

Extensions of Hirshfeld Surface-Based Tools: Decomposing Fingerprint Plots and Visualisation of Crystal Voids

J. J. McKinnon, M. A. Spackman, D. Jayatilaka

School of Biomedical, Biomolecular & Chemical Sciences, University of Western Australia, Crawley, WA, Australia

The Hirshfeld surface^[1] and associated 2D-fingerprint plot^[2] encourage a new kind of understanding of intermolecular interactions in molecular crystals by emphasising a whole-of-structure approach. The Hirshfeld surface is determined by the full local environment - the combination of intermolecular contacts - rather than concentrating on those contacts perceived to be important.

However, for crystal structures of larger molecules comprising many close intermolecular contacts, multiple interaction patterns often overlap if their contact distances coincide, making detailed analysis of these interactions more difficult.

To overcome this limitation, we have decomposed 2D fingerprint plots in order to focus on specific interaction types (for instance, O...H, CH... π , etc.) or even close contacts to individual atoms. In this way we can partition the surface into regions involving specific interaction types, leading to a more quantitative comparison between related crystal structures, in particular polymorphs.

We have also been exploring the use of an isosurface of the procrystal electron density, which forms the basis of the Hirshfeld surface, to effectively visualise and quantify the size, shape and properties of voids in the crystal structures of potential clathrate compounds.

The CrystalExplorer^[3] software package will be used to provide examples of how these techniques can provide valuable insight into intermolecular interactions in complex crystal structures.

(1) McKinnon, J. J., Spackman, M. A. & Mitchell, A. S. (2004). *Acta Crystallographica Section B* 60, 627-668.

(2) Spackman, M. A. & McKinnon, J. J. (2002). *CrystEngComm* 4, 378-392.

(3) Wolff, S. K., Grimwood, D. J., McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2006). *CrystalExplorer*. Version 1.6. <http://www.theochem.uwa.edu.au/CrystalExplorer>.