Triply Periodic Bicontinuous Cubic Microdomain Morphologies by Symmetries

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ABSTRACT: In response to thermodynamic driving forces, the domains in microphase-separated block copolymers have distinct intermaterial dividing surfaces (IMDS). Of particular interest are bicontinuous and tricontinuous, triply periodic morphologies and their mathematical representations. Level surfaces are represented by functions F: $\mathbf{R}^3 \rightarrow \mathbf{R}$ of points $(x, y, z) \in \mathbf{R}^3$, which satisfy the equation $F(x, y, z) = t$, where t is a constant. Level surfaces make attractive approximations of certain recently computed triply periodic constant mean curvature (cmc) surfaces and they are good starting surfaces to obtain cmc surfaces by mean curvature flow. The functions $F(x, y, z)$ arise from the nonzero structure factors $F_{(hkl)}$ of a particular space group, such that the resulting surfaces are triply periodic and maintain the given symmetries. This approach applies to any space group and can, therefore, yield desired candidate morphologies for novel material structures defined by the IMDS. We present a technique for generating such level surfaces, give new examples, and discuss certain bicontinuous cubic IMDS in detail.

Introduction

All periodic structures belong to one of the 230 space groups. Usually the primary goal of a structural investigation is to find the specific coordinates within the basic unit cell (a fundamental translational repeat unit) of all the various types of atoms of a material. This knowledge fully describes the structure. There are many structures that are noncrystalline at the atomic level but are crystalline at supermolecular length scales. In these mesoscopic crystalline materials, interest is not in the individual locations of the atoms and molecules but, rather, in the characterization of the interfaces separating adjacent regions of different composition. At high temperatures, entropic forces dominate and the structure is a homogeneous mixture. At lower temperatures, repulsive enthalpic interactions exert themselves, leading to the formation of ordered phases. The microdomain structure is the result of the balance between interfacial energy (which seeks to minimize surface area and favors cmc surfaces) and chain stretching energy (which seeks to minimize variation of the size of the coils and favors parallel surfaces). We therefore focus our attention on the interface between the components. We define this interface as the intermaterial dividing surface (IMDS)[1] and model it as a smooth, mathematical surface since the typical dimensions of the unit cell in block copolymer mesoscopic crystals are 50−100 nm, much larger than the typical width of the composition profile across the interface (3 nm or less).

Motivation and Overview of Triply Periodic Bicontinuous IMDS in Block Copolymer Systems. A block copolymer is a macromolecule comprised of two or more types of monomer units covalently linked in one or more junctions. The first detailed structural investigation of a periodic bicontinuous structure in a block copolymer was published in 1986.[2] The particular block copolymers examined were multiarm star diblock copolymers of polyisoprene and polystyrene. The blocks microphase separate into two nearly pure types of microdomains, one comprised of the polystyrene (PS) blocks and the other of the polyisoprene (PI) blocks. The proposed structure was cubic $Pn3m$ (space group 224) and called "OBDD", which stands for ordered bicontinuous double diamond, since the proposed structure contained two separate, connected, triply periodic, tetrahedrally coordinated networks comprised of the PS blocks in a matrix of the PI block. Both the PS and PI domains are three-dimensionally continuous. Certain TEM images[3] were later compared with two-dimensional simulations of a double diamond structure based on the cmc family of Schwarz's D surface.[4] In 1994, another bicontinuous cubic structure, the double gyroid, with space group $Ia\bar{3}d$ was discovered in a low molecular weight PS/PI diblock[5] and in a diblock/diblock blend.[6] Certain TEM images of this double gyroid (DG) structure were strongly reminiscent of the prior OBDD images, suggesting a reexamination of the star diblock structure. Improved X-ray measurements led us to revise the assignment of the star diblock structure to DG.[7]

In general, for the block copolymer microdomain structures that had been determined up to 1986, namely spheres packed on a body-centered cubic lattice, cylinders packed on a hexagonal lattice, and alternating lamellae, the actual IMDS observed is in all cases very close to a cmc surface. The fundamental reason the previously identified block copolymer microdomain structures are based on spherical, cylindrical, and planar (lamellar) structures is due to the similarity of the thermodynamic problem of microphase separation to the mathematical problem of area minimization under fixed volume (or volume fraction) constraints, which immediately leads to solutions that are periodic dividing surfaces with constant mean curvature.[1] Of course, the

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polymer physics contains other features in addition to minimization of interfacial area at fixed volume fraction. In particular, both of the component block copolymer chains must uniformly fill the various regions defined by IMDS, and these chains would prefer to have random conformations and a uniform environment, requirements which can be frustrated to various extent by an IMDS having everywhere constant mean curvature.[8]

In recent years, a number of new IMDS microdomain structures have been discovered, particularly in ABC linear and miktoarm star terpolymer systems, where the additional type of block and presence of two junctions per molecule, and/or star architecture, can strongly influence the geometry of the equilibrium microdomain morphology.[9−13] Thus, it is important to have the means to generate new models for the host of emerging complex microdomain structures owing to the ongoing synthesis of novel multicomponent, variable architecture block copolymers. The additional requirement that the candidate IMDS have precisely constant mean curvature is not of paramount importance, as a cmc surface can often be obtained by curvature flow from a surface which is not cmc,[14] and since distinctly non-cmc IMDS microdomain shapes have been found.[8,9,15,16]

I. Geometry and Symmetries of Level Surfaces

To begin, we state some basic facts concerning the geometry of level surfaces. We take on $\boldsymbol{R^3}$ the usual (x, y, z) coordinate system and the Euclidean scalar product $\langle\ ,\ \rangle_{\mathbf{R}^3}$. Let F: $\boldsymbol{R^3} \rightarrow \boldsymbol{R}$ be a smooth function. A point $p \in \mathbf{R^3}$ is a point on the surface S_t if $F(p) = t$; hence $S_t = F^{-1}(t) = \{p \in \boldsymbol{R^3}\colon\ F(p) = t\}$. If we have two level surfaces F_1 and F_2 then the level surface given by the sum $c_1F_1 + c_2F_2$ has the greatest common symmetries of F_1 and F_2, unless of course the linear combination is a constant.

An isometry in $\boldsymbol{R^3}$ is a map σ: $\boldsymbol{R^3} \rightarrow \boldsymbol{R^3}$, which preserves distances between points. The symmetries of a surface S are all the isometries which map S onto itself. In $\boldsymbol{R^3}$ the crystallographic symmetries are as follows: translations, rotations, reflections, screws, glide reflections, rotary reflections, and inversions.

We are principally interested in generating surfaces which periodically divide space into 3-D connected labyrinthine regions. Filling the labyrinths with distinct block copolymers is equivalent to coloring the IMDS differently on the inside and the outside. Thus, when choosing the appropriate space group for a given structure we do not want to include symmetry operations which would interchange the different polymer regions. For instance, we assign the space group $Pm\bar{3}m$ to Schwarz's P surface instead of a supergroup $Im\bar{3}m$, which would correspond to a single-color P surface with indistinguishable polymer regions on each side.

II. Derivation of Level Set Equations for Space Groups

To find the appropriate surface describing a given microphase-separated morphology we start with its symmetries, which can be determined from transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS) experiments. Given a set of symmetries of a periodic structure, one can determine from the *International Tables for Crystallography* (ITC) the space group of that structure.[17] To find suitable candidate functions which are invariant under the space group symmetry operations we borrow a tool from X-ray crystallography, the structure factor. The structure factor $F_{(hkl)}$ describes the amplitudes and phases of the three-dimensional diffraction pattern due to the scattering of incident radiation off of planes (hkl) of atoms in the crystalline structure. We use the structure factor terms because they have all the symmetries of the structure; however, for special values of h, k, and l, the factor $F_{(hkl)}$ can have extra symmetries. (We only consider $F_{(hkl)}$ which are nonzero since those are the allowed terms for the space group. A function which is zero everywhere has infinitely many symmetry elements.) For instance, in a noncentrosymmetric space group there can be $F_{(hkl)}$ terms that are centrosymmetric. In group $I4_132$, for example, planes (211) give rise to a structure factor which is invariant under inversion (thus the $F_{(211)}$ level surface is centrosymmetric), while the space group as a whole does not have inversion symmetry.

Another approach which can yield simple analytic expressions for periodic bicontinuous partitions of space was developed earlier by von Schnering and Nesper.[18,19] They calculated zero-potential (nodal) surfaces based on selected distributions of point charges. This method involves taking the Fourier transform of point charge distributions and leads again to the structure factor of the chosen space group. The principal aim of nodal surface calculations is to obtain simple expressions for the approximation of three-dimensional periodic minimal surfaces, since these surfaces are relevant models for amphiphilic monolayers in bicontinuous mixtures of oil, water and an amphiphile.[18] Schwarz and Gompper also have employed Fourier series to approximate nodal surfaces and have computed the variation of mean and Gaussian curvature over the surfaces.[20] Harper and Gruner used X-ray scattering to analyze lipid−water systems and constructed models for the sample electron density profile based on Fourier terms for the appropriate space group of the P, D, and G minimal surfaces.[21]

To find level set equations which could correspond to physical intermaterial dividing surfaces we consider the structure factors $F_{(hkl)}$ for small values of h, k, and l. Larger values of h, k, and l will, in general, correspond to surfaces with higher genus, which are less favorable due to their larger surface energy. Additionally, we only need to take a single permutation out of all possible ones of $\pm h$, $\pm k$, and $\pm l$ because for cubic groups these will only differ up to an exchange of axes or a sign. Moreover, we set the numerical coefficient of $F_{(hkl)}$ to unity since scaling does not affect symmetry.

Interesting new level sets can be obtained by taking combinations of several $F_{(hkl)}$ terms. To obtain surfaces which belong to a particular group and not its supergroup we need to include at least one term which only has the symmetry of that group.

The general form of $F_{(hkl)}$ is given by

$$F_{(\mathrm{hkl})} = \sum_j f_j \sum_n [\cos 2\pi\,(hx_n + ky_n + lz_n) + i \sin 2\pi\,(hx_n + ky_n + lz_n)] \quad (1)$$

where f_j is a factor corresponding to the strength of scattering of the jth type of atoms and (x_n, y_n, z_n) is the nth equivalent position of the jth type of atoms in the unit cell. The symmetry of the space group is conveyed to the structure factor through the set of $\{x_n, y_n, z_n\}$; therefore, we can set f_j equal to 1. The structure factor then becomes

$$F_{(\mathrm{hkl})} = \sum_n [\cos 2\pi (hx_n + ky_n + lz_n) + i \sin 2\pi (hx_n + ky_n + lz_n)] \quad (2)$$

The remaining requirement is to convert the structure factor in eq 1, which is in general complex, into a real level set equation. Let $F_{(hkl)} = A + iB$. If B is equal to zero, $F_{(hkl)}$ is real and the level set equation is simply $F(x, y, z) = A = t$. If A is zero, we take $F(x, y, z) = B = t$. This covers all the cases considered in this paper, however, there are space groups, for instance group No. 220, where low-order structure factor terms have both real and imaginary parts. When this occurs, we consider both the terms of the form $F^A(x, y, z) = A = t$ and $F^B(x, y, z) = B = t$.

The ITC tabulate expressions for each space group that can be used to compute the specific form of eq 1. There are 36 groups with cubic symmetry. We illustrate this procedure in detail for seven cubic space groups in the subsequent sections.

III. Level Surfaces with $Pm\bar{3}m$, $Im\bar{3}m$, and $Fm\bar{3}m$ Symmetry

The space group $Pm\bar{3}m$ (No. 221) has forty-eight general positions created by its set of symmetries. Since the origin of the unit cell can be chosen on an inversion center, $F_{(hkl)}$ is centrosymmetric, therefore, only the A term from eq 2 contributes to the level set function. The set of 48 equipoints listed for $Pm\bar{3}m$ is

$$x, y, z; \bar{x}, \bar{y}, z; \bar{x}, y, \bar{z}; x, \bar{y}, \bar{z}$$

$$z, x, y; z, \bar{x}, \bar{y}; \bar{z}, \bar{x}, y; \bar{z}, x, \bar{y}, \text{ etc.}$$

Equation 2 for the $Pm\bar{3}m$ group has 48 terms

$$\begin{aligned} F_{(hkl)} = {} & \cos 2\pi hx \cos 2\pi ky \cos 2\pi lz + \\ & \cos 2\pi h\bar{x} \cos 2\pi k\bar{y} \cos 2\pi lz + \\ & \cos 2\pi h\bar{x} \cos 2\pi ky \cos 2\pi l\bar{z} + \\ & \cos 2\pi hx \cos 2\pi k\bar{y} \cos 2\pi l\bar{z} + \\ & \cos 2\pi hz \cos 2\pi kx \cos 2\pi ly + \\ & \cos 2\pi hz \cos 2\pi k\bar{x} \cos 2\pi l\bar{y} + \\ & \cos 2\pi h\bar{z} \cos 2\pi k\bar{x} \cos 2\pi ly + \\ & \cos 2\pi h\bar{z} \cos 2\pi kx \cos 2\pi l\bar{y} + \ldots \quad (3) \end{aligned}$$

which, after dividing through by 8 to make the coefficient equal to 1, becomes

$$\begin{aligned} F_{(hkl)} = {} & \\ & \cos 2\pi hx [\cos 2\pi ky \cos 2\pi lz + \cos 2\pi ly \cos 2\pi kz] + \\ & \cos 2\pi hy [\cos 2\pi kz \cos 2\pi lx + \cos 2\pi lz \cos 2\pi kx] + \\ & \cos 2\pi hz [\cos 2\pi kx \cos 2\pi ly + \cos 2\pi lx \cos 2\pi ky] \quad (4) \end{aligned}$$

We arrange the allowed $F_{(hkl)}$ in order of increasing values of $h^2 + k^2 + l^2$. For group $Pm\bar{3}m$ the first $F_{(hkl)}$ has $h = 1$, $k = 0$, $l = 0$. Using the simplified expressions in the ITC we find that

$$F_{(100)} = \cos 2\pi x + \cos 2\pi y + \cos 2\pi z \quad (5)$$

The second term in the series has $h, k, l = (110)$ and

$$F_{(110)} = \cos 2\pi x \cos 2\pi y + \cos 2\pi y \cos 2\pi z + \cos 2\pi z \cos 2\pi x \quad (6)$$

Similarly, the third and fourth terms on the series are given by $\cos 2\pi x \cos 2\pi y \cos 2\pi z$ and $\cos 4\pi x + \cos 4\pi y + \cos 4\pi z$, respectively.

Level Surfaces of the Type $F_{(100)} = t$. We now examine the level surface family given by the first term: $F_{(100)} = t$. Figure 1a shows a three-dimensional plot of the surface with $t = 0$ over a unit cell taken from $-1/2$ to $+1/2$. This surface divides space into two continuous regions of equal volume. As previously noted by a number of authors, this level surface is quite similar in appearance to Schwarz's minimal P surface.[22] Of course, the $F_{(100)}$ level surface is not a minimal surface. Anderson et al.[4] numerically computed the cmc family based on the P surface. In the cmc family the ratio of the subvolumes varies with the mean curvature. By taking $F_{(100)} = t \neq 0$, a family of level surfaces with a strong resemblance to the cmc family of the P surface can be constructed.[23] The cmc family exists from a volume fraction of 0.5 to 0.25 with $\phi = 0.353\,99$ at pinch-off (the surface no longer subdivides space into two continuous subvolumes), while the level set family exists from 0.5 to the pinch-off at $\phi = 0.210\,29$ with $t = 1$.

$F_{(110)} = t$ Family. The surface described by

$$F_{(110)} = \cos 2\pi x \cos 2\pi y + \cos 2\pi y \cos 2\pi z + \cos 2\pi z \cos 2\pi x = t \quad (7)$$

appears similar to another minimal surface, Schoen's I−WP surface, for a certain range of t values. Figure 1b shows an I−WP surface with $t = -0.25$. Anderson et al.[4] also numerically computed a cmc family for I−WP.

Combination Level Surfaces. It is interesting to explore two-parameter families, for example, $sF_{(100)} + (1 - s)F_{(110)} = t$, where the parameter ranges are infinite for both s and t. However, for our purposes an overall scaling factor is not important, as it will only affect the frequency of the surface. Thus, we can restrict our search to s values between 0 and 1 (with the corresponding t values, limited by the bounds on the values of trigonometric functions) if we consider $sF_{(100)} \pm (1 - s)F_{(110)} = t$. Figure 1c shows an array of images obtained by varying s and t in a region which yields continuous surfaces. By changing s from 0 to 1, we obtain surfaces that change from the I−WP family to the P family. At intermediate values a new family emerges with combined features, as shown in Figure 1d. This level set resembles yet another triply periodic minimal surface, Schoen's O, CT-O surface.[24] The O, CT-O minimal surface can be regarded as a combination of Schwarz's P minimal surface and Schoen's I−WP minimal surface.

The O, CT-O surface can also be modeled within the $sF_{(110)} \pm (1 - s)F_{(111)} = t$ family. This family also yielded, for a certain range of s and t values, members of another known constant mean curvature family[4]—that based on Neovius' minimal surface.[25] An example of a level set approximation of Neovius' surface, called C(P), is shown in Figure 1e. We also found an expression for the level set approximation to a combination of the P and C(P) surfaces, previously shown by Karcher[26] to be another minimal surface with $Pm\bar{3}m$ symmetry. This surface is shown in Figure 1f and is built from a combination of F_{100}, F_{110}, F_{111}, F_{200}, F_{222} and F_{300} terms. Another interesting surface from this group resembling a minimal surface, also found by Karcher,[27] is the K surface, shown in Figure 1g.

Supergroups: $Im\bar{3}m$ and $Fm\bar{3}m$. The cubic space groups $Im\bar{3}m$ and $Fm\bar{3}m$ are supergroups of $Pm\bar{3}m$. They differ only by a body-centering translation in $Im\bar{3}m$ and face-centering translations in $Fm\bar{3}m$. The reduced terms of group $Im\bar{3}m$ are nonzero only for $h +$

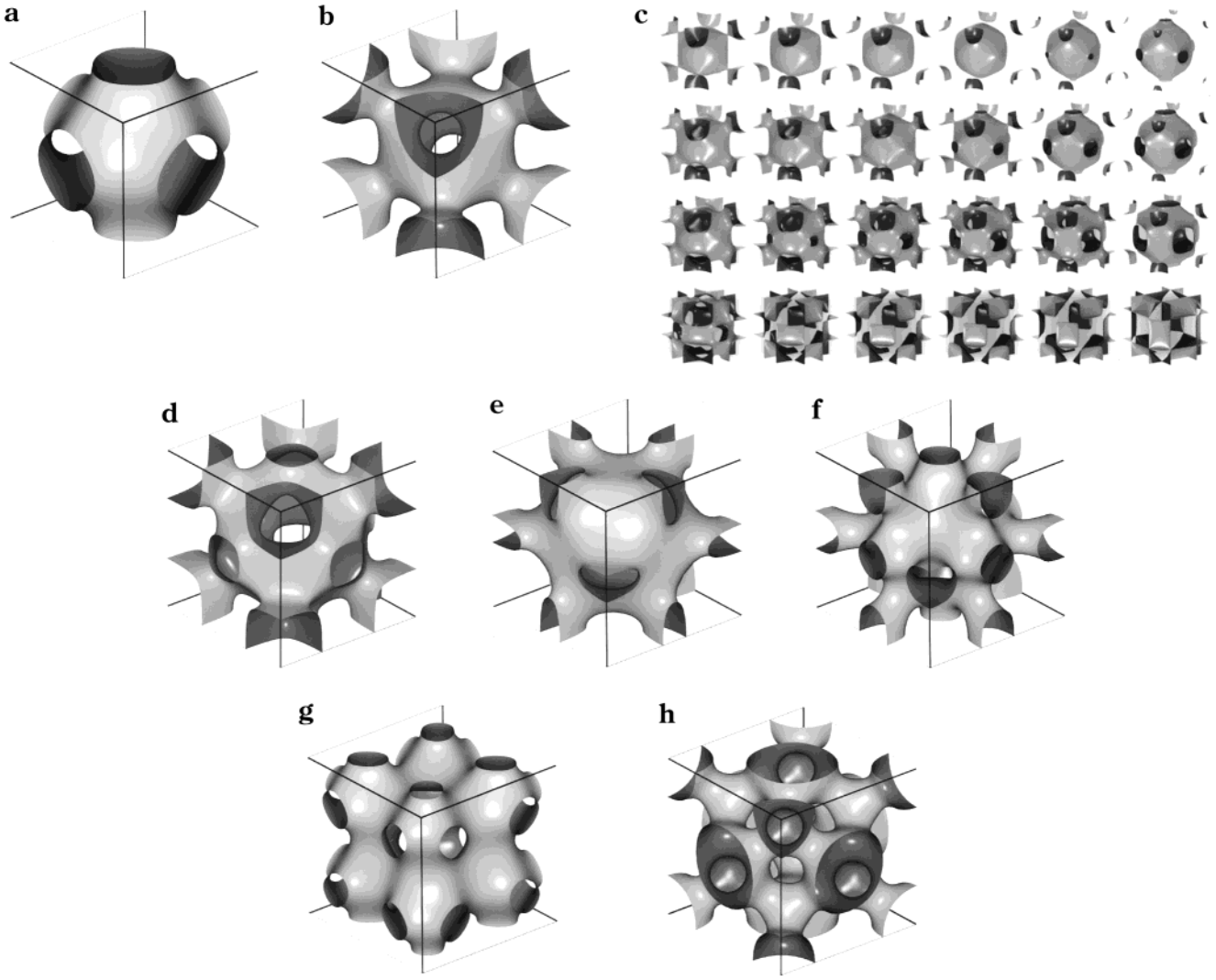

Figure 1. (a) Level set approximation for the P surface: $F(x, y, z) = F_{(100)} = \cos 2\pi x + \cos 2\pi y + \cos 2\pi z = 0$. This surface has genus 3. (b) Level set approximation to the I−WP surface: $F(x, y, z) = F_{(110)} = \cos 2\pi x \cos 2\pi y + \cos 2\pi y \cos 2\pi z + \cos 2\pi z \cos 2\pi x = -0.25$. The I−WP surface has genus 7. (c) Part of the two-parameter experiment for group No. 221. The basic equation is s (cos x + cos y + cos z) + (1 − s) (cos x cos y + cos y cos z + cos z cos x) = t, where s varies from 0 to 1. The values of t are changing along the horizontal axis, and s is varied along the vertical axis. There are distinct regions on the graph where P, I−WP, and the combination surface O, CT-O are located. (d) Approximation of the O, CT-O surface. In this part, we use the second and the third terms in the series, but it is also possible to obtain similar, though less minimal-like plots by using the first and the second terms, as shown in Figure 1c. $F(x, y, z) = 0.6\ F_{(110)} - 0.4F_{(111)} = 0.6$ (cos $2\pi x$ cos $2\pi y$ + cos $2\pi y$ cos $2\pi z$ + cos $2\pi z$ cos $2\pi x$) − 0.4 cos $2\pi x$ cos $2\pi y$ cos $2\pi z = 1$. The genus of the O, CT-O is 10. (e) Approximation to the Neovius' surface C(P). The equation is $F(x, y, z) = 0.6\ F_{(100)} - 0.4\ F_{(111)} = 0.6$ (cos $2\pi x$ + cos $2\pi y$ + cos $2\pi z$) − 0.4 cos $2\pi x$ cos $2\pi y$ cos $2\pi z = -0.3$. The genus of this surface is 9. (f) P + C(P) surface approximation. The equation is given by $F(x, y, z) = 0.35\ F_{(111)} + 0.2\ F_{(100)} + 0.2\ F_{(222)} + 0.1\ F_{(200)} + 0.05\ F_{(300)} + 0.1\ F_{(110)} = 0.35$ cos $2\pi x$ cos $2\pi y$ cos$2\pi z$ + 0.2(cos $2\pi x$+ cos $2\pi y$ + cos $2\pi z$) + 0.2(cos $4\pi x$ cos $4\pi y$ cos $4\pi z$) + 0.1(cos $4\pi x$ + cos $4\pi y$ + cos $4\pi z$) + 0.05(cos $6\pi x$ + cos $6\pi y$ + cos $6\pi z$) + 0.1(cos $2\pi x$ cos $2\pi y$ + cos$2\pi y$ cos $2\pi z$ + cos $2\pi z$ cos $2\pi x$) = 0. A minimal surface with this topology was discovered by Karcher.[25] The genus is 12. (g) K surface approximation. This surface was also discovered by Karcher.[25] The equation is given by $F(x, y, z) = 0.3F_{(100)} + 0.3F_{(110)} - 0.4F_{(200)} = 0.3$ (cos $2\pi x$ + cos $2\pi y$ + cos $2\pi z$) + 0.3(cos $2\pi x$ cos $2\pi y$ + cos $2\pi y$ cos $2\pi z$ + cos $2\pi z$ cos $2\pi x$) − 0.4 (cos $4\pi x$ + cos $4\pi y$ + cos $4\pi z$) = − 0.2. The genus of this surface is 12. (h) F−RD surface approximation. The equation is $F(x, y, z) = 0.8\ F_{(111)} + 0.1F_{(222)} - 0.1F_{(220)} = 0.8$ cos $2\pi x$ cos $2\pi y$ cos $2\pi z$ + 0.1(cos $4\pi x$ cos $4\pi y$ cos $4\pi z$) − 0.1(cos $4\pi x$ cos $4\pi y$ + cos $4\pi y$ cos $4\pi z$ + cos $4\pi z$ cos $4\pi x$) = 0. The genus of this surface is 6.

$k + l = 2n$ and for the group $Fm\bar{3}m$ are nonzero only if h, k, l are all odd or all even. Nonzero reduced $F_{(hkl)}$ terms are identical for this subgroup and its supergroups.

A combination of the first two level set terms of the $Fm\bar{3}m$ space group gives us an approximation to another triply periodic minimal surface discovered by Schoen,[23] the F−RD. Figure 1h shows an example of a member of the F−RD family using the first, third and fifth terms:

$$F_{F-RD}(x, y, z) = 0.8\ F_{(111)} - 0.1F_{(220)} + 0.1F_{(222)} = 0 \quad (8)$$

Anderson et al.[4] also computed the F−RD cmc family.

IV. The Level Surfaces with $I4_132$ and $Ia\bar{3}d$ Symmetry

Level set equations for another pair of cubic space groups, $I4_132$ space group (No. 214) and its supergroup $Ia\bar{3}d$ (No. 230), are of interest because they relate to the double gyroid microdomain structure found in many block copolymer materials.[5,6,13,16,28] The group $Ia\bar{3}d$ contains all the symmetries of $I4_132$ as well as inversion. The first few allowed reflections for $I4_132$ and for $Ia\bar{3}d$ are (110), (211), (220), and (211), (220), respectively. Schoen's infinite periodic minimal G surface, the so-

called "gyroid" surface, has the symmetries of space group $I4_132$.[23] This cubic space group does not a center of symmetry, so the $F_{(hkl)}$ can have contributions from both *A* and *B* terms. The unit cell is body-centered cubic, so in addition to the three translations along the *x*, *y*, and *z* axes there is a centering translation ($^1/_2$, $^1/_2$, $^1/_2$). The set of symmetries for $I4_132$ generates 48 equipoints for the general position. Equation 2 for the $I4_132$ group can be simplified so that its *A* and *B* components have six terms each:

$$F^A_{(hkl)}(x, y, z) = \cos 2\pi\left(\frac{h+k+l}{4}\right) \times \left\{\cos 2\pi\left(hx + \frac{l}{4}\right) \cos 2\pi\left(ky + \frac{h}{4}\right) \cos 2\pi\left(lz + \frac{k}{4}\right) + \cos 2\pi\left(hy + \frac{l}{4}\right) \cos 2\pi\left(kz + \frac{h}{4}\right) \cos 2\pi\left(lx + \frac{k}{4}\right) + \ldots\right\} \quad (9a)$$

and

$$F^B_{(hkl)}(x, y, z) = \cos 2\pi\left(\frac{h+k+l}{4}\right) \times \left\{\sin 2\pi\left(hx + \frac{l}{4}\right) \sin 2\pi\left(ky + \frac{h}{4}\right) \sin 2\pi\left(lz + \frac{k}{4}\right) + \sin 2\pi\left(hy + \frac{l}{4}\right) \sin 2\pi\left(kz + \frac{h}{4}\right) \sin 2\pi\left(lx + \frac{k}{4}\right) + \ldots\right\} \quad (9b)$$

The first allowed term is $F_{(110)}$:

$$F^B_{(110)}(x, y, z) = \sin 2\pi y \cos 2\pi z + \sin 2\pi z \cos 2\pi x + \sin 2\pi x \cos 2\pi y \quad (10)$$

Figure 2a depicts the unit cell of this surface with $t = 0$. The surface appears quite similar to Schoen's gyroid minimal surface. A level set family of $F_{(110)}$ exists for the range $t = \pm\sqrt{2}$, which corresponds to values of ϕ from 0.5 to 0.046. Since the gyroid surface does not have inversion symmetry, it cannot be approximated by terms from group $Ia\bar{3}d$.

***F*(211) = *t* Family and Combination Level Surfaces.** The next nonzero term for group $I4_132$ and the first allowed term for group $Ia\bar{3}d$ is $F_{(211)}$:

$$F_{(211)} = A = \sin 4\pi x \cos 2\pi y \sin 2\pi z + \sin 4\pi y \cos 2\pi z \sin 2\pi x + \sin 4\pi z \cos 2\pi x \sin 2\pi y = t \quad (11)$$

Setting $F_{(211)}$ equal to zero does not yield a smooth surface. However, by varying *t* we can obtain a continuous surface, G′. The surface (shown with $t = -0.5$ in Figure 2b) is a member of the C(I_2-Y**) family discovered by von Schnering. This surface is similar to the gyroid but with extra tunnels inserted along ⟨111⟩ directions to create inversion symmetry, so its space group is $Ia\bar{3}d$.

Exploration of the linear combination $sF_{(110)} \pm (1 - s)F_{(211)} = t$ does not lead to a topologically new intermediate surface. The next term in the series, $F_{(220)}$, is simply an I−WP approximation with twice the frequency of eq 7. The combination $sF_{(211)} \pm (1 - s)F_{(220)} = t$ yields two interesting surfaces—an approximation of the double gyroid microdomain structure, denoted DG (called I_2-Y** by von Schnering), and another interesting surface named the Lidinoid after S. Lidin.[29] The Lidinoid surface is shown in Figure 2e. This surface has handles to the face centers, vertexes and midpoints of all edges. The *s*, *t* array of combination images including DG and L is shown in Figure 2c. The double gyroid has the symmetries of $Ia\bar{3}d$; it consists of right- and left-handed networks of a single nonminimal gyroid, as shown in Figure 2d. Grosse-Brauckmann[30,31] computed the cmc family of gyroid surface using Brakke's Surface Evolver.[14]

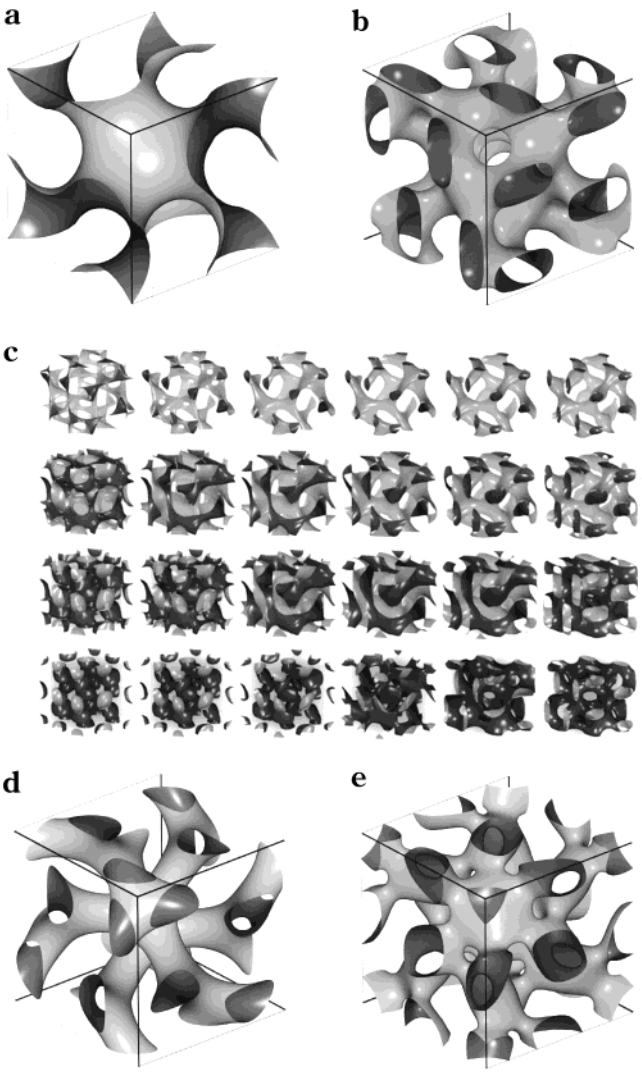

Figure 2. (a) *G* (gyroid) level surface: $F(x, y, z) = F_{(110)} = \sin 2\pi y \cos 2\pi z + \sin 2\pi z \cos 2\pi x + \sin 2\pi x \cos 2\pi y = 0$. The genus of this surface is 3. (b) G′ surface level set: $F(x, y, z) = F_{(211)} = \sin 4\pi x \cos 2\pi y \sin 2\pi z + \sin 4\pi y \cos 2\pi z \sin 2\pi x + \sin 4\pi z \cos 2\pi x \sin 2\pi y = -0.32$. G′ has several new features as compared to the gyroid, e.g., extra holes and tunnels. Unlike the gyroid, G′ belongs to space group 230. (A surface from this family which uses $F_{(211)} + 0.5\ F_{(220)}$ has been named C(I_2-Y**) by von Schnering and Nesper.[19]) The G′ surface has genus 12. (c) Part of the two-parameter experiment for space group No. 230. The basic equation is $F(x, y, z) = sF_{211} \pm (1 - s)F_{220} = t$. (d) Double gyroid surface approximation. The equation is $F(x, y, z) = 0.8F_{(211)} - 0.2F_{(220)} = 0.8(\sin 4\pi x \sin 2\pi z \cos 2\pi y + \sin 4\pi y \sin 2\pi x \cos 2\pi z + \sin 4\pi z \sin 2\pi y \cos 2\pi x) - 0.2(\cos 4\pi x \cos 4\pi y + \cos 4\pi y \cos 4\pi z + \cos 4\pi z \cos 4\pi x) = 0$. (e) Approximation to the *L* surface. The equation is $F(x, y, z) = 0.5\ F_{(211)} - F_{(220)} = 0.5(\sin 4\pi x \cos 2\pi y \sin 2\pi z + \sin 4\pi y \cos 2\pi z \sin 2\pi x + \sin 4\pi z \cos 2\pi x \sin 2\pi y) - 0.5(\cos 4\pi x \cos 4\pi y + \cos 4\pi y \cos 4\pi z + \cos 4\pi z \cos 4\pi x) = -0.15$.

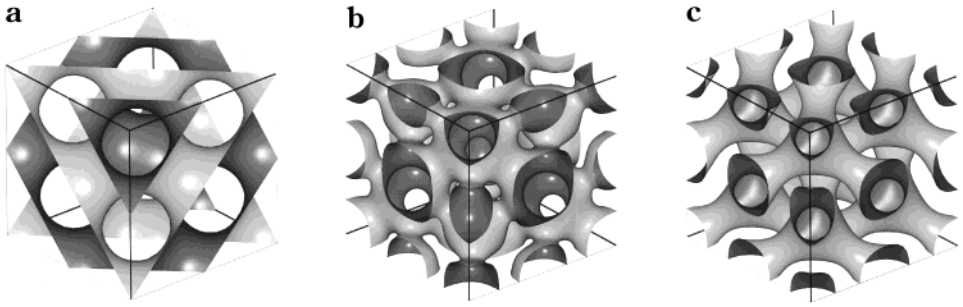

Figure 3. (a) D surface level set approximation, shifted here by $\pi/4$ for a more familiar representation: $F(x, y, z) = F_{(111)} = \cos 2\pi x \cos 2\pi y \cos 2\pi z + \sin 2\pi x \sin 2\pi y \cos 2\pi z + \sin 2\pi x \cos 2\pi y \sin 2\pi z + \cos 2\pi x \sin 2\pi y \sin 2\pi z = 0$. The genus of the D surface is 3. (b) D′ surface level set: $F(x, y, z) = 0.5F_{(111)} - 0.5F_{(220)} = 0.5(\cos 2\pi x \cos 2\pi y \cos 2\pi z + \cos 2\pi x \sin 2\pi y \sin 2\pi z + \sin 2\pi x \cos 2\pi y \sin 2\pi z + \sin 2\pi x \sin 2\pi y \cos 2\pi z) - 0.5(\sin 4\pi x \sin 4\pi y + \sin 4\pi y \sin 4\pi z + \sin 4\pi z \sin 4\pi x) = 0.2$. This is a *new* triply periodic surface with $Fd\bar{3}m$ symmetry and genus 9. (c) Double diamond surface, shown here in a shifted unit cell for easier visualization. $F(x, y, z) = 0.5F_{(110)} + 0.5F_{(111)} = 0.5(\sin 2\pi x \sin 2\pi y + \sin 2\pi y \sin 2\pi z + \sin 2\pi x \sin 2\pi z) + 0.5(\cos 2\pi x \cos 2\pi y \cos 2\pi z) = 0$.

V. Level Surfaces with $Fd\bar{3}m$ and $Pn\bar{3}m$ Symmetry

Schwarz's D surface[21] is a triply periodic minimal surface with the symmetries of space group $Fd\bar{3}m$ (No. 227). The related family of constant mean curvature surfaces was computed by Anderson et al.[4] The set of symmetries for the $Fd\bar{3}m$ group generates 192 equipoints for the general position. Equation 2 for the $Fd\bar{3}m$ becomes

$$F_{(hkl)} = \cos^2 2\pi\left(\frac{h+k}{4}\right)\cos^2 2\pi\left(\frac{k+l}{4}\right) \times \left\{\cos 2\pi(hx+ky+lz) + \cos 2\pi\left(hx+ky-lz-\frac{h+k}{4}\right) + \cos 2\pi\left(hx-ky+lz+\frac{l+h}{4}\right) + \ldots\right\} \quad (12)$$

The allowed low-order terms are (111), (220), (311), (222), etc. The first term is given by

$$F_{(111)} = \cos 2\pi x \cos 2\pi y \cos 2\pi z + \sin 2\pi x \sin 2\pi y \cos 2\pi z + \sin 2\pi x \cos 2\pi y \sin 2\pi z + \cos 2\pi x \sin 2\pi y \sin 2\pi z \quad (13)$$

Figure 3a shows the unit cell of this surface for t equal to 0, which is quite similar to the D minimal surface. A family of continuous level surfaces exists for ϕ values from 0.50 to 0.14, corresponding to t values between 0 and ± 1.

The second allowed term in this group is

$$F_{(220)} = \sin 4\pi x \sin 4\pi y + \sin 4\pi y \sin 4\pi z + \sin 4\pi x \sin 4\pi z \quad (14)$$

This term generates a surface which is similar to the I−WP surface of eq 7 but with double the frequency and a phase shift of $\pi/2$. The combination of the first two terms, $sF_{(111)} \pm (1 - s)F_{(220)}$, yields a *new* bicontinuous surface, D′, which is shown in Figure 3b. This surface has some features of the P, I−WP and C(P) surfaces.

$Pn\bar{3}m$ is a supergroup of $Fd\bar{3}m$. Its low-order nonzero terms are (110), (111), (200), (211), etc. The first term is given by

$$F_{(110)} = \sin 2\pi x \sin 2\pi y + \sin 2\pi y \sin 2\pi z + \sin 2\pi x \sin 2\pi z \quad (15)$$

The above equation also yields an I−WP-like surface with a $\pi/2$ phase shift. The second term for $Pn\bar{3}m$ group is $F_{(111)}$:

$$F_{(111)} = \cos 2\pi x \cos 2\pi y \cos 2\pi z \quad (16)$$

This surface is a periodic set of three orthogonal planes. The combination of these two terms yields a structure consisting of two offset surfaces, each one having diamond symmetry. This structure corresponds to the so-called double diamond structure, the OBDD microdomain morphology (see Figure 3c).[2,32,33]

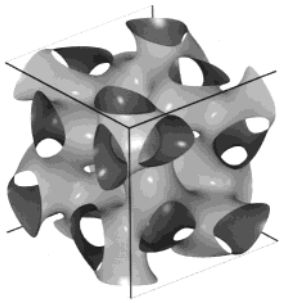

Figure 4. P2-DG surface. This *new* surface belongs to space group No. 198. It arises as a combination of terms of the double gyroid and P surface level sets. The equation for this surface is given by: $F(x, y, z) = 0.7\ F^A_{(211)} - 0.1F_{(220)} - 0.2F_{(200)} = 0.7(\sin 4\pi x \cos 2\pi y \sin 2\pi z + \sin 4\pi y \cos 2\pi z \sin 2\pi x + \sin 4\pi z \cos 2\pi x \sin 2\pi y) - 0.1(\cos 4\pi x \cos 4\pi y + \cos 4\pi y \cos 4\pi z + \cos 4\pi z \cos 4\pi x) - 0.2\ (\cos 4\pi y + \cos 4\pi z + \cos 4\pi x) = 0$. The first two terms are from space group No. 230, and the third term is from space group No. 221.

VI. Combining Level Sets from Different Space Groups

Our library of level set surfaces may also be used intuitively to generate surfaces exhibiting the greatest common symmetries of two existing level set surfaces by simply adding the respective terms and adjusting the parameters to obtain continuous surfaces. As an example of generating such new surface we consider combining the term for the P surface with twice the normal frequency ($F_{(200)}{}^{221}$) with the double gyroid terms ($F_{(211)}{}^{230} + F_{(220)}{}^{230}$). By analyzing the generators for the starting space groups, we find the new P2-DG level surface belongs to space group $P2_13$, No. 198. A plot of the surface is shown in Figure 4.

Conclusion

We have conducted a systematic search for the cubic space groups 214, 221, and 227 and their supergroups,

225, 224, 229, and 230, seeking allowed embedded, connected surfaces with the given symmetries. Searching group 221 yielded level set approximations to all the known triply periodic low genus surfaces: the P surface (see Figure 1a), I−WP (Figure 1b), their combination, the O, CT-O (Figure 1d), Neovius' surface C(P) (Figure 1e), the intermediate combination of P and C(P) (Figure 1f), and a P-like surface K (Figure 1g). We also discovered level set equations for the Lidinoid (Figure 2e) and double diamond (Figure 3c) surfaces. We found these new level set surfaces by generating arrays of surfaces: varying the free parameters over a grid and visually inspecting for interesting bi- and tricontinuous surfaces. We then refined the search in the areas of interest, investigating combinations of up to six terms to find the most physically plausible level set equations.

This investigation has shown that it is possible to find new triply periodic embedded surfaces with cubic symmetries by a simple algorithmic procedure starting from the structure factor equations from the ITC. We have found two new surfaces, in groups 198 and 227, the P2-DG and the D′ surfaces, pictured in Figures 3b and 4, respectively. It is likely that minimal surface equivalents of these surfaces exist, and thus the cmc surface families also exist. These bi- and tricontinuous structures may be useful candidate models for novel microdomain structures in block copolymers. Given the increasing interest in synthesis of well-defined, multicomponent, complex architecture macromolecules, these models may also be inspirational to both polymer chemists and also to polymer physicists due to their possible unusual transport and optical (e.g., photonic crystal) properties.[33−35]

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