

Disorder

A crystal is a potentially endless, three-dimensional, periodic discontinuum built up by atoms, ions or molecules.

Real crystals have defects and frequently parts of molecules (or whole molecules) are found in more than one crystallographically independent orientation. Possible reasons:

- $Z' > 1$
- Twinning
- Disorder

Soldier example from theory class...

The structure is always the **spatial average** over the whole crystal!

In most cases, only a small part of the molecule shows disorder.

Anisotropic displacement ellipsoids and residual electron density are best indicators for disorder.

Disorder

Disordered ethyl group.

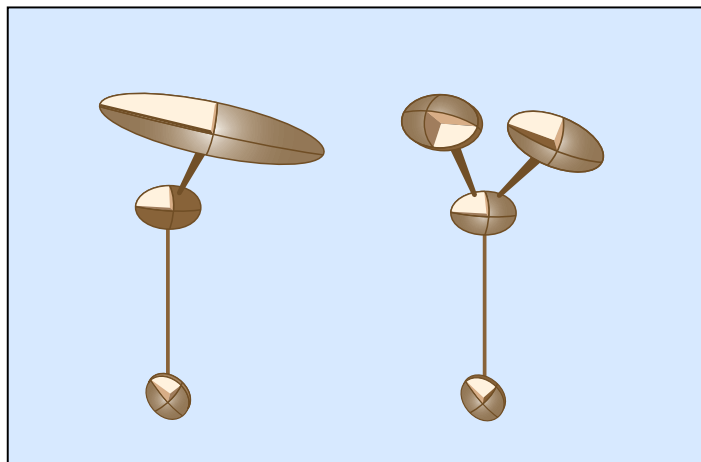


Figure by MIT OpenCourseWare.

Types of Disorder

Substitutional Disorder

The same site in two unit cells is occupied by different types of atoms

Positional Disorder

One atom occupies two (or more) sites. This can be in a single unit cell (dynamic disorder = real motion) or in two (or more) different unit cells (static disorder).

Mess

Large voids in the lattice are filled with randomly oriented solvent molecules in the fashion of amorphously frozen liquid. No contribution to diffraction pattern, only diffuse scattering.

Refinement of Disorder

The refinement program needs to know the two (or more) positions for each disordered atom (that is two sets of coordinates instead of one per disordered atom) and the relative occupancies.

Use free variables to refine occupancies.

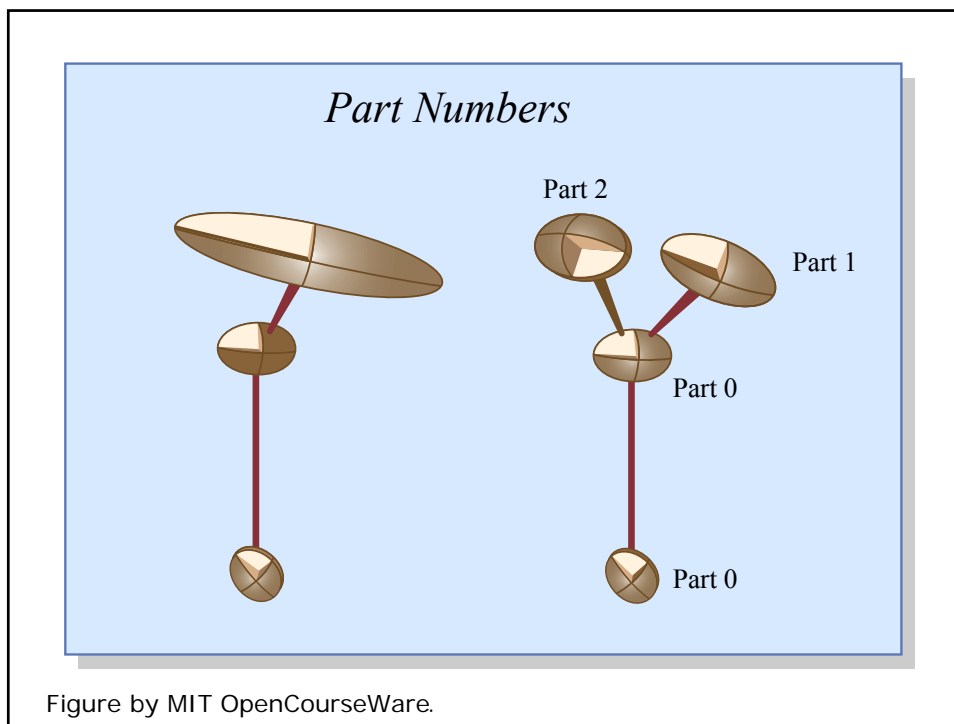
To make sure that equivalent atoms don't bind to one another use the **PART** instruction.

Per default all atoms are in **PART 0**.

Disordered atoms go into higher parts: **PART 1** and **PART 2** for a two-component disorder, for example.

Atoms bind only to atoms that are either in their own part or in **PART 0**.

It helps a lot to use similarity restraints on bond lengths and angles as well as on displacement parameters (**SAME** / **SADI** and **SIMU**, **DELU**).



Disorder Involving Special Positions

Imagine a molecule sitting on or near a special position without fulfilling the geometry of that symmetry element (e.g. toluene on inversion center).

Two possible ways of describing: either use different space group without the symmetry element(s) in question or refine a disorder about the special position.

Refinement is easy: you need only one set of coordinates, as the second one can be generated from the first by means of the symmetry operator(s) corresponding to the special position in question. Therefore instead of **PART 1** and **PART 2** you only need one component, which has to be placed in **PART -1**.

The ratio does not need to be refined as it corresponds to the multiplicity of the symmetry operator (0.5 for an inversion center, mirror and twofold axis; 0.3333 for a threefold, 0.25 for a fourfold and 0.1667 for a sixfold). Combinations of symmetry operators are possible, of course.

Disorder With More Than One Component

If you have more than two components, you need more than two parts. Say **PART 1**, **PART 2** and **PART 3**. The trick with the single Free variable using **21.000** and **-21.000** does not work for three and more components, but the **SUMP** command allows to logically relate free variables. In case of a three-component disorder (as given above) using the Free Variables number 2, 3, and 4 the correct **SUMP** command looks like that:

```
SUMP 1.0 0.001 1.0 2 1.0 3 1.0 4
```

SUMP can do more but is rarely used for anything else.

More Than One Disorder In a Structure

Each independent disorder gets its own Free Variable (beware of connected disorders!), but you use **PART 1** and **PART 2** over and over again. Higher **PART** numbers are used only for disorders with more than one component.

The format of the **.ins** file limits the number of Free Variables to 99 (that includes the **osf**).

Pseudo Symmetry

Assume $Z > 1$ (happens predominantly in low-symmetry space groups).

Most of the time there is no simple symmetry relation between the individual molecules in the asymmetric unit, but if there is, we have Pseudo Symmetry.

Two possible cases: true non-crystallographic symmetry (NCS) and global pseudo-symmetry.

NCS

NCS is the general case and not particularly difficult. Can even be beneficial, as similarity restraints can be used if the data-to-parameter ratio is low.

NCS means that two (or more) crystallographically independent molecules (or parts of molecules) are perfectly or almost perfectly related by a symmetry element that is not part of the space group symmetry. *I.e.* the symmetry element is located on a general crystallographic position.

Valid only within each unit cell and not globally (in the whole crystal).

Make sure that NCS cannot be transformed into crystallographic symmetry using an alternative unit cell setting!

Global Pseudo Symmetry

Two (or more) crystallographically independent molecules (or parts of molecules) are ***almost but not quite*** related by a crystallographic symmetry element of a higher-symmetry space group. Global Pseudo Symmetry can cause severe systematic errors and problems with correlation between parameters that are related by the pseudo symmetry.

The pseudo symmetry element is located on a special position, making it valid throughout the entire crystal (globally) and not only within the individual unit cell.

Example: Space group is $P2_1$ with $Z=4$ (i.e. $Z'=2$), and the two independent molecules are ***almost but not quite*** related by a glide plane along c and perpendicular to b . That makes the pseudo space group $P2_1/c$. The reflections of type $h0l$ with $l \neq 2n$ are going to be very weak but most of them should still be observed. This can make the space group determination a little more difficult. The biggest problem, however, are the systematic errors mentioned above.

Global Pseudo Symmetry

Two ways of treating global pseudo symmetry:

If the violation of symmetry is only marginal, it can be appropriate to choose the higher-symmetry space group (in the example given $P2_1/c$ and $Z'=1$) and refine a disorder.

In other cases refinement in the lower symmetry space group is better (in the example $P2_1$ with $Z'=2$).

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