Disordered Refinement

The most flexible and accepted refinement program for small-molecule structure determination is SHELXL written by Prof. George Sheldrick. An on-line description of all SHELXL commands is at:
http://shelx.uni-ac.gwdg.de/SHELX/shelxl_html.php

An excellent discussion of disorder is included in Peter Müller's *Crystal Structure Refinement: A Crystallographer's Guide to SHELXL*, 2006, Oxford University Press, New York.

Crystal structure determination always presumes that the same types of atoms are in the same positions in all unit cells. Thus, the crystal is assumed to have long range, 3-dimensional order. *Disorder* occurs when one or more atoms sit in one location in some unit cells and in other locations in other unit cells (or are different atom types in different unit cells).

Modeling disorder will always require more variables than are needed for an ordered model. Always confirm that there are sufficient data to refine the extra variables. If necessary, calculate R_{free} to verify that by introducing the extra variables you are not *overfitting* the data.

Observing disorder

1. Large peaks appearing in a difference map that cannot be attributed to atoms that need to be added. Often these peaks are at inappropriate distances to existing atoms to form reasonable chemical bonds (too close or too far).
2. Anisotropic displacement parameters for an atom or group of atoms may be shaped as cigars (prolate) or plates (oblate).
3. There may be a region of space that is big enough to contain the volume of one or more solvent molecules. Often these regions contain no assignable peaks. "Mother nature abhors a vacuum", so there is every likelihood that disordered solvent molecules are filling the void.

Modeling positional disorder

1. If a plausible model of another orientation of atoms can be made, first set the displacement parameters of the known atoms in the group to some reasonable, fixed isotropic value.
2. Set the occupancy of all atoms in the group to some reasonable free-variable value that is different from the occupancy of related disordered atoms.
3. Include the new atoms in the model adding PART instructions around bonded groups. Add restraints to make the geometries chemically reasonable (important!). Restrain occupancies of all parts of the disorder to add to no more than 1. Refine to convergence.
4. Restrain the ADPs (atomic displacement parameters) of atoms to be plausible. Add hydrogen atoms to the disordered atoms and refine with isotropic ADPs for disordered atoms until convergence.
5. Refine with anisotropic ADPs for the disordered atoms until convergence.
6. Check the difference map and displacement parameters of the disordered group to look for additional disorder. If more disorder is found proceed to step 1.

Modeling substitutional disorder

Substitutional disorder is difficult to model in crystallography because the shapes of the electron distribution of different types of atoms are modeled as the same. Also, there is always a rather high correlation between the refinement of occupancies with displacement parameters. When possible, set the initial values of the model parameters (occupancies) near to their final, correct values. Initially set the ADP values of the disordered atoms to reasonable fixed isotropic values when refining the occupancies. Remember, the occupancies for any region of the lattice must be ≤ 1. Next refine the ADP values isotropically, and finally anisotropically. If the atoms are near or directly on another atom, then the ADPs may be set equal using the EADP command. It is recommended that an independent analysis of the relative amounts of atom types be determined. (As a rule of thumb, X-ray occupancies really should have standard uncertainties of about 5%).

Restraints and constraints in refinement restrict some variables of the model. *Constraints* are hard restrictions, for example, placing an atom on a symmetry site such as an inversion point or a mirror plane. *Restraints* are used to set geometry or displacement parameters to "reasonable" values.

Positional restraints

DFIX restrains the distances between pairs of atoms to be a fixed value within an esd range.
DANG similar to DFIX, but is used with 1,3 distances to control an angle.
SADI restrains the distances between pairs of atoms to be equal within an esd range.
SAME restrains both 1,2 and 1,3 connections for a group of atoms to be similar to atoms later in the list.
FLAT restrains the listed atoms to be within a plane.
CHIV restrains the chiral volume of the listed atoms.

Displacement restraints

RIGU restrains the displacement parameters of bonded atoms to be similar along the bond.
DELU similar to RIGU but less strong (deprecated).
SIMU restrains the ADPs of atoms near one another to be similar.
ISOR restrains the ADPs of listed atoms to be approximately isotropic.

Occupancy restraints

SUMP restrains the occupancies of atoms to sum to a fixed value. Note that this sum can be used to restrain occupancies by total sum, by charge, etc.

Constraints

EXYZ constraint to set the positions of two or more atoms to be the same.
EADP constraint to set the ADPs of two or more atoms to be the same.

Related commands

PART separates atoms of one orientation from atoms in another orientation.
DEFS used to change the default effective standard deviation
NCSY applies non-crystallographic symmetry restraints