Boundary effects in the classical one-component plasma

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The classical one-component plasma (OCP) is investigated by molecular dynamics (MD) with spherical reflecting and periodic boundary conditions, emphasizing boundary effects on electrostatic energies and the ionic equation of state. For the bounded OCP (BOCP), simulations of up to one million ions establish a finite-size expansion of the energy with terms associated with surface effects and boundary curvature. The energies extrapolated to the thermodynamic limit for $0.03 \leq \Gamma \leq 1000$ agree with published Monte Carlo results.

Although the total electrostatic energies agree in the thermodynamic limit, their renormalized ion–ion and ion–background contributions depend on boundary conditions. In cold BOCP, the latter tends to one third of the bcc Madelung energy due to a nonlocal contribution of the electrically neutral boundary layer, whereas it vanishes for periodic OCP. For periodic OCP, direct Coulomb summation within virtual spheres confirms that the time-averaged renormalized ion–background energy vanishes even for finite spherical subvolumes, while reproducing the total energies obtained using Ewald summation.

The ionic compressibility factor determined from the renormalized energies agrees with independent Coulomb-force virial calculations and with LAMMPS. The apparent contradiction between the vanishing ionic compressibility factor in cold BOCP and its negative divergence in periodic OCP is resolved by recognizing that periodic OCP has no physical boundary: ions outside any arbitrarily chosen sphere contribute to the total forces, so the virial of the enclosed ions cannot be identified with that of the entire system.