New modelling for disordered atoms in free-form based hybrid refinement and visual representation

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Motivation

The number of structures flagged in the CSD as disordered has doubled over the last 25 years, so that the treatment of disorder has become a significant hindrance to fully automatic structure determination.

In a disordered structure, the classical partially occupied anisotropic displacement parameter model is not always appropriate [1].

Goals

A new treatment which integrates a free-form refinement of the disorder together with traditional refinement of other parameters. The method optimizes and illustrates the free-form, as well as quantifies and refines related parameters.

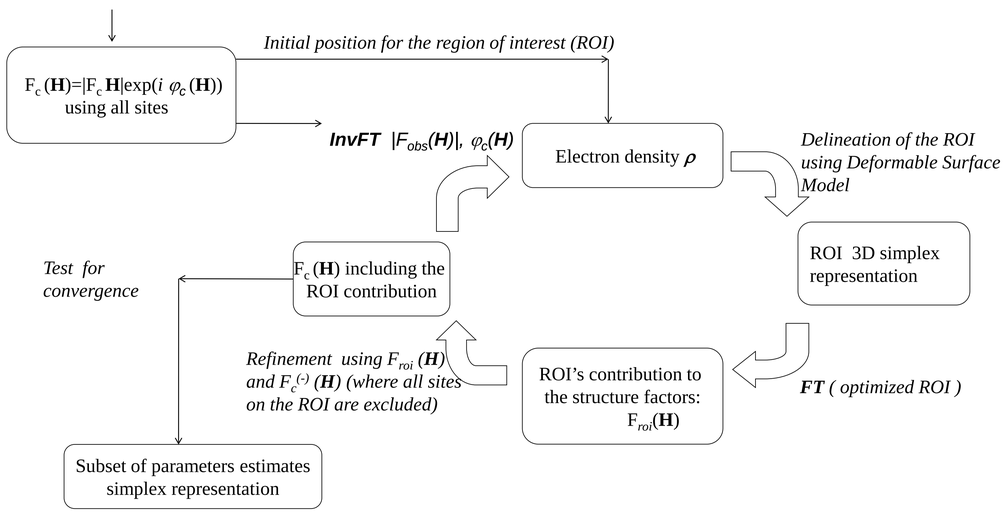
Development and implementation of a free-form disorder refinement method to optimally combine classic refinement with an iterative process between object and diffraction pattern, overwriting known information in each space to perform the structural analysis in the optimization process.

Procedure

Refinement combined with Shape Delineation

Given the results obtained from a classic refinement which indicated a potential disorder, the initial free-form configuration is defined within the ROI, in the real space where the optimization process of a deformable model will operate.

Thus, the main loop of the refinement process consists of two parts of F_c:
- one computed as known with all non-disordered sites;
- the other using the structure factors, obtained by inverse-transform of the optimized ROI.



Other parts can be included as usual, such as restraints. The resulting refined parameters and phases produce a new density which, when added to the current ROI, define a domain where a new ROI optimization operates. At the final iteration, the output will produce the refined form represented as *2-simplex meshes* jointly with the refined non-disordered sites.

Theoretical background

To optimize the Region Of Interest (ROI) boundaries (in this case, a disordered region), the ROI is modelled after each iteration as a free form with *deformable surface model*, where a surface is defined within the density domain and represented as a 2-simplex mesh, able to move under the influence of internal forces coming from within the model itself and external forces computed from the density values. We use the *gradient vector flow* (GVF) field [2] for the external force, computed as a diffusion of the gradient vectors of a density-value.

Deformable Surface Model

A deformable surface model is defined as a parameterized surface : $\boldsymbol{x}(s) = (x(s), y(s), z(s))^T$, where : $s = (s_1, s_2)$ in [0,1] , that moves through the image domain to minimize a specified energy function. Usually, the energy is formed by internal and external forces.

$$E = \int_0^1 E_{int}(\boldsymbol{x}(s)) + E_{ext}(\boldsymbol{x}(s))ds$$

$$E_{int}(\boldsymbol{x}(s)) = \frac{1}{2}(\alpha|\boldsymbol{x}'(s)|^2 + \beta|\boldsymbol{x}''(s)|^2)$$

- x' and x'' denote the first and second partial derivatives and reflect : tension and rigidity respectively

E_{ext} is derived from the image so that it takes on its smaller values at the features of interest, such as boundaries

The surface that minimizes $\boldsymbol{E}$ must satisfy the Euler equation :

$$\alpha\boldsymbol{x}''(s) - \beta\boldsymbol{x}''''(s) - \nabla E_{ext} = 0$$

This is solved by making the surface dynamic and treating x as function of s and time t: $x(s,t)$. The partial derivative of $x(s,t)$ ***w.r.t*** t :

$$x_t(s,t) = x''(s,t) - \beta\boldsymbol{x}''''(s,t) - \nabla E_{ext} \qquad \text{(I)}$$

This term vanishes when $x(s,t)$ is stabilized and the solution is achieved.

Gradient Vector Flow field

We used the GVF: $v(x)$ for the external force $-\nabla E_{ext}$, $\nu(x)$ is defined as the equilibrium solution to the vector diffusion equation:

$$\begin{cases} \boldsymbol{u}_t = g(|\nabla f|)\nabla^2\boldsymbol{u} - h(|\nabla f|)(\boldsymbol{u} - \nabla f) \\ \boldsymbol{u}(\boldsymbol{x}, 0) = \nabla f(\boldsymbol{x}) \end{cases} \qquad \text{(II)}$$

Where $f(x)$ is the edge map, g(.) , h(.) are weighting functions: $\begin{cases} g(|\nabla f|) = e^{-(|\nabla f|/K)^2} \\ h(|\nabla f|) = 1 - g(|\nabla f|) \end{cases}$

The GVF was preferred to other forces because of its large capture range and its ability to move a deformable model into boundary concavities.

Application

The first test of the method was carried out on a simulated data and also a real structure, composed of 2-disjointed parts with no disorder; one part was simulated as disorder, the other not. The method is currently in testing with real data, of which an example with BF4 ion disorder is illustrated below.

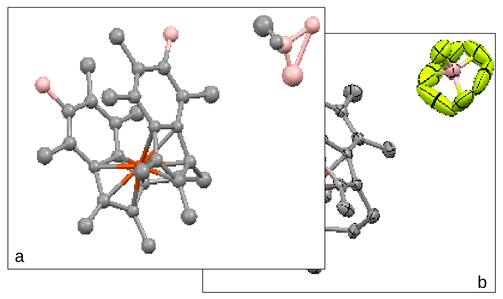


Fig.1 Structure with BF4 ion disordered part:
Input & published structure[3]

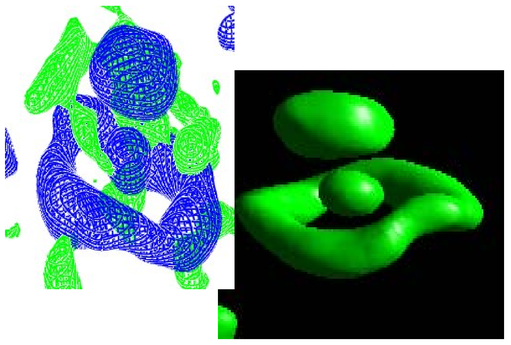


Fig.2 Visualization of the disordered part as iso-surface using a marching cube

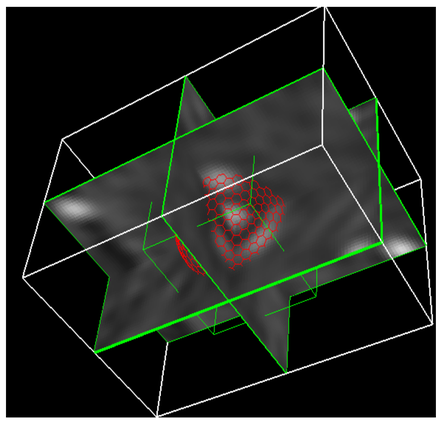


Fig.3 Initial boundaries of the ROI : Sphere represented with 2-simplex mesh in 3D map.

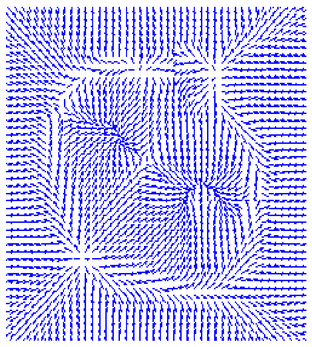


Fig.4 2D-Slice of GVF field

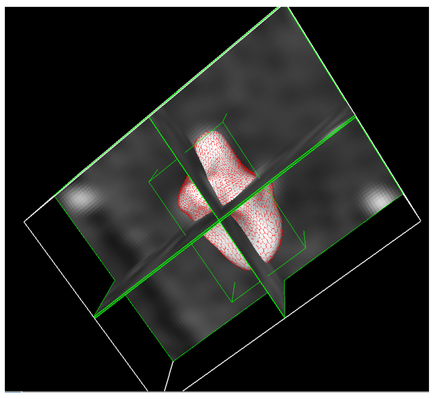
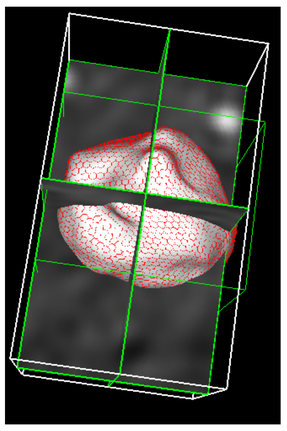


Fig.5 Optimized ROI

Fig.1b shows the disordered part in a published structure. Fig.2 shows the same region in electron density as seen when an iso-value is fixed for segmentation and visualization with a marching cube method. This also illustrates the difficulties for region segmentation in low resolution. Fig.3–5 illustrate the method as it is applied: the initial model is surrounding the ROI. Starting with an edge-map f and solving eq.I to get the *GVF* field: $\nu(x)$ (Fig.4 vector field middle-slice), $\nu(x)$ is then used to solve eq.II and evolve the surface model to the ROI's boundaries Fig.5, the form of which is Fourier transformed to contribute on F_c during classical refinement.
Although the deformable model has many parameters for tuning and requires some user intervention, it is possible to make the procedure automatic after validation. The initial results, which are both satisfactory and encouraging, indicate that with further tuning, the method will give improved parameter estimates; further tests for validation are on-going.



References

[1] P. v. d. Sluis and A. L. Spek. BYPASS, (1990) Acta Cryst. A46, 194-201.
[2] C. Xu and J. L. Prince. Snakes, shapes, and gradient vector flow. *IEEE Trans. on Image, Processing*, 7(3):359–369, March 1998.
[3] Data structure: A. Thompson, Oxford University, Chemical Crystallography group

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