CHAPTER W3

Diffraction and the Reciprocal Lattice

W3.1 Voronoi Polyhedra

The concept of Wigner–Seitz cells that is used for periodic structures may be carried over to amorphous solids except that it is given a different name, the *Voronoi polyhedra*. Select a given atom and draw lines to all other atoms. Create bisecting planes perpendicular to each of these lines. All points that can be reached from the given atom without crossing one of these planes lie within the Voronoi polyhedron of that atom. The various Voronoi polyhedra all have differing sizes and shapes, but they do collectively fill all space without overlap. In the case of a periodic solid, translational symmetry demands that the polyhedra all have the same size and shape and they reduce to the Wigner–Seitz cell. An example of a Voronoi polyhedron is given in Fig. W3.1.

W3.2 Molecular Geometry and Basis Structure from Diffraction Data

The location of the diffraction maxima for a crystalline sample provides information that allows determination of the symmetry of the reciprocal lattice and measurement of the lattice constants (i.e., the diffraction pattern specifies the Bravais lattice). In itself, it does not provide information as to the location or identity of the basis atoms comprising the unit cell. Such information, however, may be extracted from an analysis of the intensity of the diffraction spots. Since scattering experiments measure the intensity only and not the phase, the extraction of this information turns out to be a relatively difficult problem. (If an x-ray laser could be constructed, presumably an x-ray hologram could be produced that would contain both amplitude and phase information.) Imagine that one could hypothetically measure the full scattering amplitude, including the phase:

$$\begin{aligned} F(\mathbf{q}) &= \sum_{\mathbf{R}} \sum_{j} f_j(\mathbf{q}) e^{i\mathbf{q}\cdot(\mathbf{R}+\mathbf{s}_j)} \\ &= N \sum_{j} f_j(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{s}_j} \sum_{\mathbf{G}} \delta_{\mathbf{q},\mathbf{G}} \end{aligned} \tag{W3.1}$$

and assume that the atomic form factors, $f_j(\mathbf{q})$, are known from independent experiments. Restricting $\mathbf{q}$ to lie on the reciprocal lattice gives

$$F(\mathbf{G}) = N \sum_{j} f_j(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{s}_j}. \tag{W3.2}$$

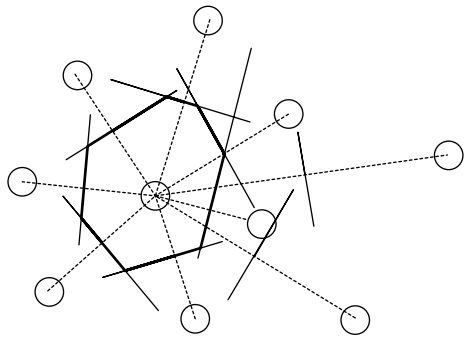

Figure W3.1. Voronoi polyhedron for a given atom in a disordered two-dimensional solid.

The unknowns are the set of vectors $\{\mathbf{s}_j\}$ and the identity of the atoms at each $\mathbf{s}_j$. One way to find them is to construct a mismatch function

$$\Delta(\mathbf{s}_1, \ldots, \mathbf{s}_{n_s}) = \left| F(\mathbf{G}) - N \sum_j f_j(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{s}_j} \right|^2 \tag{W3.3}$$

and search for the global minimum. At this minimum, if the data are perfectly accurate, $F = 0$. In principle, if one measures the complex amplitudes at $3n_s$ points in the reciprocal lattice, one should be able to determine the n_s vectors $\{\mathbf{s}_j\}$

In a realistic case, only the intensities,

$$I(\mathbf{G}) = |F(\mathbf{G})|^2, \tag{W3.4}$$

are measured and phase information is lost. Nevertheless, it is still possible to construct a mismatch function

$$\phi(\mathbf{s}_1, \ldots, \mathbf{s}_{n_s}) = \left| I(\mathbf{G}) - N^2 \left| \sum_j f_j(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{s}_j} \right|^2 \right|^2 \tag{W3.5}$$

and again search for a minimum by adjusting the set $\{\mathbf{s}_j\}$. The search for this minimum can be an arduous numerical task and limits the size of the unit cell that can be analyzed.

It is useful to introduce the *Patterson function*,

$$P(\mathbf{r}) = \sum_{\mathbf{G}} I(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}. \tag{W3.6}$$

Before simplifying this, recall some elementary properties of Fourier series. A periodic function in one dimension may be expanded as a Fourier series [(see Eq. (3.2) in the

textbook[†]]:

$$\phi(x) = \sum_{n=-\infty}^{\infty} \phi_n e^{i(2\pi n/a)x}, \tag{W3.7}$$

where the Fourier coefficients are [see Eq. (3.4)]

$$\phi_n = \frac{1}{a}\int_0^a \phi(x')e^{-i(2\pi n/a)x'}\,dx'. \tag{W3.8}$$

Inserting this into formula (W3.8) yields

$$\phi(x) = \int_0^a \phi(x')\frac{1}{a}\sum_{n=-\infty}^{\infty} e^{i(2\pi n/a)(x-x')}\,dx', \tag{W3.9}$$

implying the formula

$$\delta(x-x') = \frac{1}{a}\sum_{n=-\infty}^{\infty} e^{i(2\pi n/a)(x-x')}. \tag{W3.10}$$

The three-dimensional generalization of the formulas above, involving sums over the reciprocal lattice, leads to the result

$$\delta(\mathbf{r}-\mathbf{r}') = \frac{1}{V_{\mathrm{WS}}}\sum_{G} e^{i\mathbf{G}\cdot(\mathbf{r}-\mathbf{r}')}, \tag{W3.11}$$

where V_{WS} is the volume of the Wigner–Seitz cell.

The Patterson function becomes

$$P(\mathbf{r}) = N^2\sum_{j,j'} f_{j'}^*(\mathbf{G})f_j(\mathbf{G})V_{\mathrm{WS}}\delta(\mathbf{r}-(\mathbf{s}_{j'}-\mathbf{s}_j)). \tag{W3.12}$$

This function is seen to possess sharp peaks whenever the vector $\mathbf{r}$ matches an interatomic displacement vector $\mathbf{s}_{j'}-\mathbf{s}_j$. Thus, by studying the *Patterson map*, one may locate these vectors and attempt to reconstruct the geometric shape of the unit cell.

The use of the methods described above permit one to obtain short-range structural information about the basis of the crystal. This method is of particular value in determining the structure of crystals of biological molecules. It is also of use in studying materials with complex unit cells, such as catalysts. It is of somewhat less use in obtaining information concerning intermediate-range order.

[†] The material on this home page is supplemental to *The Physics and Chemistry of Materials* by Joel I. Gersten and Frederick W. Smith. Cross-references to material herein are prefixed by a "W"; cross-references to material in the textbook appear without the "W."

REFERENCE

Cantor, C. R., and P. R. Schimmel, *Biophysical Chemistry*, *Part II, Techniques for the Study of Biological Structure and Function*, W. H. Freeman, New York, 1980.

PROBLEM

W3.1 Define the normalized form factor for a basis by $\phi_j(\mathbf{G}) = f_j(\mathbf{G})/\Sigma_i f_i(\mathbf{G})$ and assume that it is positive and does not depend on $\mathbf{G}$. Let the normalized scattering amplitude be given by $\alpha(\mathbf{G}) = F(\mathbf{G})/N\Sigma_i f_i(\mathbf{G})$. Use the *Schwarz inequality*,

$$\left|\sum_i u_i^* v_i\right|^2 \leq \sum_i |u_i|^2 \sum_j |v_j|^2,$$

to prove the following inequalities. Show that

$$|\alpha(\mathbf{G})|^2 \leq 1.$$

Assuming inversion symmetry of the basis, show that

$$|\alpha(\mathbf{G})|^2 \leq \tfrac{1}{2}[1 + \alpha(2\mathbf{G})],$$

which is known as the *Harker–Kasper inequality*. Also prove that

$$|\alpha(\mathbf{G}) \pm \alpha(\mathbf{G}')| \leq [1 \pm \alpha(\mathbf{G} - \mathbf{G}'][1 \pm \alpha(\mathbf{G} + \mathbf{G}')].$$

As an example of the applicability of inequalities to the determination of the phase of the scattering amplitude, suppose it is known that $|\alpha(\mathbf{G})| = 0.8$ and $|\alpha(2\mathbf{G})| = 0.6$. Determine whether $\alpha(2\mathbf{G})$ is positive or negative.