Structural, vibrational and thermodynamical properties of carbon allotropes from first-principles: from graphite to nanotubes

Nicolas Mounet, Nicola Bonini, and Nicola Marzari

Department of Materials Science and Engineering, Massachusetts Institute of Technology

Cambridge, MA, USA

We studied the ground state and the finite-temperature properties of carbon allotropes using a combination of density-functional theory and density-functional perturbation theory. Equilibrium structures, elastic constants, and phonon dispersions of bulk diamond, graphene, graphite, and zigzag and armchair nanotubes are first obtained at the DFT-PBE level, showing on average an excellent agreement with experiments, with the caveat that for the case of graphite the experimental c/a ratio must be used. Thermal expansion coefficients are then determined from the minimization of the vibrational free energy in the quasi-harmonic approximation. Other thermodynamical properties such as heat capacity and the temperature dependence of the elastic constants are also obtained. Finally, the role of different phonon modes on the graphite, graphene, and nanotube thermal expansion or contraction is discussed, together with a full determination of their Grüneisen parameters.