Molecular Crystal Global Phase Diagrams

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Molecular crystals are of interest for a wide range of applications. Pharmaceuticals are often administered as crystals to take advantage of their uniformity, stability, and ease of handling. Molecular crystals are also being investigated as non-linear optical materials and as flexible organic semi-conductors. In each of these applications, the molecular arrangement within the crystal structure determines the crystal properties. Often there are multiple structures, called polymorphs, with differing properties. Crystal structure prediction is notoriously difficult because multiple polymorphs may have similar free energies and identifying the most stable crystal is dependent on an accurate and precise intermolecular potential. Small perturbations to the parameters in an intermolecular potential lead to small perturbations of the free energy surface, but discontinuous jumps in the minimum energy structure.

In the face of this extreme parameter sensitivity, we have addressed the inverse problem. Delineation of the family of intermolecular potentials consistent with an observed crystal structure is what we call Reverse Engineering of the crystal. It is a general observation that predictions hampered by extreme parameter sensitivity are good candidates for the inverse problem. In our case, the constraints can be quite tight since perturbations to the potential lead to different crystal structures. Therefore, the extreme parameter sensitivity that hinders structure prediction aids reverse engineering. During last year's meeting I presented the algorithm used to construct Molecular Crystal Global Phase Diagrams. In the oral presentation of this work, I briefly describe the diagrams and use them to rationalize the observed crystal structures of tetrahedral molecules from the Cambridge Structural Database. Extensions to other point group symmetries, including asymmetric structures, is also to be discussed. A brief description of our methods may be found in Ref. [1] and a thorough description of the method details in Ref. [2].

[1] J. B. Keith, J. Mettes and R. B. McClurg, Molecular Crystal Global Phase Diagrams, *Cryst. Growth and Design,* In Press (2004).
[2] J. A. Mettes, J. B. Keith and R. B. McClurg, Molecular Crystal Global Phase Diagrams: I. Method of Construction, *Acta Cryst. A,* In Press (2004).