Stacking of conjugated oligomers and polymers in vacuum and in solution from first-principles

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The elucidation of the intermolecular interactions between conjugated polymers and oligomers in the condensed phase is essential to understand and design novel organic semiconductors and electro-active polymers. The stacking of charged layers and the spatial arrangement of the chains are determining factors in charge-transfer processes and in the electronic and optical properties of these materials. In this work we address these issues from first-principles using different electronic-structure techniques in vacuum and in solution. We also apply a novel implementation of the Car-Parrinello method at the density-functional theory level which couples self-consistently the Kohn-Sham equations with a dielectric continuum. This approach is contrasted with other well established, quantum-chemistry solvation models in the investigation of charged thiophene oligomers and polymers in different solvent fields. We assess the role of the dielectric polarizability in the stacking of the charged layers, that of surface tension, and show how the balance between electrostatics, cavitation, and covalent forces can be determined by the solvation environment leading to either stable stacking or repuslive interactions.