Precision Quantification of Phonons and Vibrational Free Energies

K. Refson[1] Rui Guo and Sarah. L. Price[2]

[1] Department of Physics, Royal Holloway University of London, Egham, Surrey, TW20 0EX and ISIS Neutron Facility, Chilton, Didcot, OX11 0QX

[2] Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ.

Computing phonon frequencies and vibrational free energies within a DFT/lattice dynamics framework presents considerable additional computational challenges above those encountered in ground-state calculations. Accurate free energy calculations are essential to establish polymorph stability of molecular crystals where the internal energies differ by meV [1]. These crystals are characterised by very low-frequency (THz) intramolecular modes which give the largest entropic contribution to the vibrational free energy.

Phonon frequencies are the result of near-complete cancellation of large terms in the dynamical matrix, and the difference is exquisitely sensitive to computational grids, basis-set size, SCF residual, Brillouin-Zone sampling and more. Furthermore the use of electron-density-dependent dispersion corrections to DFT introduces additional convergence issues.

We will present a study of convergence challenges aimed at determining the precision limits of free energies for organic molecular polymorphs. Using the CASTEP plane-wave DFT code[2] we have calculated phonons for several systems, including desloratadine, coronene and naphthalene, and established a variatey of criteria necessary to approach convergence.

References

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