Anharmonic effects in graphene, graphite and carbon nanotubes: thermal expansion and phonon lifetimes

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We study anharmonic effects in graphene, graphite and carbon nanotubes using a first-principles approach based on density-functional theory and density-functional perturbation theory. In particular, we investigate thermal expansion and phonon lifetimes, which are key quantities to understand thermomechanical and transport properties of these systems. The thermal expansion coefficients are calculated from a minimization of the vibrational free energy in the quasi-harmonic approximation. Our results predict that carbon nanotubes contract both in the axial and radial directions at low and room temperature and expand at higher temperatures. The role of different phonon modes in the thermal contraction is discussed, together with their Grüneisen parameters. Anharmonic phonon lifetimes are evaluated from the cubic terms in the interatomic potential, using density-functional perturbation theory and the 2n+1 theorem. Finally, we present preliminary results for the temperature-dependent frequency shift of the Raman G peak in graphite—calculated from both third- and fourth-order anharmonic terms in the crystalline potential.