

# Utilising MaXrd in the Study of Inclusion Compounds

## Abstract

The Mathematica X-ray diffraction package *MaXrd* [1] has now been expanded with the capability to compose “custom” crystal structures, particularly aimed at facilitating the embedment of a guest phase into a host lattice. After importing the required crystallographic information from a cif file, one can extend the asymmetric unit to a desired number of unit cells while inserting atoms, molecules or other structures in the process. The embedded phase can also be distorted and/or rotated by a specified or random amount when placed into the host. The resulting structure can be visualised in three dimensions in direct space and the information may be utilised automatically by *DISCUS* [2] to obtain a simulated diffraction pattern. A consequence of this technique is that the space group of the guest phase becomes independent of that of the host (essentially having P1 symmetry). This gives the means to test hypotheses on the crystal structure and simultaneously investigate reciprocal space for any implied characteristics in a relatively swift and easy manner. This functionality is used in our ongoing study of a thiourea-ferrocene clathrate, which has proven challenging with regard to its phase transitions and the five-fold symmetry of the cyclopentadienyl rings [3, 4].

## References

- [1]: Ramsnes, S., Larsen, H. B. & Thorkildsen, G. (2019). *J. Appl. Cryst.* 52, 214–218.
- [2]: Proffen, T. & Neder, R. B. (1997). *J. Appl. Cryst.* 30, 171–175.
- [3]: Hough, E. & Nicholson, D. G. (1978). *J. Chem. Soc., Dalton Trans.*, 15–18.
- [4]: Lorson, L. C.; Tai, O. & Foxman, B. M. (2018). *Crystal Growth & Design*, 18, 409–415.
- [5]: R. Clement, R. Claude, and C. Mazieres, “Clathration of ferrocene and nickelocene in a thiourea host lattice,” *J. Chem. Soc., Chem. Commun.*, pp. 654–655, 1974.
- [6]: M. Sorai, K. Ogashara, and H. Suga, “Heat capacity and phase transitions of thiourea-ferrocene channel inclusion compound,” *Molecular Crystals and Liquid Crystals*, vol. 73, no. 3-4, pp. 231–254, 1981.
- [7]: M. G. B. Drew, A. Lund, and D. G. Nicholson, “Molecular modelling studies on the thiourea/ ferrocene clathrate,” *Supramolecular Chemistry*, vol. 8, no. 3, pp. 197–212, 1997.

## Functionality

The latest version, *MaXrd 1.7.0*, comes with a handful of functions which simplify the process of building and tweaking a “custom” crystal structure and visualising it in both direct and reciprocal space. A typical workflow starts by using `ImportCrystalData` to import the relevant content of a cif file to *Mathematica*. Next one can use `ExpandCrystal` to grow the asymmetric unit to a desired number of unit cells. At this point one can apply `ImportCrystalData` to the object for an inspection in direct space, or use `DISCUSPlot` which feeds the structural information into *DISCUS* and outputs a 2D plot of a reciprocal space simulation. Interactive examples are found in the documentation.



### ImportCrystalData

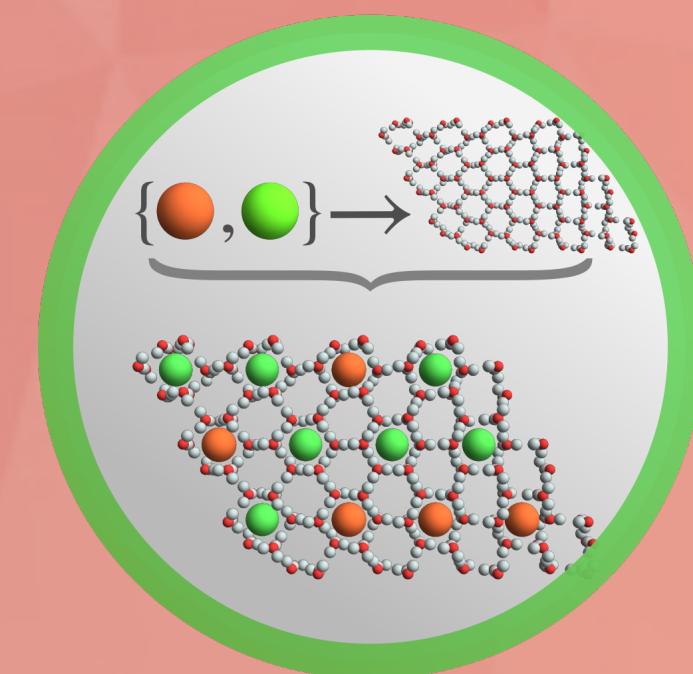
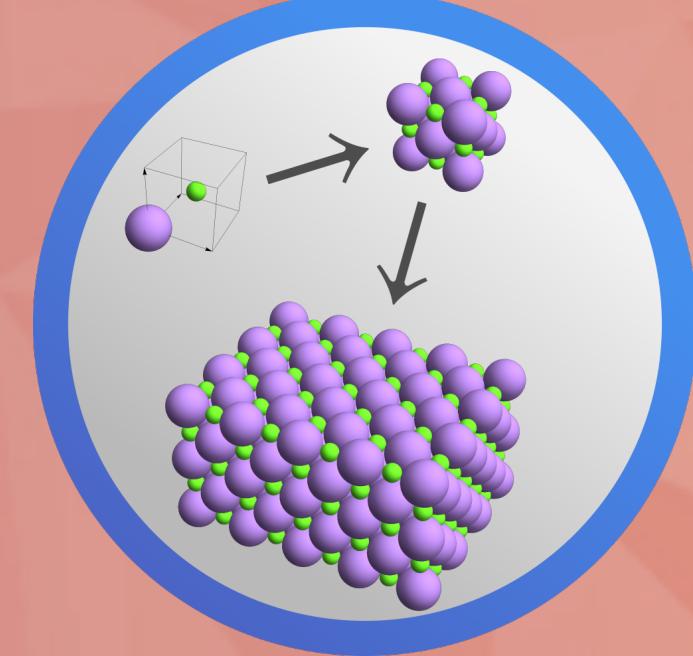
A straightforward but necessary step is to import the relevant crystallographic information to *Mathematica*.

The simplest way is to use this function with a `cif` file, but one also has the option to enter the required information programmatically or through a dialogue window.

### ExpandCrystal

With the asymmetric unit, lattice and space group in place, this function will simply grow the structure to a desired number of unit cells.

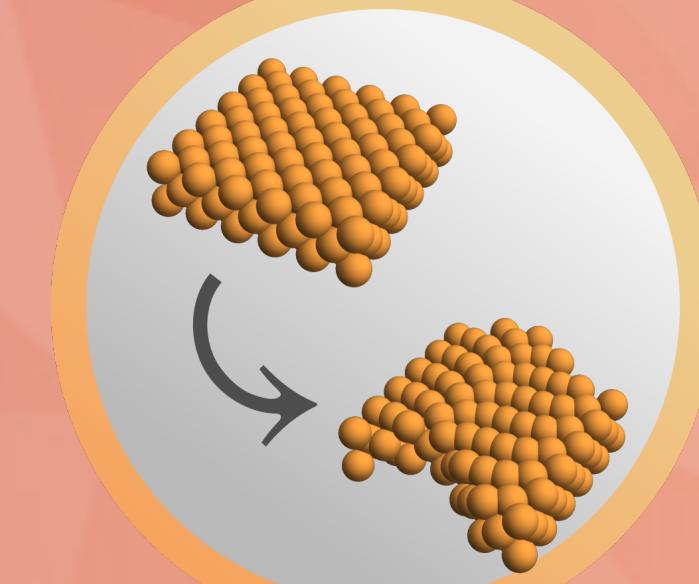
One of the main purposes is to create the host phase of the structure, and also to prepare the crystal for visualisation. It is flexible for creating both stand-alone structures or pieces that are to be part of a larger or more complicated structure.



### DistortStructure

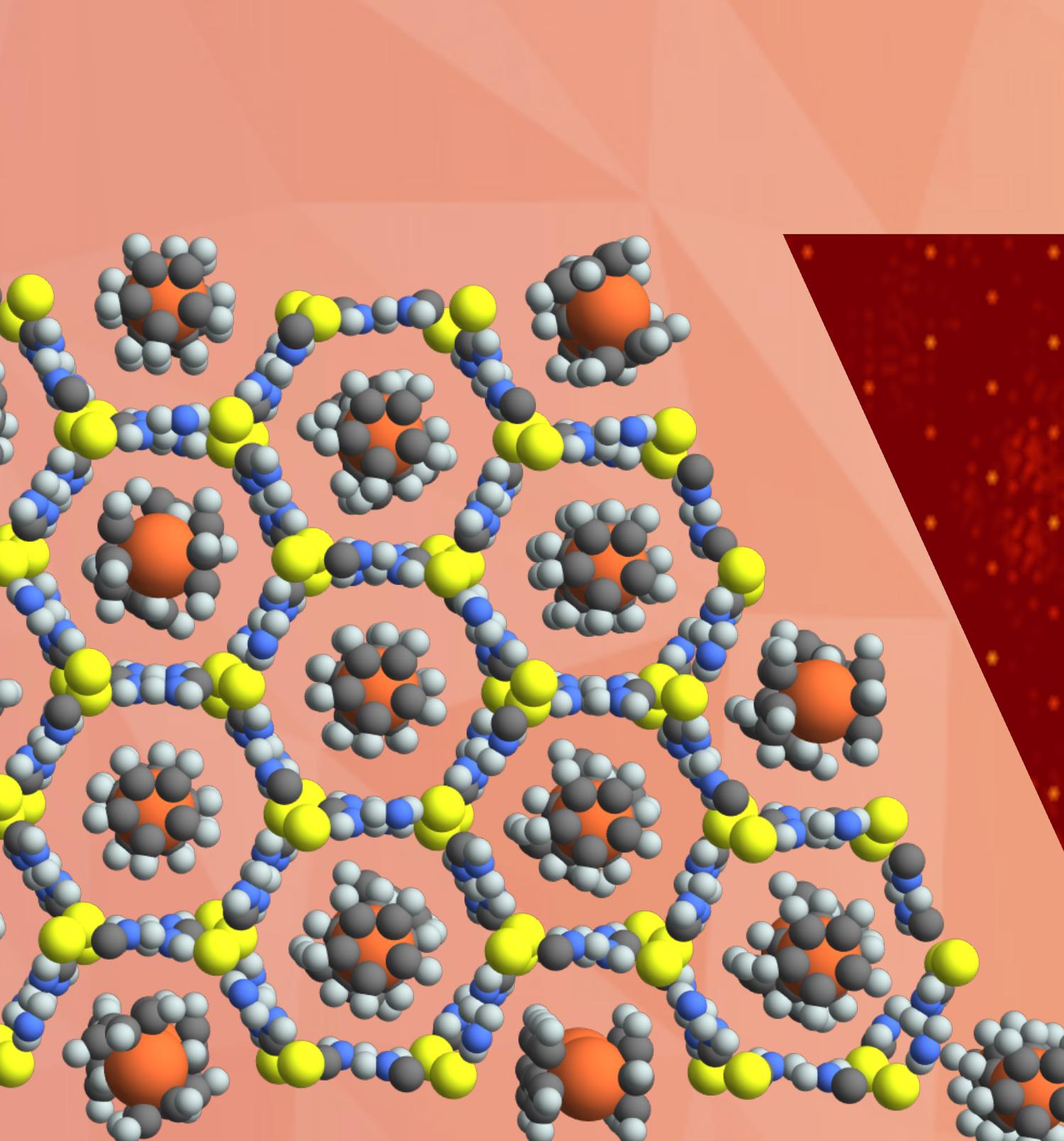
With this function, the user specifies a displacement field that shifts every atom relative to their present location. The flexibility in *Mathematica* makes it easy to configure the vector field to work periodically or in specific domains.

This function works well with the built-in `Manipulate` function to tweak the distortion parameters dynamically.



### EmbedStructure

Once a host structure has been defined, the guest phase can easily be embedded. The targeted positions specified are automatically matching the host size by default. Guest entities can be placed randomly, sequentially or conditionally. Furthermore, the entities can be shifted or rotated—by a constant or random amount—at placement.



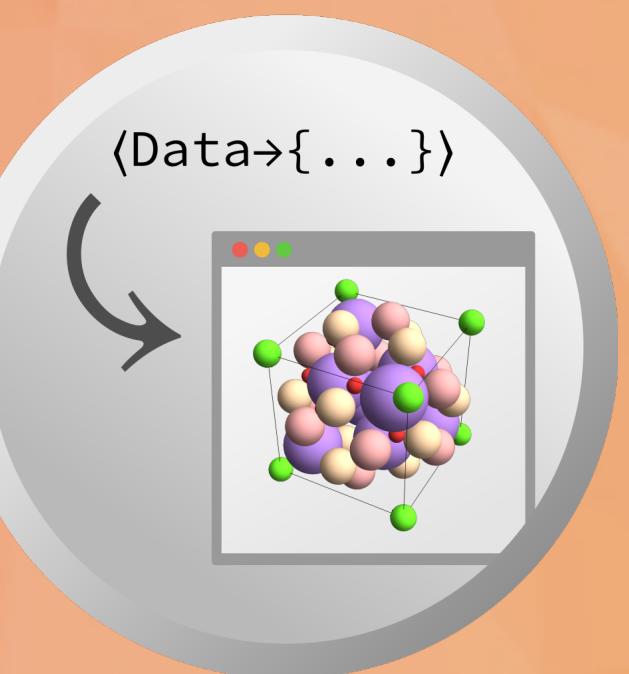
### DISCUSPlot

If *DISCUS* is installed, the user needs only input a structure name and Miller indices to obtain a simulated diffraction pattern. This function will automatically generate the input code of *DISCUS* and run it through a terminal/command prompt in the background, then present the resulting plot.



### SynthesiseStructure

If the structure is made from a set of smaller substructures, this function can synthesise the overall structure by assembling the blocks automatically. These items can also be placed sequentially or in random order. Normally they are assembled “edge-to-edge”, but there is also an option for using a buffer between them (which may be useful for cubic structures).



### CrystalPlot

This plot function can be called on every crystal/structure object to give a simple 3D representation of it. All direct space plots of crystals on this poster (and in the package documentation) have been created using this function.

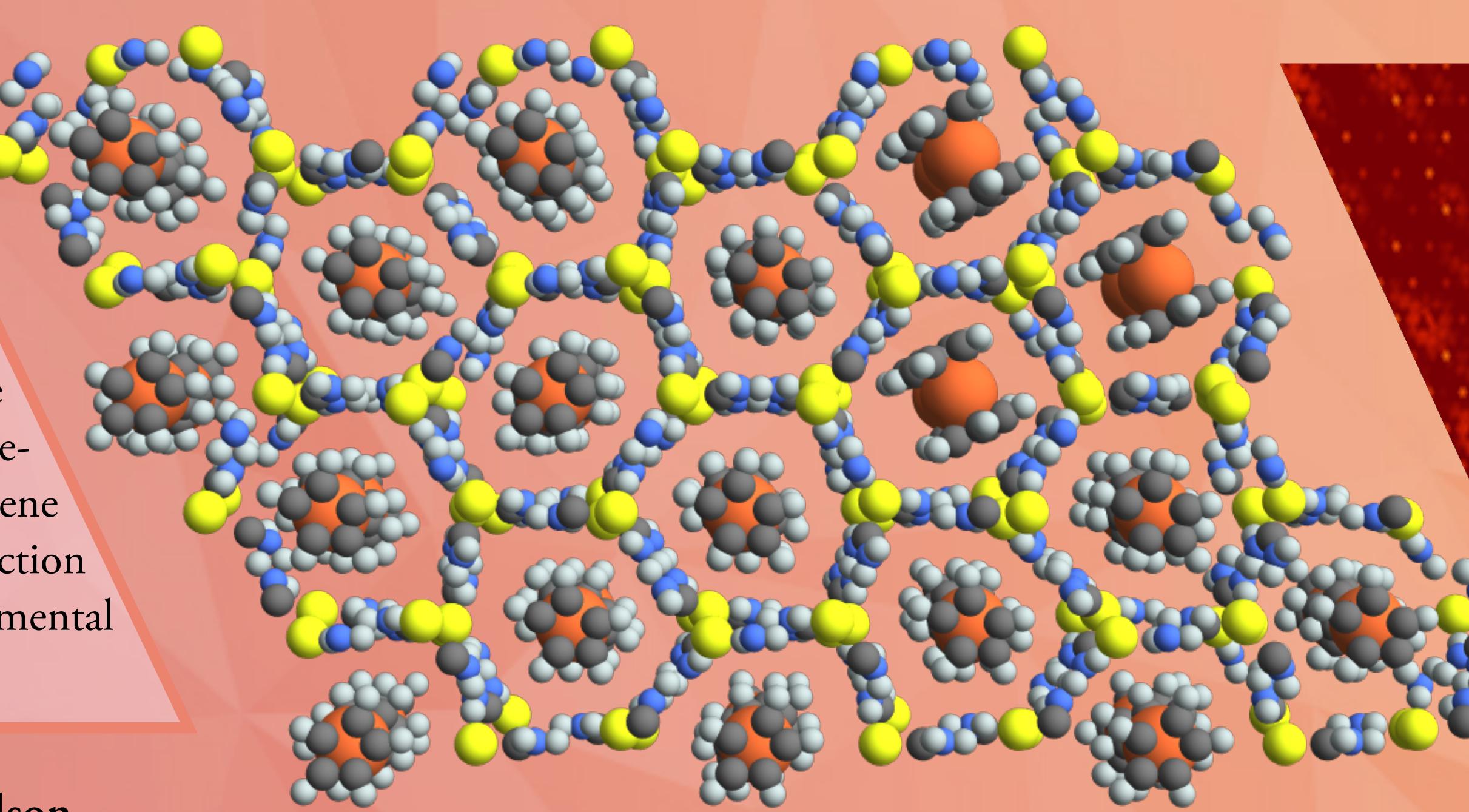
In this research context it provides an easy way of checking the current status of embedding or distortions.

## Simulations

In the literature we find reports of 60/40% distribution of the ferrocene molecules in parallel and perpendicular orientations, respectively [7]. Simulating this is a fitting task for the discussed tools. It is easy to try out different weighting schemes or switching between a random embedding or trying for instance a herringbone pattern. Another idea is to model incommensurability between the guest and host by imposing a random shift in the tunnel direction when placing the ferrocene molecules. Additionally, it is not too difficult to form the ferrocenes in a repeating spiral structure along the tunnel.

The lower figures demonstrate the use of the distortion function to simulate the lower-temperature phase of the structure. The hypothesis is that the ferrocenes become more static at this point and distorts the thiourea host in a more jagged way, bringing it in to an orthorhombic structure.

[GitHub repository](#)



The main connection to the reciprocal space is through the *DISCUS* (Diffuse Scattering and Defect Structure Simulation) program written by R. B. Neder and Th. Proffen [2].

## Conclusion

The presented tools enable users to perform simple inspections and adjustments of crystal structures with particular emphasis on host-guest systems. The functions are first and foremost user-friendly, but also sufficiently versatile to fine-tune complex structures. In our case, we try out various arrangements of ferrocene and distortion of the thiourea frame aiming to recreate features seen in diffraction images. We have not yet arrived at a definitive simulation matching experimental records, but believe these tools are useful to test or disprove models.

**Motivation**

The thiourea-ferrocene clathrate has been studied since 1974 [5], and its rhombohedral lattice and reversible phase transition at 162 K has been known since then. Four other phase transitions have been reported in 1981 [6]. Nevertheless, the dynamics of ferrocene in this tunnel inclusion complex has been the topic of research papers up to this day. Discussion have mainly revolved around the orientation of ferrocene as a function of temperature, effects of different conformations and the disordered ferrocene’s impact on the overall thiourea structure at the transitions.

We still seek a more complete and intuitive understanding of the low-temperature phase as well as the transition mechanism and overall disorder.

