\mu \simeq 0.26$ and -0.044 are revealed for the RPM and HCSW.

To understand multivalency the previous Debye-Hückel, Bjerrum ion-pairing, ion-solvation theory has been extended to 2:1 and 3:1 equisized models by analyzing larger ion clusters, their kinematics, and solvation. In contradistinction to all other theories, the correct trends of $T_c(z)$ and $\rho_c(z)$ are generated. *Neutral* ion clusters always predominate near criticality: that enables the z-dependence to be derived semiquantitatively.

At fluid criticality the density-density correlation length ξ_N (T, ρ) diverges strongly: but what happens to charge-screening? Simulation shows that the *Lebowitz length*, $\xi_L(T, \rho)$, of the RPM remains *finite* (but displays a *weak* entropy-like singularity). More general answers emerge from exactly soluble 1:1 ionic spherical models. Breaking the artificial RPM size and charge symmetry proves significant: the *charge screening length,* ξ_Z (T, ρ), then diverges like ξ_N. Furthermore, the Stillinger-Lovett sum rule may fail at criticality. Additional power-law interactions, $\sim 1/r^{d+\sigma}$, can be handled yielding insights into *quantum-mechanical* effects.

[1] *Phys. Rev. Lett., Phys. Rev. E, J. Phys. A, Chem. Phys. Lett. and Comp. Phys. Commun*., 2004-5.