FAST COMMUNICATIONS

Contributions intended for this section should be submitted to any of the Co-editors of the Journal of Applied Crystallography. In the letter accompanying the submission, authors should state why rapid publication is essential. The paper should not exceed two printed pages (about 2000 words or eight pages of double-spaced typescript including tables and figures) and figures should be clearly lettered. If the paper is available on a 3.5 or 5.25 in IBM PC compatible or 3.5 in Apple Macintosh diskette, this should be sent with the manuscript together with details of the word-processing package used. Papers not judged suitable for this section will be considered for publication in the appropriate section of the Journal of Applied Crystallography.


Using a structure envelope to facilitate structure solution from powder diffraction data

SIMON BRENNER, LYNN B. MCCUSKER* and CHRISTIAN BAERLOCHER at Laboratorium für Kristallographie, ETH Zentrum, CH-8092 Zürich, Switzerland. E-mail: lynne.mccusker@kristall.erdw.ethz.ch

(Received 8 May 1997; accepted 20 August 1997)

Abstract

Given just a few strong low-index reflections, a periodic nodal surface (PNS), which divides the unit cell into regions of high and low electron density, can be generated. Fourteen known zeolite structures were examined to verify the validity of the procedure developed and in all cases the framework atoms were found to lie on just one side of the calculated curved surface. In other words, the surface defines a structure envelope. The same approach was applied to a few ionic and organic structures and was found to be equally valid. Since these reflections, with large d spacings, are precisely the ones that are least likely to be involved in overlap in a powder diffraction pattern, such a PNS can also be calculated using powder data. The resulting restriction in the region of the asymmetric unit in which atoms are likely to be found has immediate implications for any of the direct-space methods of structure determination from powder data. The use of this structure envelope as a mask in a straightforward grid search procedure reduced the computer time required to solve several framework structures by as much as two orders of magnitude.

1. Introduction

The existence of a relationship between crystal structures and infinite periodic minimal surfaces (PMS) was recognized over a decade ago by Mackay (1985) and Andersson (1983). These surfaces have the property whereby the mean curvature at each point on the surface is exactly zero and they are the simplest of the three-periodic hyperbolic surfaces. Hyde (1993) established that the atoms of framework structures lie on or near a minimal surface. That is, a zeolite framework can be considered to be a decoration of a two-dimensional non-Euclidean object, whose geometry is hyperbolic. This implies that if the appropriate hyperbolic surface could be determined for a zeolitic material of unknown structure, structure solution could be reduced to the determination of the decoration of that surface. Since single crystals are relatively rare in zeolite science, this property of framework structures could significantly simplify the structure elucidation of novel zeolite structures, for which only powder diffraction data are available.

Unfortunately, the determination and mathematical description of the correct hyperbolic surface for an arbitrary space group is a nontrivial exercise. However, the concept of periodic zero potential surfaces (POPS) and periodic equipotential surfaces (PEPS), introduced by von Schnerring & Nesper (1987), provides an alternative to the complicated mathematics. These surfaces can closely resemble PMS and have the advantage of being somewhat easier to calculate. While they no longer have the elegant description within non-Euclidean space, they do provide a straightforward link between hyperbolic surfaces and common crystallographic formalisms. They can be generated as periodic nodal surfaces (PNS) using the structure-factor amplitudes and phases of a few selected reflections in a Fourier summation (von Schnerring & Nesper, 1991).

The connection between crystal structures and these hyperbolic surfaces has been demonstrated. They have been shown to serve as space partitioners separating the negatively from the positively charged ions in ionic crystals (von Schnerring & Nesper, 1987) or separating the interpenetrating networks in Cu2O or ice VII (Mackay, 1985) and as indicators of diffusion pathways (Andersson, Hyde, Larsson & Lidin, 1988). Phase transitions have also been characterized using these surfaces (von Schnerring & Nesper, 1987; Leone & Nesper, 1997). It should be noted, however, that all of these studies have been based on known structures, where the surface best fitting the structure was easily recognized by eye. The set of reflections most suitable for the generation of the appropriate surface was established intuitively by trial and error.

It was hoped that surfaces generated using a few (three to five) single (nonoverlapping), low-index reflections from a measured zeolite powder diffraction pattern would approximate the hyperbolic surface for that zeolite and that this surface could then be used to facilitate structure solution. Of course, the phases of these few reflections would have to be determined since only the structure-factor amplitudes can be gleaned from the powder pattern, but this did not appear to be an insurmountable problem. If such an approach should prove to be applicable to zeolite structures, adaptation to encompass other classes of materials might also be possible.

2. Simulation of periodic minimal surfaces for zeolites

Initially, surfaces were generated according to the formalism described by von Schnerring & Nesper (1991), where the
summation
\[ \rho(x) = \sum_{h} F(h) \cos[2\pi(hx) - \alpha(h)] \] (1)

over all equivalents of a few selected reflections \( h \), with phase angle \( \alpha(h) \), is used to produce a density distribution \( \rho(x) \). Normally, the structure-factor amplitudes are simply set at an arbitrary value of 1.0. The points at which the density is zero (i.e. the roots of the equation) describe a PNS. The number of reflections needed for the summation depends upon the symmetry of the space group. That is, in a higher space group, fewer nonequivalent reflections are necessary to obtain a good fit of the surface to the structure than in a lower one. In the cubic case, for example, usually only one set of \( \{hkl\} \) is needed.

It should be mentioned that a PNS is not necessarily a hyperbolic surface. However, if the appropriate set of reflections is used, the mathematical formalism for the generation of a PNS can be applied and a hyperbolic surface calculated. In this way, a PNS can also be an excellent approximation of a PMS.

A series of known zeolite structures was investigated to establish some objective criteria for the selection of reflections to be used in the summation. In each case, a surface that fitted the structure could be generated, but a set of generally applicable rules for reflection selection could not be discerned. It was obvious that the reflections and their symmetry equivalents must describe all dimensions of reciprocal space and that their indices should be low, but the exact combination needed to generate the surface that best described the framework could not be determined without using the structural model as a guide. In some cases, it was even found that systematically absent reflections yielded the best surface (e.g. \( \{100\} \) for sodalite, which is body-centred cubic). Furthermore,

![Fig. 1. The framework structure of AlPO₄-D and the periodic nodal surface generated using two origin-defining reflections with high \( |E| \) values and large \( d \) spacings (see Table 1). All atoms of the framework are situated on the positive (green) side of the surface.](image)

![Table 1. Zeolite structures tested and the reflection(s) used to generate the structure envelope](image)

| Name† | Space group | \( \{hkl\} \) | \( |E(hkl)| \) | Phase (°) |
|-------|-------------|-------------|-------------|----------|
| ANA   | Ia3d        | 112         | 1.02        | 0        |
| APD   | Cmca        | 021†        | 1.52        | 0        |
| DDR   | R₃m         | 101†        | 1.07        | 0        |
| DOH   | P6/mmm      | 111†        | 0.77        | 0        |
| EDI   | P₄m2        | 010‡        | 1.44        | 0        |
| FAU   | Fd₃m        | 111†        | 0.98        | 0        |
| GOO   | C222₁       | 110†        | 1.48        | 0        |
| LEV   | R₃m         | 012‡        | 1.07        | 0        |
| MFI§  | Pnma        | 011†        | 1.19        | 180      |
| PAU§  | Im₃m        | 013         | 1.88        | 180      |
| RTE   | C2/m        | 110‡        | 1.13        | 180      |
| SGT   | I₄1/amd     | 121†        | 1.50        | 0        |
| SOD   | Im₃m        | 011†        | 0.91        | 180      |
| VFI   | P6/mcm      | 221†        | 1.49        | 180      |

† Three-letter codes taken from the *Atlas of Zeolite Structure Types* (Meier, Olson & Baerlocher, 1996). ‡ Reflections used to define the origin. § Reflections used which overlap with others in the powder diffraction pattern (see text).

![Fig. 2. Two periodic nodal surfaces for CsCl (Cs red, Cl green) generated (a) using the weak \( \{100\} \) reflections in equation (1) and (b) using the strong \( \{110\} \) reflections in equation (2). The surface in (a), which separates the cations from the anions, approximates both the well known periodic minimal surface known as the P surface and the periodic zero potential surface (POPS), while that in (b) has the centres of both the cations and the anions on the same (yellow) side of the surface.](image)
some structures fitted a surface with a higher density level better than they did a surface at zero density. Consequently, the concept of creating a hyperbolic surface that could be decorated with a four-connected net had to be abandoned.

3. Generation of a structure envelope

Fortunately, during the testing phase described above, an alternative approach emerged. It became apparent that by assigning the correct phases to the low-order reflections with the highest $E(h)$'s, a well defined PNS could be generated. The (arbitrary) structure factor $F(h)$ in (1) was replaced by the true normalized structure factor $E(h)$ (since these allow a better estimation of whether a reflection is strong or weak) to yield the equation

$$\rho(x) = \sum_h E(h) \cos[2\pi(hx) - \alpha(h)].$$

Within a small tolerance, the periodic nodal surface calculated from the roots of this equation, using only a few strong reflections, was found to separate the framework atoms from the void space. A number of zeolites with different symmetries were examined (see Table 1) to verify the general validity of this observation. In all cases, the framework was found to lie on just one side of the PNS. As an example, the surface generated for the framework of AlPO$_4$-D using just two reflections is shown in Fig. 1. Further examples, including all of those listed in Table 1, can be found on the WWW at http://kristall.erdw.ethz.ch/research/zeolite_group/PNS.

These surfaces no longer approximate a PMS, but they can be generated in a rational manner and they do have a potentially exploitable property (i.e. the partitioning of the unit cell into regions where atoms are likely to be found and those where they are not). For CsCl, for example, the PMS known as the P surface can be used to separate the cations from the anions. That is, it closely resembles the POPS, which can be generated using $|F_{100}| = 1$ in equation (1). However, the 100 reflection is extremely weak. If, on the other hand, $E_{110}$, which is the strongest of the low-order reflections, is used in equation (2), a different PNS is produced. In this case, the cations and anions are located on the same side of the surface. The difference between these two surfaces is illustrated in Fig. 2.

The summation (2) can be viewed as a severely truncated Fourier series and the resulting density distribution as a very low-resolution electron-density map. However, a true low-resolution $E$-map would be calculated using all reflections up to a certain $d$ spacing (and an $E_{000}$ term) and not just a handful of strong reflections. The PNS generated using the procedure outlined above simply separates the regions of high electron density from those of low electron density. In this sense, it can be compared with the molecular envelope used in protein

![Fig. 3. Projection of the structure of a cyclic tetramer of a β peptide (Seebach et al., 1997) along [001], showing the periodic nodal line calculated using $E_{220}$ and $E_{310}$ in equation (2).](image1)

![Fig. 4. (a) The crystal structure of the organic molecule cimetidine, (b) with the periodic nodal surface calculated using the four strongest low-index reflections, and (c) with an iso-surface with a negative value [circa 20% of the most negative $\rho(x)$] calculated using just the three origin-defining reflections.](image2)
crystallography (Bricogne, 1976) to define the approximate boundary between the protein molecule and the solvent in a low-resolution electron-density map (see, for example, Coulombe & Cygler, 1997, or Subbiah, 1993 and references therein), but of course the number of reflections needed to generate the PNS described here is significantly less and the surface does not necessarily have a closed form. However, the two are closely related, so we have adopted the term 'structure envelope' for this partitioning PNS.

4. Using the powder diffraction data

Although the PNS described in the previous section was generated using simulated single-crystal data [i.e. calculated \( |E(h)| \) s and phases], the implications are obvious. Measured diffraction data could be used to determine which reflections should be selected for the generation of the structure envelope. The reduction of the space in the asymmetric unit in which the diffraction data could be used to determine which reflections should be selected for the generation of the structure envelope. The reduction of the space in the asymmetric unit in which the diffraction data could be used to determine which reflections should be selected for the generation of the structure envelope.

In 12 of the 14 zeolite structures tested (Table 1), the reflections used to generate the PNS can be extracted from the powder pattern without difficulty. They are the strongest low-index reflections and they are at least 0.5 FWHM (full width at half-maximum) from neighbouring reflections, so their intensities could be extracted reliably from the powder pattern. An advantage of using low-index reflections is the fact that they tend to lie in the low-angle (high \( d \) spacing) region of the powder diffraction pattern, which is less prone to reflection overlap. In the cases of MFI and PAU, alternatives would have to be considered. Either the relative intensities of the overlapping reflections would have to be estimated using other methods (e.g. David, 1987, 1990; Jansen, Peschar & Schenk, 1992; Cascaro, Favia & Giacovazzo, 1992; Estermann & Gramlich, 1993; Hedel, Bunge & Reck, 1994), or a different set of reflections would have to be used.

5. Reflection selection and the phase problem

Normally, there are several reflections with \( |E| \geq 1 \) in the high \( d \)-spacing region of the diffraction pattern. Precisely which reflections are used is not critical, but a few rules of thumb have emerged from preliminary tests. (i) The number of reflections used should be kept to a minimum. If too many reflections are included, the surfaces are moderated by the superfluous reflections and unless all reflections of similar resolution are included, these modulations can be misleading. (ii) The \( d \) values of the chosen reflections should be in the same range as the expected density fluctuations (e.g. the pore size of a zeolite, or the ‘thickness’ of an organic molecule). (iii) All directions in reciprocal space should be represented.

Depending on the group space in question, up to three reflections can be selected as origin-defining reflections and their phases assigned arbitrarily. In some cases, these reflections alone suffice to produce a useful PNS (see Table 1 and the example of the organic compound cimetidine in the next section). However, further phases must be determined if fewer reflections are needed to define the origin than are required for the calculation of the surface and/or if the strongest low-index reflections cannot be used as origin-defining reflections (e.g. structure semi-invariants).

The phase determination is not trivial. A direct method approach requires the input of reliable intensity data for a relatively large number of reflections in order to construct the tree of phase relationships, even if the phases of only a few reflections are needed. Furthermore, it must be borne in mind that the \( E \) values of the strongest low-order reflections are not necessarily among the highest \( E \) values when the whole pattern is taken into consideration. Unlike direct methods, the maximum entropy approach to phasing is independent of resolution (Gilmore, 1996), so this may be the more appropriate method to use.

An alternative, less complicated solution to the problem is presently under investigation and preliminary results for centrosymmetric structures are promising. The phases for a set of approximately 20 nonoverlapping strong reflections (\( |E| \geq 1 \)) with a maximum \( d \) spacing of circa 2.7 Å are permuted systematically, a figure-of-merit for each set is calculated and similarities in the phase relationships for those sets with the higher figures-of-merit are evaluated. In this way, the most likely phases for at least a few additional reflections can be extracted relatively easily and quickly.

Usually, no more than one or two reflections are required to supplement the origin-defining ones to generate a useful partitioning surface; thus, in the centrosymmetric case, it is also feasible to consider simply permuting the signs of these reflections and generating all of the corresponding PNS. Some of the surfaces are likely to contradict known chemical information [e.g. the experimentally determined size and dimensionality of a zeolite’s channel system, the fact that voids in a zeolite are found around points of highest symmetry (Brunner, 1990), or geometric considerations] and can therefore be discarded. The remaining surfaces can then be further investigated.

For noncentrosymmetric space groups, the fact that there are often planes with centrosymmetric symmetry (e.g. perpendicular to a twofold axis) can also be exploited by using only those reflections for which \( \alpha \) must be 0 or 180°. In this way, periodic nodal lines (PNL), which are the two-dimensional equivalents of PNS, can be generated within the centrosymmetric planes. The PNL for a cyclic tetramer of a β peptide (Seebach et al., 1997), generated from the \{220\} and \{310\} reflections in the noncentrosymmetric space group \( \Gamma 4 \) is shown in Fig. 3. The presence of a ring structure and the approximate location of the methyl groups are easily discerned from the shape of the PNL.

6. Application to nonzeolite structures

The example above indicates that this procedure can be applied not only to zeolites, but also to other classes of materials. A few organic and ionic structures were examined and as for the zeolites, the centres of the atoms were found to be situated on only one side of the curved surface (see Figs. 2b and 3). The PNS generated using the strongest low-index reflections separates regions of high electron density from those of low electron density, whatever the chemical composition of the material. Of course, the higher the fluctuations in the electron density within the asymmetric unit, the easier it is to generate
To illustrate this fact, the PNS calculated for the organic molecule cimetidine (Fig. 4a) (Hädicke, Frickel & Franke, 1978) using only four reflections is shown in Fig. 4(b). All nonhydrogen atoms of the molecule lie on the positive side of the PNS. Even if only the three origin-defining reflections are used, most of the molecule lies on the positive side of the surface. By changing the partitioning surface from the zero-level PNS to an iso-surface with a slightly negative value [circa 20% of the most negative $\rho(x)$ present], no penetration of the surface occurs and all non-H atoms again lie on one side of the surface (Fig. 4c). Similar effects have been observed in other cases where more reflections were needed to obtain an optimal surface. Of course, the latter approach entails a decrease in the volume that can be excluded in a structure solution algorithm (from circa 50% to circa 40%), but the information is still very useful.

7. Structure solution using the structure envelope

To demonstrate the effectiveness of using the structure envelope in the structure determination process, three of the zeolites listed in Table 1, AlPO$_4$-D (APD topology), Sigma-2 (SGT topology) and RUB-3 (RTE topology), with orthorhombic, tetragonal and monoclinic crystal systems, respectively, will be discussed in more detail. The zeolites have two, four and three tetrahedrally coordinated framework atoms in the asymmetric unit, respectively. The procedure used consisted of the following steps. (i) A set of origin-defining reflections with high $E$ values and large $d$ spacings, which do not overlap in $2\theta$, were selected. (ii) A PNS was generated using these reflections. (iii) An exhaustive search for feasible framework topologies on fixed grid points within the region of the asymmetric unit defined by the structure envelope, using a subroutine of the FOCUS program (Grosse-Kunstleve, 1996), was performed. (iv) The geometries of any topologies found were optimized using a distance least-squares (DLS) procedure (Baerlocher, Hepp & Meier, 1977). (v) If the search was not successful, additional high $E$-value, large $d$-spacing reflections were added to the origin-defining ones.

For these tests, a simple grid search (circa 0.5 Å grid and 0.5 Å tolerance on interatomic distances) was used in step (iii), but of course a more sophisticated approach using the Fourier recycling loop that is built into the FOCUS suite of programs (Grosse-Kunstleve, McCusker & Baerlocher, 1997) would include the information from the powder diffraction pattern and automatically eliminate some of the spurious results that had to be filtered out in the geometry optimization step used here. All calculations were performed on a Silicon Graphics Solid Impact R10000 computer.

For AlPO$_4$-D (APD), two origin-defining reflections can be chosen and the two with the highest $|E|$ values and large $d$ spacings, $\{021\}$ and $\{131\}$, were selected. These sufficed to produce a useful structure envelope (see Fig. 1). For Sigma-2 (SGT), the $\{121\}$ reflection was selected to define the origin, but the PNS generated with just this reflection did not allow the structure to be found, so the phase of a second strong reflection, $\{116\}$, was determined using the permutation/figure-of-merit method outlined earlier, and both reflections were then used to generate a useful PNS. The grid searches were completed in 6 min for APD and in 1.8 min for SGT, and the DLS geometry optimization of the topologies generated singled out the correct topology very clearly. For comparison, grid searches were also performed over the whole asymmetric unit without the structure envelope mask and these took 43 and 123 min, respectively. In other words, the use of the PNS mask increased considerably the efficiency of the topology search.

In the lower symmetry case of RUB-3 (RTE), more than just the two origin-defining reflections were required. A list of the ten reflections with the largest $d$ spacings is given in Table 2. Initially, $\{110\}$ and $\{111\}$ were selected for the generation of the PNS. However, the grid search with this mask did not yield a satisfactory framework topology. Consequently, a third reflection, $\{201\}$, was added to the origin-defining ones. Two surfaces were generated: one with the phase for 201 set at 0° and one with it set at 180°. For the former combination, none of the 56 topologies generated had a satisfactory geometry. For the latter (the correct phase set), the RTE topology emerged as the only geometrically sensible one out of the 15 generated. The two grid searches with the structure envelope mask required 25 min of CPU time. The search without the structure envelope mask was still not finished after more than 48 h. These time differences illustrate very clearly the advantage offered by the structure envelope.

8. Conclusions

It has been demonstrated that a periodic nodal surface (PNS) that partitions a unit cell into regions of high and low electron density can be calculated. This structure envelope can be used to facilitate structure solution from powder diffraction data because the low-index reflections used to generate the PNS lie in the low-angle region of the powder diffraction pattern, where reflections are less prone to overlap. Phases not fixed by the definition of the origin have to be determined, but since there are only a few reflections involved, this obstacle can be overcome. The resulting restriction in the region of the asymmetric unit in which atoms are likely to be found not only reduces the space in which a molecule can be placed (e.g. in a Monte Carlo, simulated annealing or computer modelling
procedure), but also defines the shape of this space. The latter,
in particular, severely limits the number of orientations and
conformations that the molecule can adopt. A few tests on
zeolite framework structures demonstrate that the use of these
surfaces in a direct-space approach to structure solution can
reduce the amount of computer time required by as much as two
orders of magnitude. Thus, the exploitation of this structure
envelope may allow far more complicated structures to be
determined from powder data than has been possible in the past.

We thank G. O. Brunner for providing the impetus for this
study and S. Leone and R. Nesper for many helpful discussions
and for their willingness to share their considerable expertise in
the field of periodic nodal surfaces. We are particularly indebted
to R. W. Grosse-Kunstleve for his assistance with the
modifications to the FOCUS program and to both referees of
the original manuscript for their very valuable comments and
suggestions. This work was supported in part by the Swiss
National Science Foundation.

References
88, 221–242, and references therein.
Program for the Simulation of Crystal Structures by Geometric
Refinement. Institut für Kristallographie, ETH, Zürich, Switzerland.

25, 310–317.
3222–3232.
157–162, 2067–2074.
Geoscience Applications, The McLaren Volume, edited by J. N.
26, 1059–1080, and references therein.
407–412.
Seebach, D., Matthews, J. L., Meden, A., Wessels, Th., Baerlocher, Ch.