Resolving the inconsistency between the virial and thermodynamic pressure of Coulomb systems

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The expression for the pressure of Coulomb systems $P_F V/(Nk_BT) = 1 + U/(3N)$ can be obtained by differentiating the free energy by the volume. In atomistic simulations, the pressure is often calculated using an internal virial [1], which is called the virial pressure, P_W. In the case of the Coulomb potential, the $P_F = P_W$. However, due to the long-range nature of the Coulomb potential, the Ewald summation technique is often applied in simulations [2,3]. Using forces from the Ewald potential, P_W can differ from P_F by several orders of magnitude and has no N-convergence [4]. For volume-dependent potentials, we found that an additional contribution to the virial pressure should be accounted for [5,6]. We show [7] that, due to the homogeneity of the Ewald potential over the particle coordinates and the computational cell length, the corrected virial pressure coincides with the thermodynamic one and is equal to P_F.

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