

Generalizations and ramifications induced by the counterion structure in the strong and weak-coupling electrostatic interactions

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We present general arguments for the importance, or lack thereof, of the structure in the charge distribution of counterions for counterion-mediated interactions between bounding symmetrically charged surfaces. We show that on the mean field or weak coupling level, the charge quadrupole contributes the lowest order modification to the contact value theorem and thus to the intersurface electrostatic interactions. The image effects are non-existent on the mean-field level even with multipoles. On the strong coupling level the quadrupoles and higher order multipoles contribute additional terms to the interaction free energy only in the presence of dielectric inhomogeneities. Without them, the monopole is the only multipole that contributes to the strong coupling electrostatics. We explore the consequences of these statements in all their generality.