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Finite-size effects in simulations of electrolyte solutions under periodic boundary conditions[1] JEFFREY THOMPSON, ISAAC SANCHEZ, Univ of Texas, Austin — The equilibrium properties of charged systems with periodic boundary conditions may exhibit pronounced system-size dependence due to the long range of the Coulomb force. As shown by others [S. Chiesa *et al.*, Phys. Rev. Lett. **97**, 076404 (2006)], the leading-order finite-size correction to the Coulomb energy of a charged fluid confined to a periodic box of volume V may be derived from sum rules satisfied by the charge–charge correlations in the thermodynamic limit $V \to \infty$. In classical systems, the relevant sum rule is the Stillinger–Lovett second-moment (or perfect screening) condition. This constraint implies that for large V, periodicity induces a negative bias of $-k_{\mathrm{B}}T(2V)^{-1}$ in the total Coulomb energy density of a homogeneous classical charged fluid of given density and temperature [J. P. Thompson and I. C. Sanchez, J. Chem. Phys., in press]. We present a careful study of the impact of such finite-size effects on the calculation of solute chemical potentials from explicit-solvent molecular simulations of aqueous electrolyte solutions.

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