

Title	Hyperbolic Tiling on the Gyroid Surface in a Polymeric Alloy (Mathematics of Quasi-Periodic Order)
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Citation	数理解析研究所講究録 (2011), 1725: 80-91
Issue Date	2011-02
URL	http://hdl.handle.net/2433/170488
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

Hyperbolic Tiling on the Gyroid Surface in a Polymeric Alloy

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1 Introduction

Biological amphiphilics (lipids) or synthetic surfactants in aqueous solutions self-assemble to bilayers centered on the multiply connected surface dividing the space into two interpenetrating and nonintersecting “bicontinuous” subspaces[1]. At high concentration of lipids or surfactants, these bilayers can organize cubic phases based on mathematically well-characterized surfaces, namely, triply periodic minimal surfaces: e.g., Schoen-Luzatti gyroid (G), Schwarz diamond (D), Schwarz primitive (P), and Neovius surface ($C(P)$)[2]. Moreover, it is known that these surfaces abound in biological cells such as the endoplasmic reticulum, the mitochondrion and the nucleus of certain cells[3]. For high polymeric block copolymer systems[4], bicontinuous cubic phases had attracted much attention as well[5, 6], and it is believed that only the G phase has been established in most block copolymer systems[7, 8].

Recently, Hayashida et al. have found a gyroid surface related structure in an ABC star polymer system. Interestingly, the gyroid surface is decorated and the structure can be regarded as a hyperbolic Archimedean tiling structure[9]. The present paper discusses the mathematical aspects of the hyperbolic Archimedean tiling on the Gyroid surface in an ABC star block copolymer system.

2 Self-organization of AB block copolymers

A block copolymer is a polymer consisting of at least two large connected blocks of different polymer types, say, A-B diblock copolymer:



For example, famous one is a styrene-isoprene diblock copolymer composed of plastic (polystyrene) and rubber (polyisoprene) polymer types. Suppose that A and B are immiscible with each other, molten copolymers can undergo microphase separation exhibiting spatially periodic structures like lamellar structures, bicontinuous double gyroid structures, hexagonal arrays of cylinders, body-center-cubic arrays of spheres depending upon the volume fraction of A and B as shown in Fig.1.[4] Such a morphological phase behavior is common to surfactant or lipid systems.

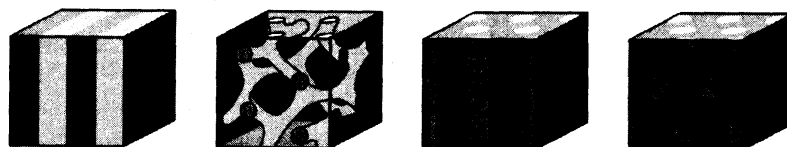


Figure 1: Morphology of AB block copolymer systems. Light and dark gray correspond to A and B components of AB block copolymers, respectively. With decreasing the fraction of the A component, the shape of A component becomes lamellae, bicontinuous double gyroid struts, cylinders, and spheres. The lattice constants (periodic lengths) are the order of 10-100 nm.

The gyroid phase is called “bicontinuous phase” because domains of both A and B components go to infinity. It is also called “gyroid”, because the dark gray domain of the bicontinuous phase displayed in Fig.1 contains the gyroid minimal surface as a mid-surface. Notice that each polymer chain is very flexible and random in its chain shape in the domains; each domain is made up of a random mixture of polymer chains of the same polymer type.

3 Self-organization of ABC star block copolymers

Particular interests have focused on the possibility of creating new materials having new morphologies by controlling composition, molecular weight, and molecular architecture, such as multiblock copolymers and branched or star block copolymers. For instance, ABC three-arm star-shaped[10, 11] copolymer systems (Figure 2(a)) have shown to have very fascinating morphologies. The ABC star block copolymer consists of three different polymer types connected at one junction. Because of this topological constraint, several polygonal cylindrical phases called “Archimedean tiling” phases have been obtained. See Fig.2.

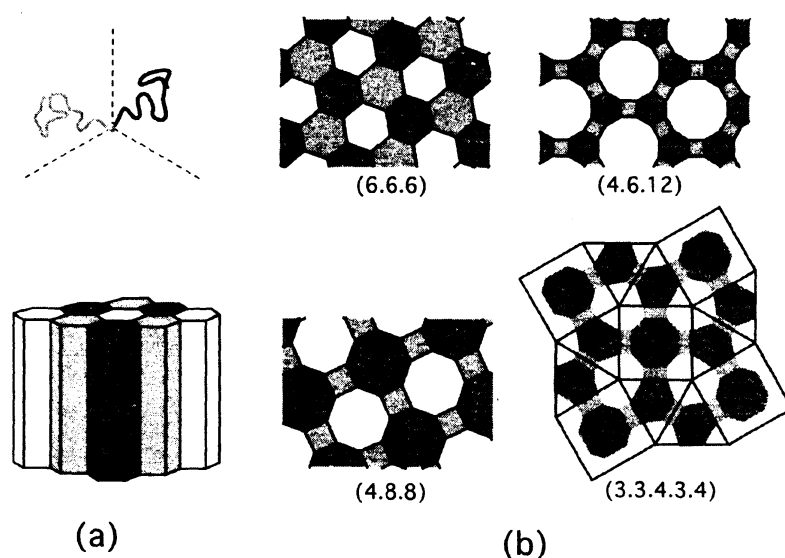


Figure 2: (a) ABC star block copolymer consists of three different polymers linked at a junction point. Cylindrical phases called Archimedean tiling phases (b) are obtained when the fractions of A, B and C components are not too different.

For generic microphase-separated structures, there is a recent established scenario that bicontinuous phases exist in the boundary region between cylindrical and lamellar phases. In the case of a star polymer, the gyroid-type phase exists between a lamellar phase and a cylindrical phase [9]. The problem here is the decoration on the gyroidal membrane.

4 The gyroid surface and its symmetry via hyperbolic geometry

The gyroid surface S is a triply periodic minimal surface given by the Weierstrass-Enneper formula ([12])

$$\begin{cases} x = x_0 + \Re \left(\exp(i\theta) \int_0^\omega \frac{1-w^2}{\sqrt{w^8-14w^4+1}} dw \right), \\ y = y_0 + \Re \left(\exp(i\theta) \int_0^\omega \frac{i(1+w^2)}{\sqrt{w^8-14w^4+1}} dw \right), \\ z = z_0 + \Re \left(\exp(i\theta) \int_0^\omega \frac{2w}{\sqrt{w^8-14w^4+1}} dw \right). \end{cases} \quad (1)$$

The angle θ is given by

$$\theta = \cot^{-1} \frac{K(\frac{\sqrt{3}}{2})}{K(\frac{1}{2})},$$

where $K(k)$ is the complete elliptic integral of the first kind with modulus k .

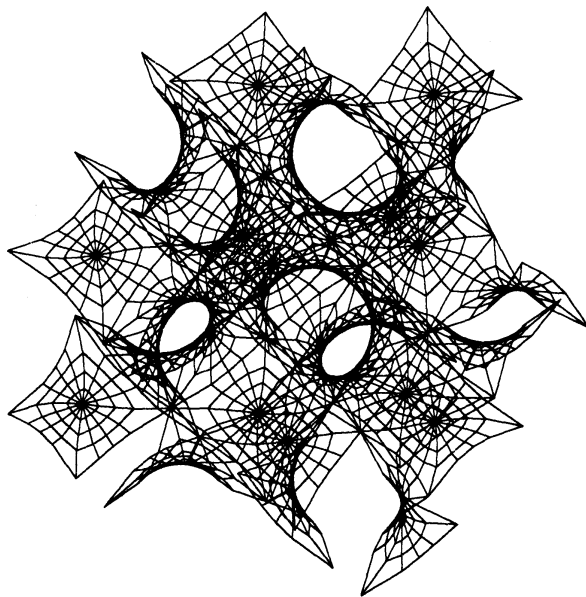


Figure 3: The gyroid surface.

To study the symmetry of the gyroid surface, it is useful to regard S as

a Riemann surface. Thus we recall a description of the gyroid surface as a Riemann surface.

The representation (1) of S enables us to regard S as a covering space of a Riemann surface of genus 3 as follows.

Let Σ be the Riemann surface of the function $\sqrt{w^8 - 14w^4 + 1}$, which is the two-sheeted covering surface of the Riemann sphere S^2 branched at 8 points which correspond to the zeros $\{\pm\alpha^{\pm 1}, \pm i\alpha^{\pm 1}\}$ ($\alpha = (\sqrt{3} - 1)/\sqrt{2}$) of the equation $w^8 - 14w^4 + 1 = 0$,

$$\pi : \Sigma \longrightarrow S^2.$$

Then the 1-forms in (1)

$$\frac{1 - w^2}{\sqrt{w^8 - 14w^4 + 1}}dw, \frac{i(1 + w^2)}{\sqrt{w^8 - 14w^4 + 1}}dw, \frac{2w}{\sqrt{w^8 - 14w^4 + 1}}dw$$

are holomorphic on Σ and the integrations of these holomorphic 1-forms define the multiple-valued functions on Σ . The multiple-valuedness arises from the integrations of the 1-forms around homotopically nontrivial loops on Σ : period integrals, which gives the translational symmetry (periodicity) of the gyroid surface S . Thus S is considered as a covering surface of Σ with covering map $p : S \rightarrow \Sigma$ whose covering transformation group is just the translational symmetry group of S (Fig. 4).

Since the universal covering space of Σ is the hyperbolic plane, there exists the covering map φ of the Poincaré disc D to the Gyroid surface S ,

$$\varphi : D \longrightarrow S.$$

Let Γ be the symmetry group of S : the space group $Ia\bar{3}d$ (No. 230, see [13] as for the notation). Since an isometry f of S are conformal automorphism, there exists a conformal automorphism \tilde{f} of D such that the projection φ satisfy

$$\varphi \circ \tilde{f} = f \circ \varphi. \quad (2)$$

Thus we define $\tilde{\Gamma}$ to be the group of conformal automorphisms g of D such that there exists an element f of Γ satisfying $\varphi \circ g = f \circ \varphi$. Then φ is an equivariant mapping with respect to the actions of $\tilde{\Gamma}$ and Γ . Furthermore φ induces a group homomorphism

$$\varphi_* : \tilde{\Gamma} \longrightarrow \Gamma,$$

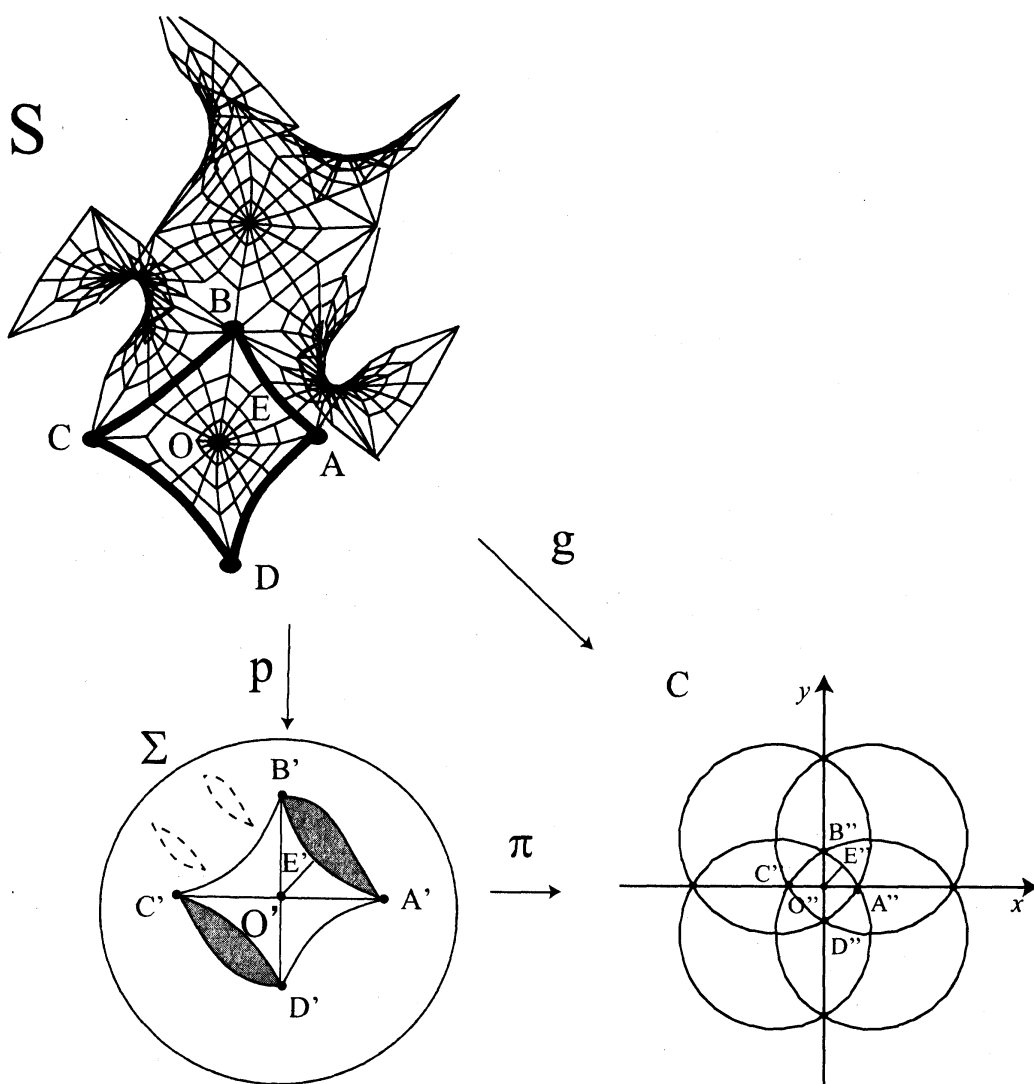


Figure 4: The gyroid surface S and the Riemann surface Σ . The mapping p is the covering map and g is the composition of the Gauss map of S to S^2 and stereographic projection of S^2 to \mathbb{C} . Bottom left is one sheet of the Riemann surface Σ . Bottom right is the complex plane. The 8 intersection points $\{\pm\alpha^{\pm 1}, \pm i\alpha^{\pm 1}\}$ ($\alpha = (\sqrt{3} - 1)/\sqrt{2}$) of 4 circles are the zeros of the equation $w^8 - 14w^4 + 1 = 0$, which are the branch points of π . The points O', A', B', C', D' of Σ are mapped to the points O'', A'', B'', C'', D'' by the projection π .

whose kernel is isomorphic to the fundamental group $\pi_1(S)$ of S .

The description of S as a covering surface of the Riemann surface Σ gives the explicit representation of $\tilde{\Gamma}$ and Γ as follows.

The representation (1) of the gyroid surface S shows that the Gauss map of S to the unit sphere S^2 factors through a mapping of Σ to S^2 . Therefore we can find the triangle OAB on S with angles $(\frac{\pi}{6}, \frac{\pi}{6}, \frac{\pi}{2})$ such that OAB is mapped onto a triangle $O'A'B'$ on Σ with same angles by p and the triangle $O''A''B''$ with angles $(\frac{\pi}{3}, \frac{\pi}{3}, \frac{\pi}{2})$ on \mathbf{C} by the Gauss map, where O'' is the origin, A'', B'' are the branch points of the covering $\pi : \Sigma \rightarrow \mathbf{C}$ indicated in Fig. 4, and the covering π maps $O'A'B'$ onto $O''A''B''$.

The quadrilateral $A''B''C''D''$ on \mathbf{C} (Fig. 4) is transformed into 6 copies quadrilaterals in the Riemann sphere $\mathbf{C} \cup \{\infty\}$ by successive reflections in the sides of the quadrilaterals. Thus the 12 copies of the quadrilateral $A'B'C'D'$ forms the Riemann surface Σ . This tiling is lifted to the Gyroid surface S and gives a tessellation on S by the copies of OAB .

The triangle OAB is nothing but a fundamental domain of the symmetry group Γ of S : Γ is generated by the rotations w_1 of order 4 around O and w_2 of order 2 around E

$$\Gamma = \langle w_1, w_2 \rangle,$$

where E corresponds to the midpoint on the arc $A''B''$ (Fig. 4). The action of Γ is easily seen from the view point of hyperbolic geometry. To do this we consider the $(2, 4, 6)$ tiling on the universal covering space of S : the Poincaré disc D ([14], [15]) (Fig. 5).

The covering map φ maps the triangle PQR with angles $(\frac{\pi}{6}, \frac{\pi}{6}, \frac{\pi}{2})$ onto OAB . The group $\tilde{\Gamma}$ defined above is the subgroup of index 2 in the Schwarz triangle group $\tilde{\Gamma}'$ of type $(2, 4, 6)$:

$$\tilde{\Gamma}' = \langle s_1, s_2, s_3 \mid s_1^2 = s_2^2 = s_3^2 = (s_1s_2)^2 = (s_2s_3)^4 = (s_3s_1)^6 = 1 \rangle,$$

where s_1, s_2, s_3 are the reflections in the sides of the triangle PQM with angles $(\frac{\pi}{2}, \frac{\pi}{4}, \frac{\pi}{6})$. The subgroup $\tilde{\Gamma}$ consists of orientation-preserving elements of $\tilde{\Gamma}'$ and is generated by the rotations through angles $\frac{2\pi}{2}, \frac{2\pi}{4}, \frac{2\pi}{6}$ around the vertices of the triangle PQM .

$$\begin{aligned} \tilde{\Gamma} &= \langle s_1s_2, s_2s_3 \rangle \\ &\simeq \langle a, b \mid a^2 = b^4 = (ab)^6 = 1 \rangle. \end{aligned}$$

Then the mapping φ_* is given by $\varphi_*(s_1s_2) = w_2, \varphi_*(s_2s_3) = w_1$.

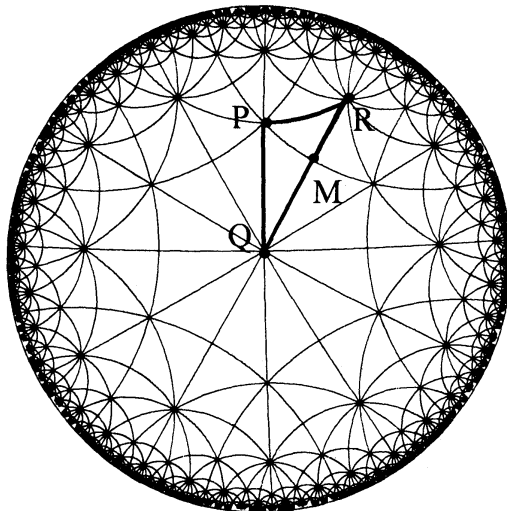


Figure 5: $(2,4,6)$ tiling on the Poincaré disc D . Angles of the triangle PQR and PQM are $(\frac{\pi}{6}, \frac{\pi}{6}, \frac{\pi}{2})$ and $(\frac{\pi}{2}, \frac{\pi}{4}, \frac{\pi}{6})$.

5 Hyperbolic Archimedean tiling

In the $(2, 4, 6)$ tessellation on D given by the triangle with angles $\frac{\pi}{2}, \frac{\pi}{4}, \frac{\pi}{6}$, we can find a dodecagonal region indicated in Fig. 6. This region is mapped to the domain in the gyroid surface S whose translations cover S ([14]).

If we put two adjacent triangles together to form a triangle Δ with angles $(\frac{\pi}{4}, \frac{\pi}{4}, \frac{\pi}{3})$. This is a fundamental domain of the action of $\tilde{\Gamma}$. Let $\tilde{\Gamma}_0$ be the subgroup of $\tilde{\Gamma}$ generated by s_2s_3 and $(s_2s_3s_1s_2)^2$

$$\tilde{\Gamma}_0 = \langle s_2s_3, (s_2s_3s_1s_2)^2 \rangle,$$

where s_2s_3 and $(s_2s_3s_1s_2)^2$ are both rotations through angle $\frac{\pi}{2}$ around P and angle $\frac{2\pi}{3}$ around Q in Fig. 5. The image $\Gamma_0 = \varphi_*(\tilde{\Gamma}_0)$ is isomorphic to the space group $I\bar{4}3d$ (No. 220), which is the subgroup of index 2 in the space group $\Gamma = Ia\bar{3}d$.

Since the index of $\tilde{\Gamma}_0$ in $\tilde{\Gamma}$ is 2, the action of $\tilde{\Gamma}_0$ on D gives two colored tiling (Fig. 6).

The orbit Ω of a point in a fundamental domain (shaded region in Fig. 6) by the action of $\tilde{\Gamma}_0$ defines a new tiling structure on D as follows (see Fig. 7 A).

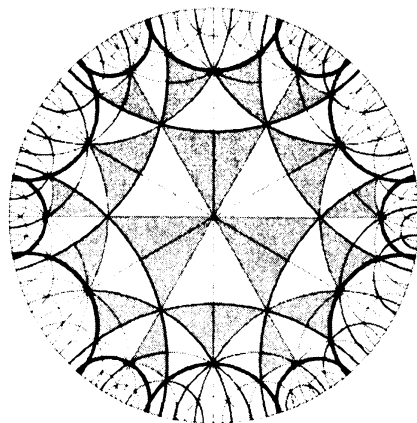


Figure 6: Two colored tiling on the Poincaré disc D .

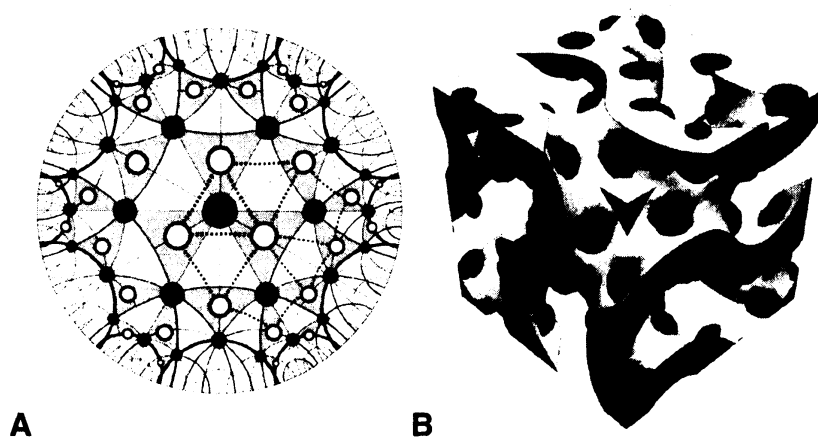


Figure 7: **A**, Hyperbolic Archimedean tiling on the Poincaré disc D . The circles on the shaded triangles form the tiling of vertex type $(3^3.4.3.4)$. **B**, ABC star-shaped block copolymer system. The I (balls) and the S (membrane surrounding the balls) components forming the gyroid membrane. Remaining parts are filled with the P component.

Every point P of Ω is surrounded by 6 faces: 4 triangles and 2 quadrilaterals. We denote its vertex type by $(3.3.3.4.3.4)$ or $(3^3.4.3.4)$ which indicates the numbers of vertices of the consecutive faces around P . We call it hyperbolic Archimedean tiling, because it can be considered as a simple analogue of the Archimedean tiling of type (3^6) on a plane.

By the results of transmission electron microscopy and small-angle X-ray scattering, we can find the geometry of the gyroid surface in the geometric structure of an ABC star-shaped block copolymer system, which is composed of polyisoprene (I), polystyrene (S), and poly(2-vinylpyridine) (P): the I and S components form a gyroid membrane and the complement of the membrane is filled with the P component (Fig. 7 B). The I component consists of isolated domains that form a new tiling structure on the gyroid surface corresponding to the hyperbolic Archimedean tiling introduced above. Furthermore this tiling is characterized in three-dimensional Euclidean space as follows.

Let P be a point on the gyroid surface S and Ω_P the orbit of P under the action of $\tilde{\Gamma}_0$. Then we have

Theorem *There exists a unique point P in the triangle $\varphi(\Delta)$ (a fundamental domain of the action of $\Gamma_0 = I\bar{4}3d$) on the gyroid surface S such that Ω_P forms a hyperbolic Archimedean tiling $(3^3.4.3.4)$ in which the edges are all the same length.*

Outline of the proof. By the symmetry, points of Ω_P are assembled in the same way around each point. Thus when the faces surrounding one point of Ω_P satisfy the conditions, all faces satisfy the conditions. Let $P = (x, y, z)$ be a point of Ω_P . Then the conditions that all edges connecting to P have the same length are given by two quadratic equations. Let C be the intersection of two quadric surfaces defined by the quadratic equations. It is not hard to show that the curve C and S intersect at one point in the triangle $\varphi(\Delta)$.

We show the tiling of the theorem in Fig. 8.

References

- [1] S. Hyde, S. Andersson, K. Larsson, Z. Blum, T. Landh, S. Lidin, B. W. Ninham, *The language of Shape* (Elsevier, Amsterdam 1997); W. Gòzdž and R. Hołyst, *Macromol. Theory Simul.* **5**, 321 (1996) and a

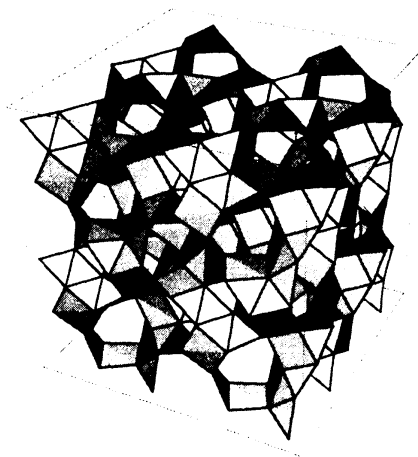


Figure 8: Hyperbolic Archimedean tiling of type $(3^3.4.3.4)$ in three-dimensional Euclidean space whose vertices are on the gyroid surface.

short history of the periodic minimal surfaces therein; T. Dotera, *Phys. Rev. Lett.* **89**, 205502 (2002).

- [2] P. Ström and D. M. Anderson, *Langmuir* **8**, 691 (1992); T. Landh, *J. Phys. Chem.* **98**, 8453 (1994).
- [3] T. Landh, *FEBS Letters.* **369**, 13 (1995). See also for a review: J. M. Seddon, *Ber. Bunsenges. Phys. Chem.* **100**, 380 (1996).
- [4] I. W. Hamley. *The Physics of Block Copolymers* (Oxford, New York, 1998); F. S. Bates and G. H. Fredrickson, *Phys. Today* **52**, 32 (1999); M. W. Matsen, *J. Phys.: Condens. Matter* **14**, R21 (2002).
- [5] E. L. Thomas, D. B. Alward, D. J. Kinning, D. C. Martin, D. L. Handlin, Jr., and L. J. Fetters, *Macromolecules* **19**, 2197 (1986); H. Hasegawa, H. Tanaka, K. Yamasaki, and T. Hashimoto, *Macromolecules* **20**, 1651 (1987).
- [6] Y. Mogi *et al.*, *Macromolecules* **25**, 5408 (1992); **25**, 5412 (1992).
- [7] D. A. Hajduk *et al.*, and L. J. Fetters, *Macromolecules* **27**, 4063 (1994); **28**, 2570 (1995); M. W. Matsen and F. S. Bates, *Macromolecules* **29**, 1091 (1996); H. Hückstädt *et al.*, *Macromolecules* **33**, 3757 (2000);

- [8] Y. Matsushita, J. Suzuki, M. Seki, *Physica* **B248**, 238 (1998); J. Suzuki, M. Seki, Y. Matsushita, *J. Chem. Phys.* **112**, 4862 (2000); M. W. Mat- sen, *J. Chem. Phys.* **108**, 785 (1998).
- [9] T. Dotera, K. Hayashida, J. Matsuzawa, A. Takano, Y. Matsushita, preprint.
- [10] N. Hadjichristidis, *J. Polym. Sci., Part A* **1999**, *37*, 857.
- [11] T. Gemma, A. Hatano, T. Dotera, *Macromolecules* **35**, 3225-3237 (2002), references therein; K. Ueda, T. Dotera, T. Gemma, *Phys. Rev. B* **75**, 195122 (2007).
- [12] A. H. Shoen, , Infinite periodic minimal surfaces without self- intersections, *NASA Techn. Rep.*, **D-5541** (1970) .
- [13] International table for crystallography, vol A: Space-group symmetry, International Union of Crystallography,
- [14] J.-F. Sadoc, and J. Charvolin, *Acta Cryst.*, **A45**(1989), 10–20.
- [15] V. Robins, S. J. Ramsden, and S. T. Hyde. *Eur. Phys. J. B*, **48** (2005), 107–111.