# High Genus Periodic Gyroid Surfaces of Nonpositive Gaussian Curvature

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In this paper we present a novel method for the generation of periodic embedded surfaces of nonpositive Gaussian curvature. The structures are related to the local minima of the scalar order parameter Landau-Ginzburg Hamiltonian for microemulsions. The method is used to generate six unknown surfaces of $Ia\bar{3}d$ symmetric (gyroid) of genus 21, 53, 69, 109, 141, and 157 per unit cell. All of them but that of genus 21 are most likely the minimal surfaces. The Schoen-Luzzati gyroid minimal surface of genus 5 (per unit cell) is also obtained.

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The surfactant molecules which are the main ingredient of soaps and detergents have the ability to solubilize oil in water, two liquids which in the binary mixture at normal conditions are immiscible. This ability stems from their chemical structure; a surfactant molecule has polar and nonpolar segments at two ends and thus is simultaneously hydrophobic and hydrophilic. The term amphiphilic (from the Greek work for loving both) molecule is used since one end (polar) of the molecule is well solubilized in water while the other (nonpolar) is in oil. Hence the molecule preferably stays at the oil-water interface, forming a monolayer. At high concentration of surfactant the physical interface made of these molecules orders, forming periodic structures of various symmetries. Similar behavior is observed in systems of biological molecules (lipids) which in water solutions self-assemble into bilayers. In 1967–68 Luzzati *et al.* [1–3] observed that the type of ordering in the lecithin-water and lipid-water systems cannot be described by the arrangement of simple surfactant aggregates such as cylinders, planes, or spheres. They observed the cubic bicontinuous phase of the $Ia\bar{3}d$ symmetry (gyroid) where the lipid bilayers formed a highly curved smooth (embedded) surface of the same symmetry. Such surface divides the volume into two disjoint subvolumes. The NMR, SAXS (small angle x-ray scattering), and surfactant concentration measurements indicate that these surfaces closely resemble triply periodic minimal surfaces [4–7], i.e., surfaces characterized by zero mean curvature at every point. The latter belongs to the broader class of periodic surfaces of nonpositive Gaussian curvature. Since the discovery of minimal periodic surfaces in 1865 by Schwarz only one periodic embedded gyroid surface of cubic symmetry and genus 5 (per unit cell) has been discovered and fully characterized [4]. Apart from that six more of $Pn\bar{3}m$ and $Im\bar{3}m$ symmetry and known, all of low genus. *Here we present the general method which can be used to generate periodic surfaces of nonpositive Gaussian curvature. We prove the efficiency of this method by generating six new gyroid structures of genus 21, 53, 69, 109, 141, and 157. All these surfaces but that of genus 21 are minimal; we have also generated the Schoen-Luzzati gyroid minimal surface of genus 5 per unit cell.*

We point out that the unique characterization of the periodic surfaces using standard x-ray scattering methods is very difficult if the motif in the unit cell is not precisely known [8–12]. Our theoretical method combined with experimental technique will be extremely helpful in future discoveries of new surfaces in biological systems.

The surfaces of surfactant systems find application in the production of the mesoporous silicate systems, where in the synthesis process the ordered surfactant surface is used as a template for the three-dimensional polymerization of silicate [13,14]. One obtains an ordered silicate pore system with the symmetry and geometry of the surfactant template. We believe that our method can also be used for the design of new mesoporous structures.

Our method is based on the Landau-Ginzburg model which has been proposed by Teubner and Strey [15] and Gompper and Schick [16,17] on the basis of neutron scattering experiments performed on microemulsion (homogeneous ternary mixture of oil, water, and surfactant) and later experiments and theory of their wetting properties [18,19]. The Landau-Ginzburg free energy functional has the following form:

$$F[\phi] = \int d^3r[|\Delta\phi|^2 + g(\phi)|\nabla\phi|^2 + (\phi^2 - 1)^2(\phi^2 + f_0)], \quad (1)$$

where $g(\phi) = g_2\phi^2 - g_0$. Here $\phi$, the order parameter, has the interpretation of the normalized difference between oil and water concentrations; $g_2, g_0$ are positive constants and $f_0$ can be of either sign. The last term in Eq. (1) is the bulk free energy and describes the relative stability of the pure water phase ($\phi = -1$), pure oil phase ($\phi = 1$), and microemulsion ($\phi = 0$). The stability of the bulk microemulsion phase depends on $f_0$: for $f_0 > 0$ microemulsion is a metastable bulk phase, whereas pure

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water phase or pure oil phase is stable; for $f_0 \leq 0$ microemulsion is stable. We note that in general $g(\phi)$ can be a polynomial in $\phi^2$.

For $g_0 > 2$ the system can undergo a transition to periodically ordered phases where water rich domains and oil rich domains order. The interface between the domains corresponds to $\phi(\mathbf{r}) = 0$. The different structures (stable or metastable) correspond to the minima of the functional (1). The following simple argument shows that among the surfaces, inside these structures, we might expect minimal surfaces. The mean curvature of the surface at point $\mathbf{r}$ is given by the divergence of the vector normal to the surface at this point [20,21],

$$H = -\frac{1}{2}\nabla\left(\frac{\nabla\phi}{|\nabla\phi|}\right) = -\frac{1}{2}\frac{\Delta\phi}{|\nabla\phi|} + \frac{\nabla_n|\nabla\phi|}{2|\nabla\phi|}. \quad (2)$$

Here $\nabla_n$ denotes the derivative along the normal to the surface. It follows from the second term of Eq. (1) that $F[\phi]$ is minimized when $|\nabla\phi|$ has the maximal value for $\phi(\mathbf{r}) = 0$ since at that point $g(\phi)$ has the lowest value. For the maximum of $|\nabla\phi|$ its normal derivative vanishes, and consequently the second term in Eq. (2) does so. We also know that in the case of $\phi$, $-\phi$ symmetry, $H$ averaged over the whole surface should be zero. It means that either $\Delta\phi$ is exactly zero at the surface or it changes sign. From the first term of Eq. (1) it follows that the former can be favored, and consequently $H = 0$ at every point at the surface. Hence we can expect that some of the surfaces are minimal. This argument does not take into account the global distribution of the field $\phi$; nonetheless it provides a useful hint for our studies.

In order to find the minima of the functional we have discretized Eq. (1) on the cubic lattice. Thus the functional $F[\phi(\mathbf{r})]$ becomes a function $F(\{\phi_{i,j,k}\})$ of $N^3$ variables, where $Nh$ is the linear dimension of the cubic lattice and $h$ is the distance between the lattice points. Each variable $\phi_{i,j,k}$ represents the value of the field $\phi(\mathbf{r})$ at the lattice site $(i, j, k)$, and the indices $i, j, k$ change from 1 to $N$. In our calculations we use $N = 17, 33, 65$, and 129; final results are shown for $N = 129$. Please note that $N = 129$ results in over $2 \times 10^6$ points per unit cell. The first and second derivative in the gradient and Laplacian terms of the functional (1) were calculated on the lattice according to the three point formula for the first derivatives and five point formula for the second derivatives [22]. We impose on the field $\phi_{ijk}$ the periodic boundary conditions and the symmetry of the structure we are looking for, by building up the field inside a unit cubic cell from a smaller polyhedron, replicating it by reflections and rotations combined with translations, since the gyroid symmetry involves glide planes. Such procedure enables substantial reduction of independent variables.

The initial configuration needed for the minimization is set up by building the field $\phi(\mathbf{r})$ first on a small lattice $N = 3$ or 5. It is done by analogy to the structure of a two component $(A, B)$ molecular crystal. The value of the field $\phi_{i,j,k}$ at a lattice site $(i, j, k)$ is set to 1 if in the molecular crystal an atom $A$ is in this place. It is set to $-1$, if there is an atom $B$, and to 0, if there is an empty place at $(i, j, k)$. Next the small lattice can be enlarged to the desired size by changing the number of points from $N$ to $2N - 1$ and finding the values of $\phi_{i,j,k}$ in new lattice sites by interpolation.

We have used the conjugate gradient method [23] to find a minimum of the functional $F(\{\phi_{i,j,k}\})$. It is highly unlikely, because of numerical accuracy, that a value of the field $\phi_{i,j,k}$ at a lattice site $(i, j, k)$ is exactly zero. Therefore the points of the surface have to be localized by linear interpolation between the neighbor sites of the lattice. This approximation is legible because the field $\phi(\mathbf{r})$ is very smooth. The points on the surface are used for the triangulation. From the triangles covering the surface we get the surface area and the Euler characteristic, $\chi$. The latter is given by the Euler relation $\chi = F - E + V$, where $F$ is the number of faces, $E$ is the number of edges, and $V$ is the number of vertices of the triangles covering the surface. The edges and vertices has to be taken with weight 1, $1/2$, or $1/4$ if they appear inside, at the face, or at the edge of the unit cell, respectively.

We have performed the detailed study of the phase diagram, checking the Landau free energy of almost *30 different structures of various symmetries* and found that the only stable ordered structure is the lamellar phase. The phase boundaries for the lamellar phase are given by Gompper and Zschocke [24]. The gyroid phase of genus 5 has the second lowest energy (after lamellar phase) among all the structures (Table I). We have noted that this phase has larger area per unit volume than the lamellar phase, thus in the case of very sharp interfaces it should have smaller energy than the lamellar phase, since from the second term of Eq. (1) it follows that at $\phi(\mathbf{r}) = 0$ the gradient term gives large and negative contribution to the energy. This negative contribution is not canceled by the bulk or Laplacian terms. Unfortunately the size of the interface scales with the size of the unit cell. We have performed the same calculations for the new function $g(\phi)$ given by $g(\phi) = g_2\phi^4 - g_0$. Increasing the power of $\phi$ by a factor of 2 indeed sharpens the interface between oil and water but at the same time reduces the size of the unit cell. The net result is the larger relative difference in energies between the gyroid and lamellar phase. We note that in the case of multiparameter Landau models introduced in recent years [16,25] we may expect the stabilization of the various phases which here are only metastable.

Among the local minima of the functional [Eq. (1)] we have found four known minimal surfaces: P, D, I-WP, and G [26]. Here we present the detailed study of the surfaces of gyroid symmetry. In all these structures a surface is characterized by nonpositive (zero or negative) Gaussian curvature. In Table I the main characteristics

TABLE I. The gyroid surfaces of nonpositive Gaussian curvature. The symmetry of all the structures is $Ia\bar{3}d$. In all cases the volume fraction is 0.5 by construction. Here $g_2 = 4\sqrt{1 + f_0} + g_0 + 0.01$, $g_0 = 3$, and $f_0 = 0$. At this point the energy of the stable phase (lamellar phase) is $-0.2077$ and the size of the unit cell is $d = 3.4$. In column 2 the energy per unit volume is given. In the third column the dimensionless linear size of the unit cell $d$ is given. The surface area $S$ (fourth column) is divided by $V^{2/3} = d^2$, i.e., is calculated per face of the unit cubic cell. The surface area per unit volume, $S/d^3$, is almost constant for all the structures. The genus $g$ (fifth column) has been calculated from the formula $1 - \chi/2$, where $\chi$ is the Euler characteristic per unit cell. We give in the last column the quantity $\delta = |\chi|^{1/3}d^2/S$. This quantity characterizes not only the ordered phase, but also the fluctuating microemulsion [28]. We think that it can be used as a test for the structure of microemulsion. We find these structures practically for all values of the parameters where the lamellar phase is also stable [24], although most easily they are generated close to the microemulsion stability region. The genus, surface area per side of the unit cell $S/d^2$, symmetry, volume fraction, and $\delta$ do not depend on the parameters, $g_0$, $f_0$, and $g_2$. Only the energy, size of the unit cell, and surface area per unit volume are model dependent.

| Name | Energy | Cell length | Surface area | Genus | $\delta$ |
|---|---|---|---|---|---|
| GM5 | −0.190 | 10.08 | 3.092 | 5 | 0.6469 |
| G21 | −0.183 | 18.32 | 5.484 | 21 | 0.6236 |
| GM53 | −0.186 | 26.16 | 7.907 | 53 | 0.5947 |
| GM69 | −0.183 | 26.48 | 8.081 | 69 | 0.6364 |
| GM109 | −0.181 | 31.72 | 9.657 | 109 | 0.6213 |
| GM157 | −0.178 | 34.40 | 10.519 | 157 | 0.6448 |
| GM141 | −0.186 | 41.32 | 12.460 | 141 | 0.5251 |

of the gyroid surfaces are given. Here we have used $N = 129$ points per edge of the unit cell. In order to estimate the errors we have compared the results obtained for $N = 65$ and 129; for the surface area the largest errors (gyroid 141 and 157) are smaller than 0.3%, for the energy the largest error is smaller than 1% for the gyroid 5 structure and a few percent for other structures. Of course these are the upper limits and most probably the errors are much smaller. In Figs. 1 and 2 two gyroid structures are shown together with the histograms of their mean curvature. Please note that for the minimal surface the mean curvature is peaked around 0 in the histograms, but due to the numerical accuracy the peak has a finite width. We note that as the genus of the surface increases the surface area per unit volume ($S/d^3$) and the energy per unit volume does not change very much (Table I). Some authors [27] ruled out the possibility of the existence of high genus surfaces in real systems, because of expected high curvature regions. We have checked the Gaussian curvature in high genus surfaces and found that it is not much different from the low genus surfaces. This is due to the sufficiently large size of the unit cell for the former structures. We also observe that the gyroid structures of high genus are most easily generated (from any initial configuration and sufficiently large unit cell) close to the stability region of microemulsion.

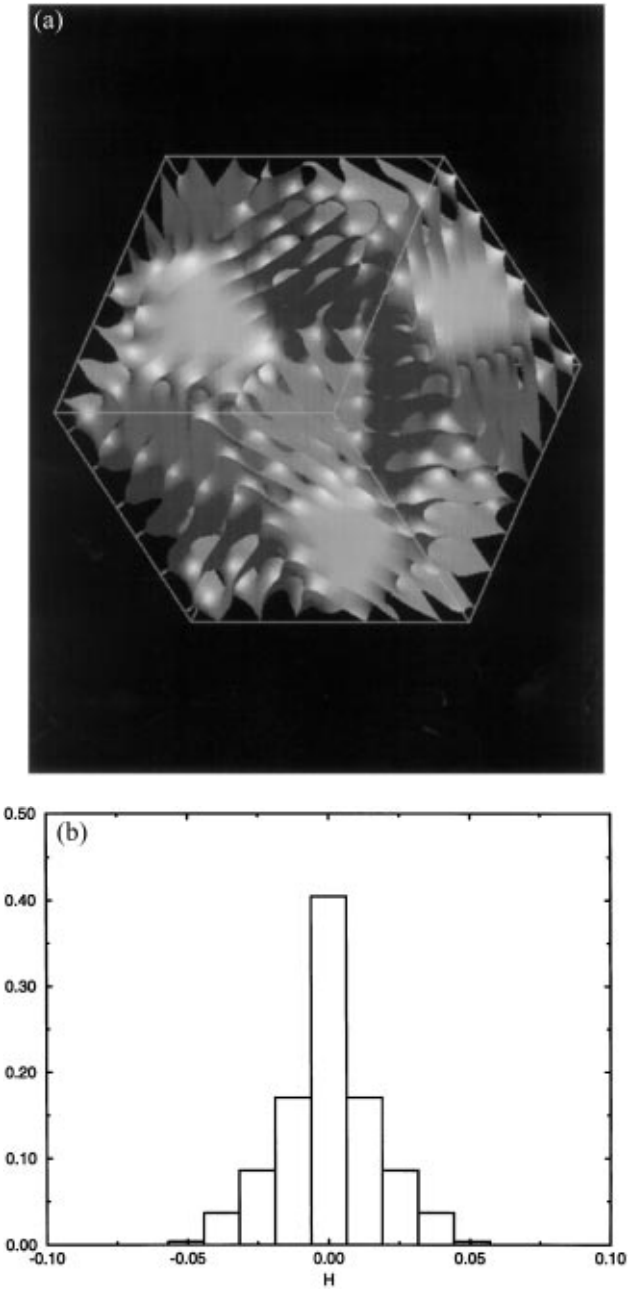


FIG. 1. G141 gyroid structure (see Table I). (a) One unit cell. (b) The histrogram of the mean curvature $H$. The size of the unit cell is given in Table I. Here the typical curvature, $1/R = \pm\sqrt{-K}$, is $\pm 0.1$ ($K$ is the Gaussian curvature).

In summary, we have used the Landau-Ginzburg Hamiltonian for microemulsions to generate periodic surfaces of nonpositive Gaussian curvature. Using this model we have studied seven periodic gyroid surfaces: One of them is the Schoen-Luzzati minimal gyroid surface of genus 5. The remaining six structures are new. The model can be well applied by physicists working

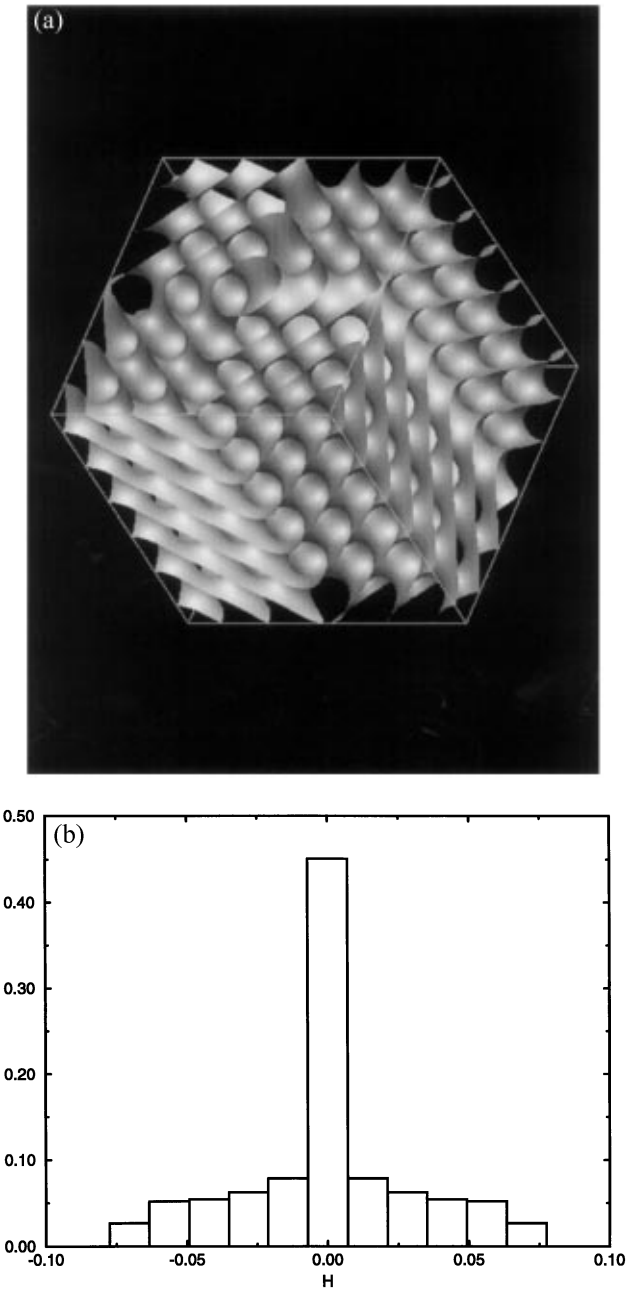


FIG. 2. GM157 gyroid structure. Legend as in Fig. 1. Here the typical curvature is $\pm 0.5$.

in soft condensed matter, mathematicians working in topology, biologists, and crystallographers. We are positive that its richness is far from being explored by our work.

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