Three-dimensional Periodic Nodal Surfaces which Envelope the Threefold and Fourfold Cubic Rod Packings

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Two novel three-dimensional periodic nodal surfaces are calculated from simple Fourier series, corresponding to the space group symmetries $Pm\bar{3}n$ and $Ia\bar{3}d$, respectively. The surfaces are intersection-free space partitioners and they have the unique property of enveloping the well-known threefold and fourfold rod packings, which represent important structural principles. Indeed, in the labyrinths the appropriate Fourier series generate maximal amplitudes along quasi-continuous lines or line segments which correspond to the graphs of well-known networks.

Dedicated to Professor Sten Andersson on the occasion of his 60th birthday.

Recently it was shown by von Schnering and Nesper that periodic nodal surfaces of Fourier series, PNS,[1–3] can be understood as fundamental invariants of structured matter. Of course, close relationships exist to periodic potential surfaces, POPS,[4] as well as to periodic minimal surfaces, whose fundamental significance to chemical structures was recognized by Andersson.[5–8] However, there is one important property of the periodic nodal surfaces which makes them different from the POPS: The PNSs are space partitioners which require no assumptions about a structure. Because of the zeros of the Fourier series, they do not contribute to any physical or chemical force in a structure. They only contain the symmetry in space, which is included in the phase angles α_{hkl} of the few Fourier coefficients.[3]

$$\sum_h |S_h| \frac{|\Phi|^2}{|h|^2} \cos(2\pi hr - \alpha_h) = 0 \qquad (1)$$

The general *Ansatz*[3] is given in eqn. (1), where $|S|$ is the structure factor, α_h is the phase angle, h and r are coordinates in reciprocal and real space and $|\Phi|/|h|$ is a measure of the relative reciprocal length.

When considering this idea, we first tried to reproduce the periodic zero potential surfaces (POPS) by eqn. (1) with as few Fourier coefficients as possible. The first astonishing result was the perfect reproduction of Schoen's gyroid (corresponding to the POPS Y**) only with $|S(100)| = 1$, $\alpha = \pi/2$ and generating symmetry $I4_132$.[9] Eqn. (1) simply becomes eqn. (2), where $X = 2\pi x$ etc.[3] Numerous other examples were tested,[10] and lead at least to the general concept of the periodic nodal surfaces as fundamental invariants of structured matter.[3]

$$\sin X \cos Y + \sin Y \cos Z + \cos X \sin Z = 0 \qquad (2)$$

The cubic POPS I_2–Y** was found in the course of systematic studies carried out to understand the influence of distinct point configurations, PK.[10,11] This surface, which is shown in Fig. 1, looks like a *Weihnachtsstern* (Christmas star) along [111], and runs 'parallel' to the gyroid Y** like an envelope. As a POPS, the surface was first generated with the formal point charge distribution: (1+) at position I_2(16a) and (1−) at position Y**(16b) of space group $Ia\bar{3}d$. The corresponding structure factor listing shows that, close to the reciprocal origin, the reflections (211) and (220) are mainly important, with $F(211) = 1$, $\alpha = 0$ and $F(220) = 2$, $\alpha = 0$.[10] With these two coefficients the surface I_2–Y** is well-reproducible from eqn. (1). Later is was found that with the ratio $F(211)/F(220) = 1$, the topological essentials will not be changed,[3] but that now the resulting amplitudes of the Fourier series indicate very important alterations of the quasi-charge distribution in space. Namely, the amplitudes remain nearly constant when changing the positional parameters within the paths of the line segment configuration spanned by the Y** points, i.e. one moves on a graph between the equivalent points of the configuration Y** ($\frac{1}{8}\,\frac{1}{8}\,\frac{1}{8}$ etc.) in the space group $Ia\bar{3}d$ (cf. Fig. 1). In other words, the PNS of simple Fourier series may correspond to "charge distributions" which are not necessarily distributions of "point charges". The PNS obviously yield a procedure to define in general the shape of the topological pattern, which generates the space partitioner and which is formed by these (Tables 1 and 2).

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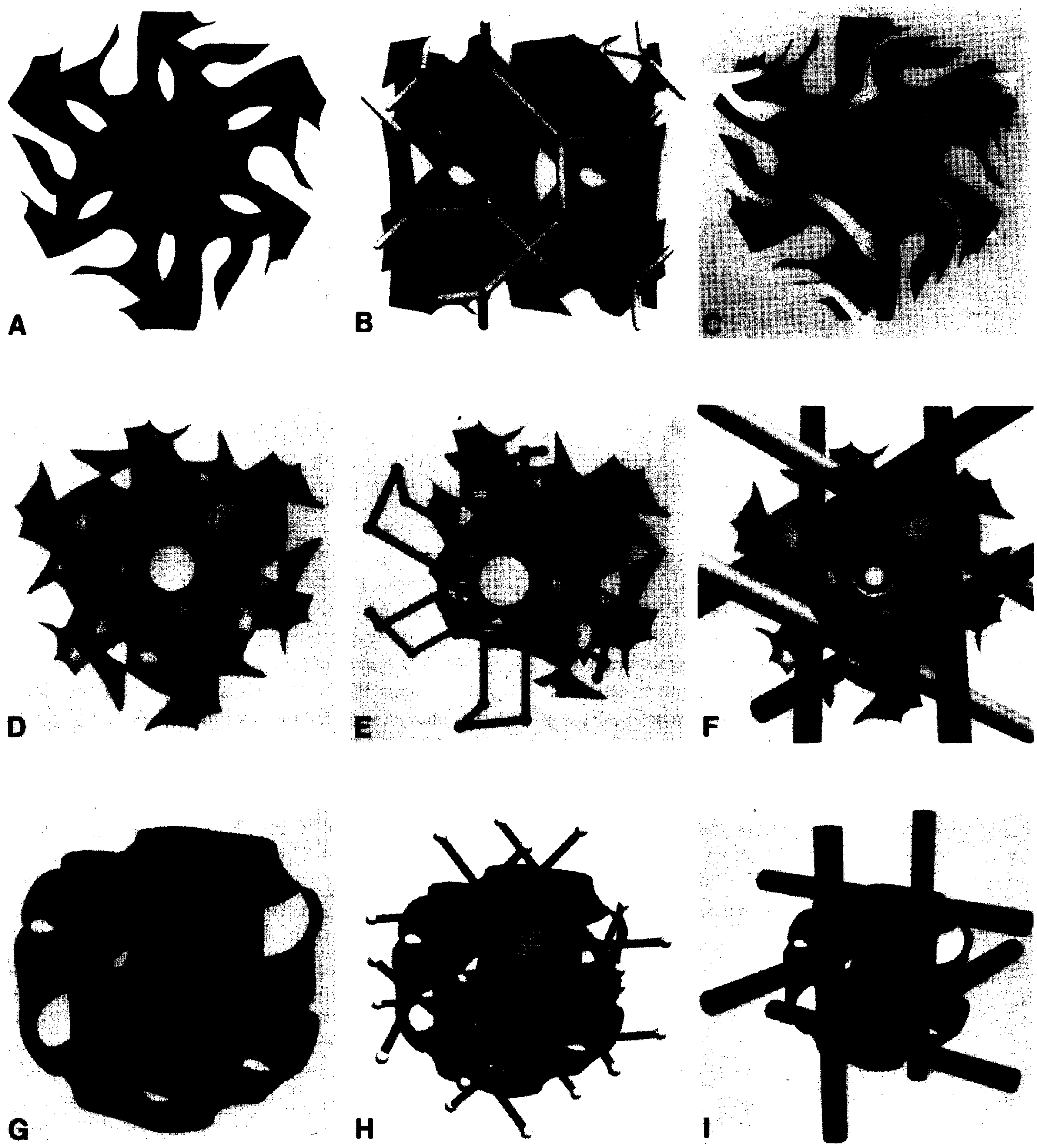

Fig. 1. Periodic nodal surfaces, PNS, and their relationship to line and line segment configurations. (A) The I_2–Y^{**} surface (*Weihnachtsstern*) which is a 'parallel' surface to the gyroid-like Y^{**} surface along [111]. (B) Part of the I_2–Y^{**} surface and the graph of the line segment configuration Y^{**}_{xx} in the red labyrinth along [001]. (C) The I_2–Y^{**} and Y^{**} surfaces together along [111]. (D) The new surface $C(I_2$–$Y^{**})$ along [111]. (E) Part of $C(I_2$–$Y^{**})$ and the graph of the line segment configuration S^* in the red labyrinth along [111]. (F) $C(I_2$–$Y^{**})$ and the graph of the line configuration Y^{**}_{xxx} in the blue labyrinth along [111]. The Y^{**}_{xxx} line configuration corresponds to the famous fourfold cubic rod packing. (G) The new surface W_zI–W_{xx}. (H) W_zI–W_{xx} and the graph of the line segment configuration W_{xx} in the blue labyrinth. This graph corresponds exactly with the Pt_3O_4 partial structure of $Na_xPt_3O_4$. (I) The W_zI–W_{xx} surface envelopes the threefold cubic rod packing in the yellow labyrinth, represented by the line configuration W_z.

Table 1. Representations of the three-dimensional nodal surfaces ($w = |\Phi|^2/|h|^2$).

Name	*hkl*	$\lvert S\rvert \cdot w$	α	Generating space group	$f(x,y,z) = 0$	Symmetry of surface
Y**	110	1	$\pi/2$	$I4_132$	$\sin X \cos Y + \sin Y \cos Z + \cos X \sin Z = 0$	$Ia\bar{3}d$
I_2–Y**	211 220	1 1	0 0	$Ia\bar{3}d$	$-2[\sin 2X \cos Y \sin Z + \sin X \sin 2Y \cos Z + \cos X \sin Y \sin 2Z]$ $+ \cos 2X \cos 2Y + \cos 2Y \cos 2Z + \cos 2X \cos 2Z = 0$	$Ia\bar{3}d$
C(I_2–Y**)	211 220	1 1	π 0	$Ia\bar{3}d$	$+2[\sin 2X \cos Y \sin Z + \sin X \sin 2Y \cos Z + \cos X \sin Y \sin 2Z]$ $+ \cos 2X \cos 2Y + \cos 2Y \cos 2Z + \cos 2X \cos 2Z = 0$	$Ia\bar{3}d$
W_zI–W_{xx}	110 200 210	2 4 1	π π 0	$Pm\bar{3}n$	$-2[\cos X \cos Y + \cos Y \cos Z + \cos X \cos Z]$ $-2[\cos 2X + \cos 2Y + \cos 2Z]$ $+[\cos 2X \cos Y + \cos 2Y \cos Z + \cos X \cos 2Z]$ $-[\cos X \cos 2Y + \cos Y \cos 2Z + \cos 2X \cos Z] = 0$	$Pm\bar{3}n$

Table 2. Relative amplitudes $f(xyz)$ of the Fourier series.

Surface name	Point configuration and Wyckoff position				
	I_2 16a 000	Y** 16b $\frac{1}{8}\frac{1}{8}\frac{1}{8}$	V* 24c $\frac{1}{8}0\frac{1}{4}$	S* 24d $\frac{3}{8}0\frac{1}{4}$	–
Y**	$f=0$ (flat point)	$f=\pm 3$ (point config.)	$f=\pm 2.83$	$f=0$ (saddle)	–
I_2–Y**	$f=+3$ (point config.)	$f=-3$ $\frac{\text{line segments}}{\text{along } \frac{1}{8},\, y,\, \frac{1}{4}-y}$	$f=-3$	$f=+1$	–
C(I_2–Y**)	$f=4$ $\frac{\text{line}}{\text{along } xxx}$	$f=+3$	$f=+1$	$f=-3$ (point config.)	–
	I 2a 000	J* 6b $0\frac{1}{2}\frac{1}{2}$	W 6c $\frac{1}{4}0\frac{1}{2}$	W 6d $\frac{1}{4}\frac{1}{2}0$	P_2 8e $\frac{1}{4}\frac{1}{4}\frac{1}{4}$
W_zI–W_{xx}	$f=-6$ (point config.)	$f=-2$ $\frac{\text{line}}{\text{along } x0\frac{1}{2}}$	$f=-2$	$f=+2$ $\frac{\text{line segments}}{\text{along } \frac{1}{4},\, y,\, \frac{1}{2}+y}$	$f=+3$

Now one can request the topology of space partitioners which are suitable for organizing rod packings. The importance of the threefold and fourfold rod packing to chemical structures was indicated and discussed in detail by O'Keeffe and Andersson[12] and by Hyde and Andersson.[13] The threefold rod packing corresponds to the symmetry group $Pm\bar{3}n$, which is the symmetry of important materials like the so-called A15 superconductors (Nb_3Sn etc.). The fourfold rod packing has $Ia\bar{3}d$ symmetry, and corresponding compounds are also important materials (e.g. garnet).

From the black–white symmetry of the space divided by PNSs, one can see that only such solutions of the problem are possible *where all rods are in the same labyrinth!* The appropriate symmetry of the cubic fourfold rod packing is $Ia\bar{3}d$, and here the four groups of non-intersecting rods correspond to the four groups of non-intersecting threefold axis. The graph which describes this type of line configuration is defined by the infinite number of points 32e xxx with $-\infty < x < +\infty$. The enveloping surface of this line configuration (which represents the central lines of all rods) must have open channels along xxx. This is in contrast to the I_2–Y** surface, which closes these channels at the points Y^{**}_{xxx} with $x = 1/16$. Our idea was that the missing surface may be a complementary one to I_2–Y**. This is true: one only needs to change one of the phase angles from 0 to π to calculate the PNS (Table 1). The surface C(I_2–Y**) is shown in Fig. 1, and it is seen how beautifully this surface envelopes the rod packing. Calculating the amplitudes of the Fourier series according to Table 1, one can show that indeed a continuous "charge distribution" extends along the Y^{**}_{xxx} line graph forming one labyrinth (Table 2). The second labyrinth is characterized by the point configuration S*(24d).

The names I_2–Y** and C(I_2–Y**) were taken to indicate the former point configurations, as well as to show that there exists a type of complementarity (Table 2). Now, with the knowledge of the existence of quasi-continuous line configurations and line segment configurations in the labyrinths, a better description may be given by I_2–Y^{**}_{xx} and S*–Y^{**}_{xxx}.

The cubic three-fold rod packing belongs to the space group $Pm\bar{3}n$. We first found[10] a sufficient surface via a POPS, generated by the point charges (+1) at position J*(6b) and (−1) at position W(6d) of the space group

$Pm\bar{3}n$. Proceeding as shown above, one can simulate this POPS with high accuracy by a PNS calculated with $|S(110)| = 2$, $\alpha = \pi$, $|S(200)| = 4$, $\alpha = 0$ and $|S(210)| = 1$, $\alpha = \pi$ (generating symmetry $Pm\bar{3}n$, Table 1). This surface is shown in Fig. 1, and again the "charge distribution" in the two labyrinths corresponds to nearly continuous graphs (Table 2). One labyrinth is indeed spanned around the line configuration $W(x0\frac{1}{2})$ centred at the point configuration W(6c). This part perfectly envelops the rod packing. The second labyrinth is also organized by a nearly continuous "charge distribution" which substitutes the original "point charges". It is a line segment graph which is exactly the well-known $(8,\frac{3}{4})$a net described by Wells.[14] The line segments connect the positions $6d(\frac{1}{4}\ \frac{1}{2}\ 0)$ and $8e(\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4})$ following the twofold axis $24j(\frac{1}{4}, y, y+\frac{1}{2})$ between $y = \frac{1}{4}$ and $y = \frac{1}{2}$ etc. This line segment configuration may be described (Fig. 1) by $W(\frac{1}{2}, y, y + \frac{1}{2})_{y=1/4}^{y=1/2}$. With respect to all maximal amplitudes (Table 2), the surface will be named $W_xI\text{–}W_{xx}$.

The interpenetrating parts of the rod packings have no intersections, and therefore they were not included in the general systematics of three-dimensional nets.[14] However, it is seen from our discussion that the rod packings can be understood as special cases of three-dimensional nets, where the missing "intersections" are substituted by the symmetry-governed organisation of the whole pattern. We have no doubt that the periodic nodal surfaces, PNS,[3] will contribute to a better understanding of the organisation in crystalline matter by revealing more about the fundamental pattern hidden in graphs of general shape.

The calculations were made on a GX4000/SUN 4 graphic work station.

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