Abstract Submitted
for the MAR06 Meeting of
The American Physical Society

Charge fluctuations and correlations in finite electrolytes YOUNG C. KIM, Laboratory of Chemical Physics, NIDDK, NIH, Bethesda, 20892, MICHAEL E. FISHER, Institute for Physical Science and Technology, University of Maryland, College Park, 20742 — Charge fluctuations, $\langle Q_\Lambda^2 \rangle$, for the 1:1 equisize hard-sphere electrolyte with the diameter a are computed via grand canonical Monte Carlo simulations, where Q_Λ is the total charge inside a subvolume Λ contained in a simulation box of dimensions $L \times L \times L$ with periodic boundary conditions. The charge fluctuations increase like the surface area $|\partial\Lambda|$ as Λ increases, even for small system sizes $L \leq 12a$. For slabs of dimensions $L \times L \times \lambda L$ with $0 < \lambda < 1$, the scaled charge fluctuations, $\langle Q_\Lambda^2 \rangle / |\partial\Lambda|$, approach the thermodynamic limits exponentially fast. The extrapolations to $L \to \infty$ then yield the Lebowitz length, $\xi_{\rm L}(T, \rho)$, where densities $\rho \lesssim 3\rho_c$ and temperatures $T \gtrsim T_c$ have been studied. An exact asymptotic expression is obtained for $\langle Q_\Lambda^2 \rangle$. This enables one to compute the charge correlation length $\xi_Z(T, \rho)$ precisely. The results for $\xi_Z(T, \rho)$ agree with Debye-Hückel-type theories at low densities, but show deviations as the density increases. Charge oscillations at higher densities are also observed, as anticipated theoretically.
[1] Y. C. Kim, E. Luijten, and M. E. Fisher, Phys. Rev. Lett. **95**, 145701 (2005).

Young C. Kim
Laboratory of Chemical Physics, NIDDK, NIH, Bethesda, 20892

Date submitted: 11 Jan 2006 Electronic form version 1.4