Chapter 4

Results

We have generated lots of unknown structures as well as few known. Among the generated surfaces are the triply periodic minimal surfaces. These surfaces have been considered paradigms of the internal interface in the ordered phases formed in the mixtures containing surfactant. We describe these surfaces in Section 4.1. To the best of our knowledge the results we present are the first ones showing that a triply periodic minimal surface can be the solution of a physical model. In Section 4.2 we present unknown surfaces of low genus resulted from our model. We speculate that some of these surfaces can be new triply periodic minimal surfaces. The surfaces of high genus are presented in Section 4.3. The pictures of these surfaces strongly resemble the pictures of microemulsion taken during freeze fracture microscopy studies. In Section 4.4 we describe new type of structures, **the multiply continuous ones.** Our discovery calls for new experiments confirming or rejecting the existence of such structures in real systems (so far only bicontinuous structures have been considered). The phase diagram of the model is presented in Section 4.5.

4.1 Minimal Surfaces

The following simple experiment can be used for the direct visualization of a simple patch of minimal surface: Take a metal non-planar frame and immerse it in the water solution of soap. The soap bubble which forms on this frame assumes the shape that minimizes its surface free energy associated with the surface tension and consequently it forms a surface of least area. Thus these surfaces are called minimal surfaces. Such experiments can be traced back to Leonardo da Vinci but in fact the detailed studies of this type were done and published by Plateau [41] and hence later the problem of surface of least area spanning a given loop has been named the Plateau problem.

The history of physics and mathematics of minimal surfaces ran in parallel. Lagrange in 1761 (before Plateau) derived the equations for a surface of least area that is equivalent to the condition of vanishing mean curvature at every point on the surface. The representation of these surfaces in terms of harmonic functions was given by Weierstrass in 1866 and this representation has served many researchers up to date for their generations. A new qualitative insight into the mathematics of the problem was obtained by Schwarz and his student Neovius, who showed that simple patches of minimal surfaces can be put together to give smooth periodic three dimensional structures, which are called now triply periodic minimal surfaces (TPMS) or sometimes infinite periodic minimal surfaces (IPMS). They identified five phases three of which were of the cubic symmetry i.e. P, D and C(P). Plateau and Schwarz in fact entertained scientific contacts, but none of them had envisaged the role of these surfaces as physical interfaces. Rediscovery of the problem is due to Schoen [39], who identified 4 new surfaces of cubic symmetry(G, I-WP, F-RD and O,C-TO). In 1976 Scriven [42] hypothesized that such surfaces could be used for the description of physical interfaces appearing in ternary mixtures of water, oil and surfactants. In 1967/68 Luzzati et al [43, 44, 45, 46] observed this type of ordering in the lecithin-water and lipid-water systems. One of the phases observed by them was the phase of the same symmetry as the G Schoen minimal surface. It seems that both Schoen's and Luzzati discovery were made independently. In fact this phase appears to be very common in biological systems. Another example of such surfaces is found in the system of diblock copolymers, commercially important materials for the production of plastics. AB diblock copolymer consists of two macromolecules chemically bonded together. At low temperatures the system forms ordered A-rich and B-rich domains, with the points of bondage at the interface between the domains. In 1988 Thomas et al [47] observed that the PS/PI (polystyrene/polyisoprene) diblock copolymer forms a structure of the same symmetry as the D (diamond) Schwarz surface and argued on the basis of the relative volume fraction of PS and PI component that the resulting physical interface must be the surface of constant mean curvature at every point of the surface. Such surface belongs to the family of minimal surfaces [39, 32, 48].

Surfaces are ubiquitous. Even in the ionic crystals one can imagine a periodic zero potential surfaces (POPS in short), having same symmetry as the crystal [49]. Although, POPS do not have usually the same geometry as minimal surfaces (their mean curvature varies along the surface), nonetheless they share the same topology (genus etc) and symmetry as the latter.

The minimal surfaces are usually described in terms of Weierstrass integral equations. The Weierstrass representation gives the coordinates (x, y, z) on a minimal surface of the point represented by ω on the complex plane [50]

$$
\begin{aligned}
x &= Re \int_{\omega_0}^{\omega_1} (1-\omega^2) R(\omega) d\omega, \\
y &= Re \int_{\omega_0}^{\omega_1} i(1+\omega^2) R(\omega) d\omega, \\
z &= Re \int_{\omega_0}^{\omega_1} 2\omega R(\omega) d\omega,
\end{aligned}
\tag{4.1}
$$

where $R(\omega)$ is the Weierstrass characteristic function for the surface, Re stands for "real part", $\omega = \omega_a + i\omega_b$ and $i = \sqrt{-1}$. When the function $R(\omega)$ is replaced with $R(\omega)e^{i\theta}$ the surface described by the function $R(\omega)$ is transformed into another surface called the adjoint surface. Such transformation is called the Bonnet transformation [51] and θ is known as the Bonnet angle. The Bonnet transformation preserves the Gaussian and mean curvatures.

4.1.1 Schwarz surfaces D, P and Schoen surface G

The Schwarz primitive surface P and Schoen gyroid surface G are related to the D-surface by the Bonnet transformation: the Bonnet angle for the P-surface is 90° and for the G-surface is 38.015°. The Weierstrass function for the fundamental element of the surfaces D is given by [50, 52]

$$R(\omega) = (\omega^8 - 14\omega^4 + 1)^{-1/2}, \tag{4.2}$$

with an integration domain given by the points around the origin limited by 4 circles with radius $\sqrt{2}$ and centers at $\pm\sqrt{2}, \pm i\sqrt{2}$.

Here we use our model to generate surfaces. The fact that the P,D,G surfaces are adjoint means that the histograms of the Gaussian curvature for these surfaces should be the same. In fact the histograms look very similar (see Figs. 4.6, 4.10, 4.14), the small differences result form the numerical accuracy. The mean curvature of the minimal surface is zero at every point, thus its histogram should be a single infinitely sharp peak at $H = 0$. Here it is smeared (see Figs. 4.7, 4.11, 4.15) due to numerical accuracy. In fact it serves as a good estimate of the errors for curvatures.

It is interesting that the value of the free energy in our model (2.9) for each of these structures is the lowest for all the structures of given symmetry, i.e. among all structures of the symmetry of gyroid phase G, this phase has the lowest free energy. These phases are generated independently of the initial configuration, provided that the unit cell length is set close to the minimal length. If the cell length is taken close to multiple length of of the unit cell then multiple images of a given structure are created.

The fact that the G and D structures are the most stable among structures of a given symmetry suggest that they can be found in real system. In fact the phases, diamond D and gyroid G, have been discovered in real systems in diblock copolymers [47, 53, 54, 55, 56]. However, the discovery of the gyroid phase, after the diamond phase had been found real systems, was not straighforward. It took the researchech about six years to find the gyroid phase.

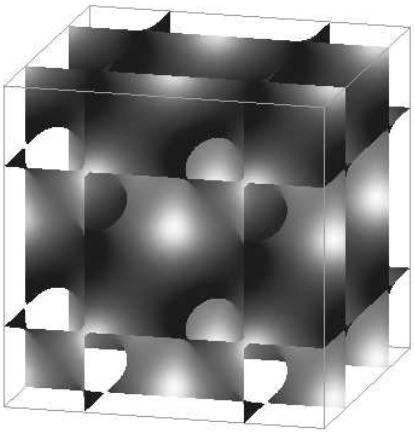

Figure 4.1: Schwarz diamond surface D generated from the functional (2.9). The unit cell. Off front view.

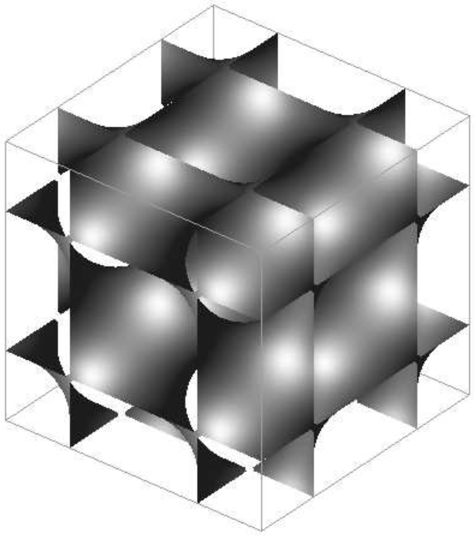

Figure 4.2: Schwarz diamond surface D generated from the functional (2.9). The unit cell. Off diagonal view.

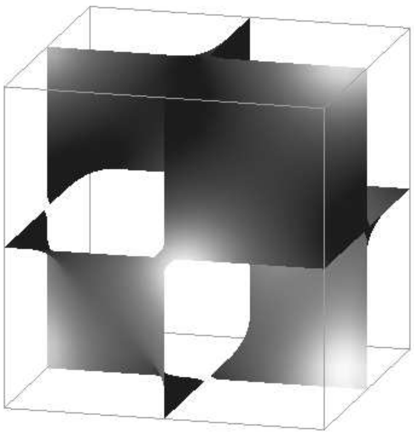

Figure 4.3: Schwarz diamond D surface generated from the functional (2.9) 1/8 of the unit cell. Off front view.

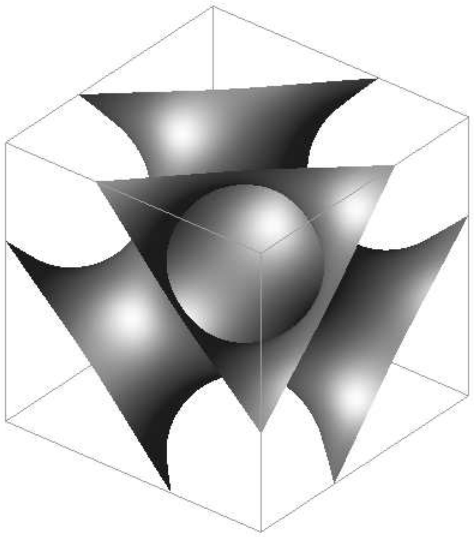

Figure 4.4: Schwarz diamond surface D generated from the functional (2.9) The middle element of the unit cell. Off diagonal view.

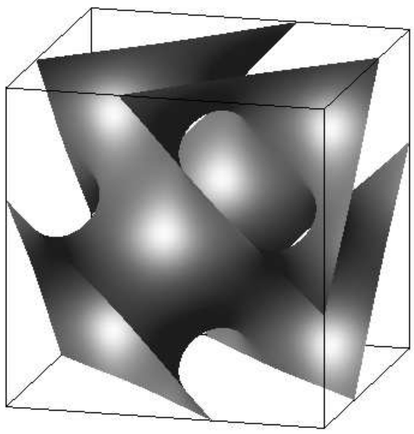

Figure 4.5: Schwarz diamond surface D generated from the functional (2.9) The middle element of the unit cell. Off front view.

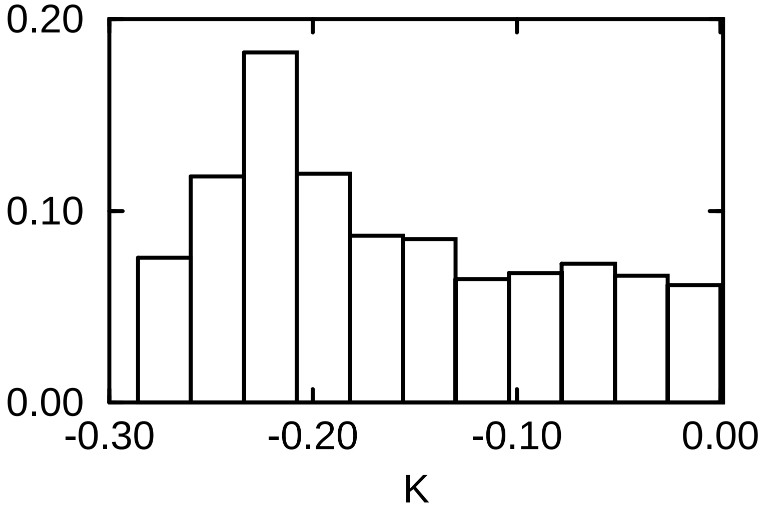

Figure 4.6: The histogram of the Gaussian curvature for the surface D

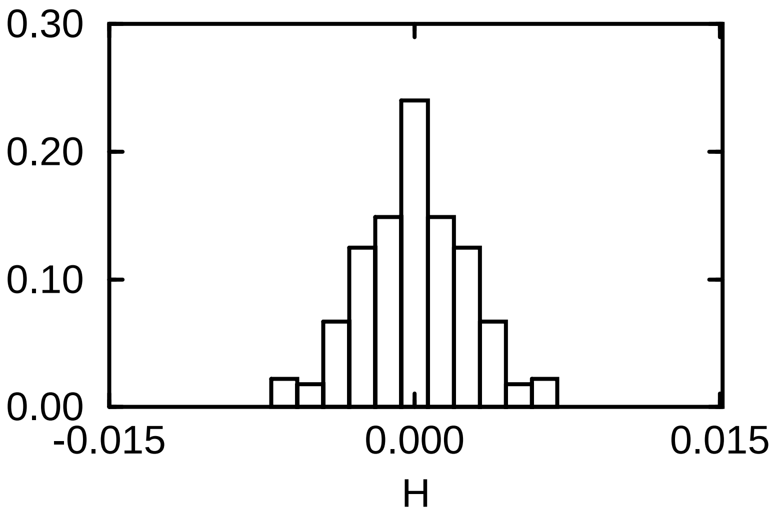

Figure 4.7: The histogram of the mean curvature for the surface D

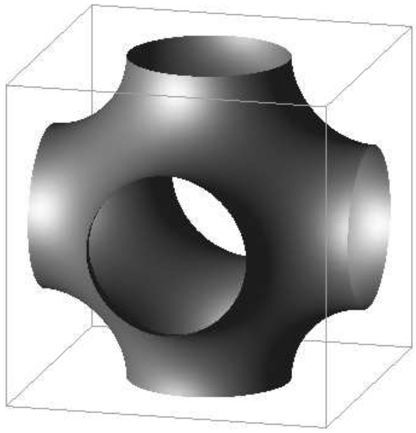

Figure 4.8: Schwarz surface P generated from the functional (2.9). The unit cell. Off front view.

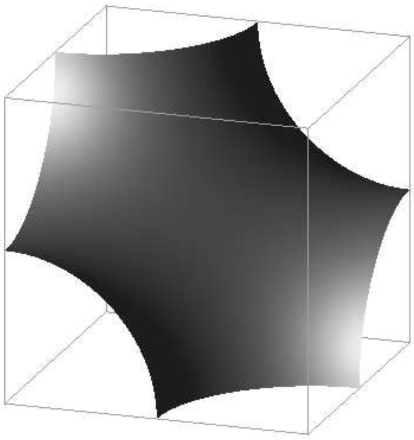

Figure 4.9: Schwarz primitive surface P generated from the functional (2.9) 1/8 of the unit cell. Off front view.

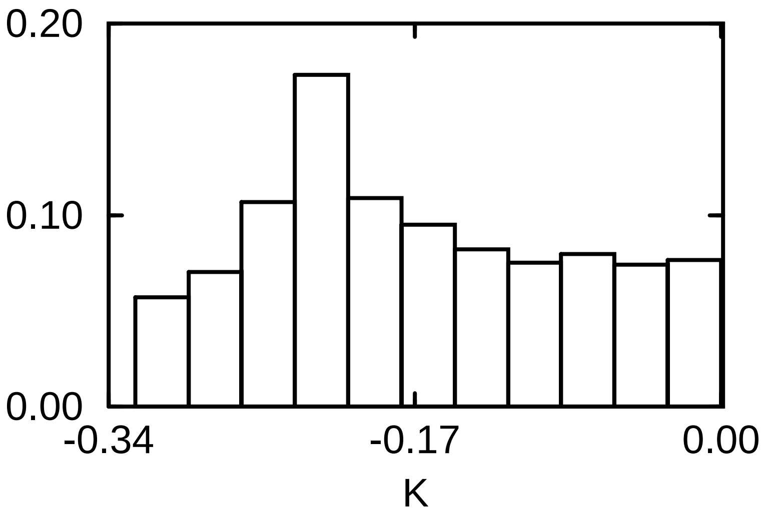

Figure 4.10: The histogram of the Gaussian curvature for the surface P

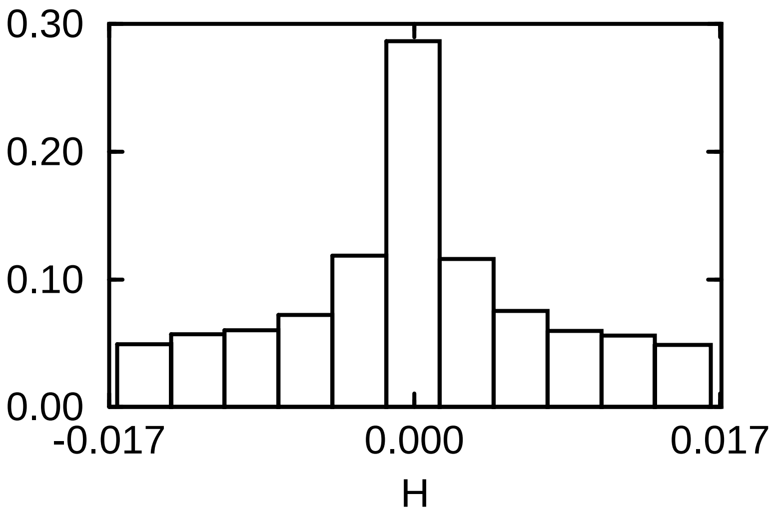

Figure 4.11: The histogram of the mean curvature for the surface P

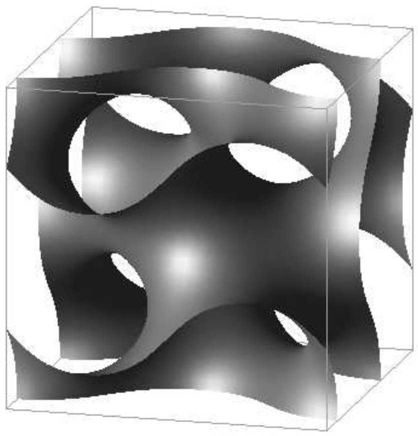

Figure 4.12: Schoen gyroid surface G generated from the functional (2.9) The unit cell. Off front view.

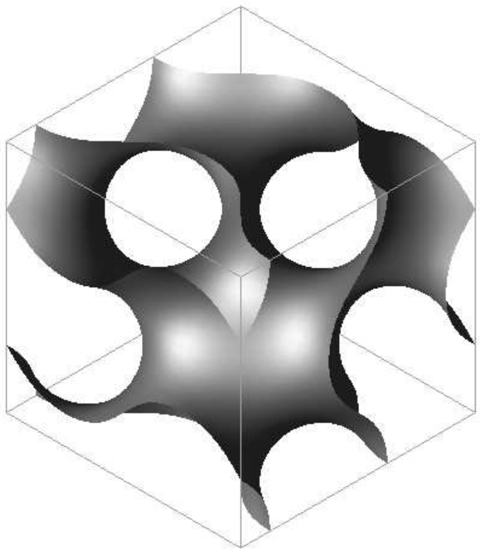

Figure 4.13: Schoen gyroid surface G generated from the functional (2.9) The unit cell. Off diagonal view.

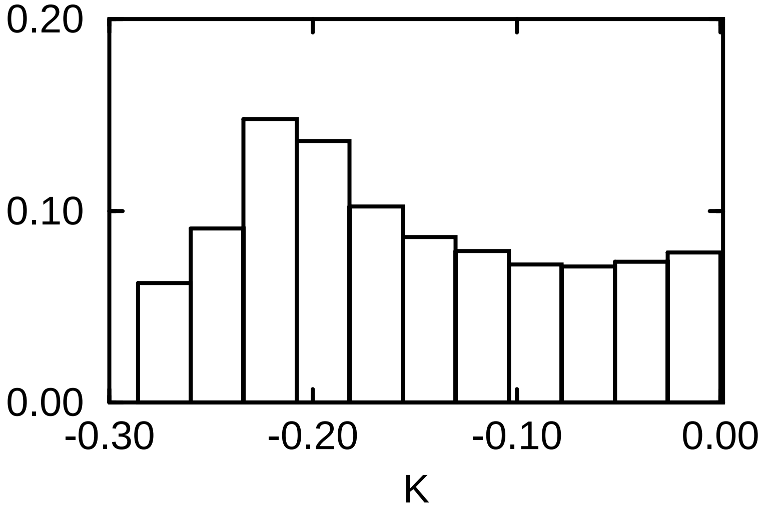

Figure 4.14: The histogram of the Gaussian curvature for the surface G

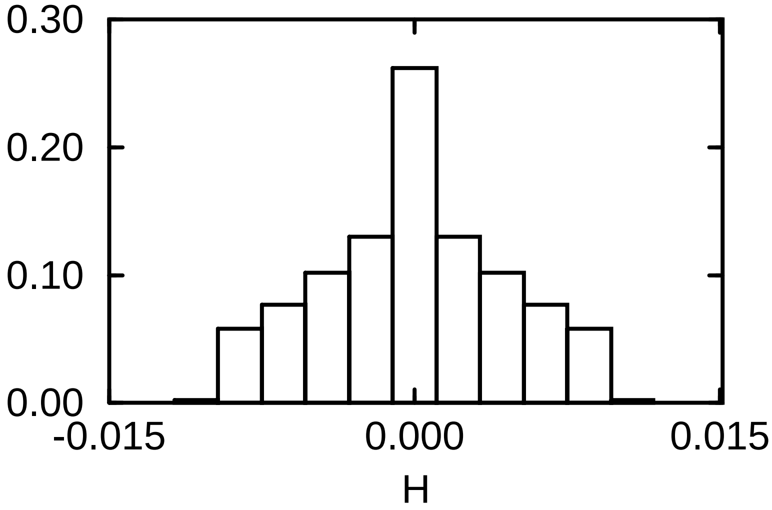

Figure 4.15: The histogram of the mean curvature for the surface G

4.1.2 Schoen I-WP and O,C-TO minimal surface

The I-WP surface was discovered by Schoen [39]. He built the models of the surface, identified its space group as $Im\bar{3}m$. That is why the letter I is in the first part of the name given by him to this surface. The WP stands for "wrapped package" because of the resemblance of finite portions of the graph to the arrangement of string on a simply wrapped package. The Weierstrass characteristic function for I-WP surface is [51, 57]:

$$R(\omega) = (\omega^6 - 5\omega^4 - 5\omega^2 + 1)^{-2/3} \tag{4.3}$$

The I-WP surface was found in star block co-polymers [58]. The results of our study suggest that it can also be found in the ternary surfactant mixtures.

The O,C-TO surface was discovered by Schoen [39]. The Weierstrass function for this surface is not known and no other information except genus and the symmetry are described in the literature. Here we report for the first time the volume fraction of the two subvolumes divided by the OCTO surface, see Table 4.1. Nobody so far has shown the existence of this structure in real systems. The surface obtained from the functional (2.9) strongly resembles the one described by Schoen. The histogram of the mean curvature suggest that this surface can be minimal. However, this is the only structure which cannot be minimized with respect to the cell length. For all structures except this one we were able to find the minimal cell length, i.e. varying the cell length we were able to find such length for which the free energy density of

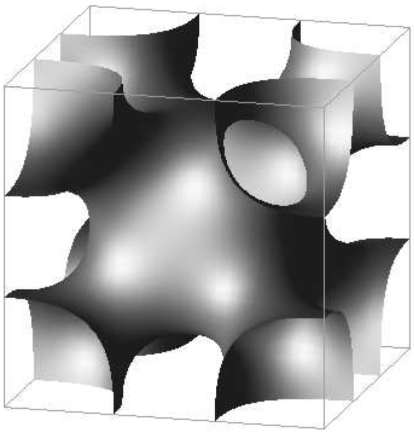

Figure 4.16: Schoen surface I-WP generated from the functional (2.9) The unit cell. Off front view.

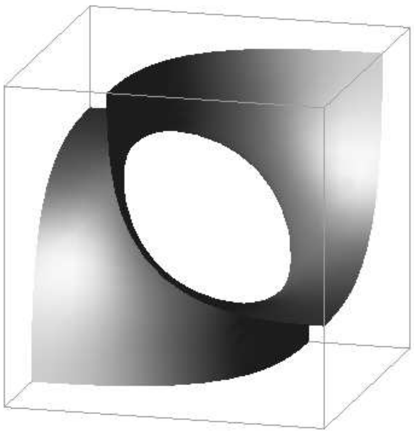

Figure 4.17: Schoen surface I-WP generated from the functional (2.9) 1/8 of the unit cell. Off front view.

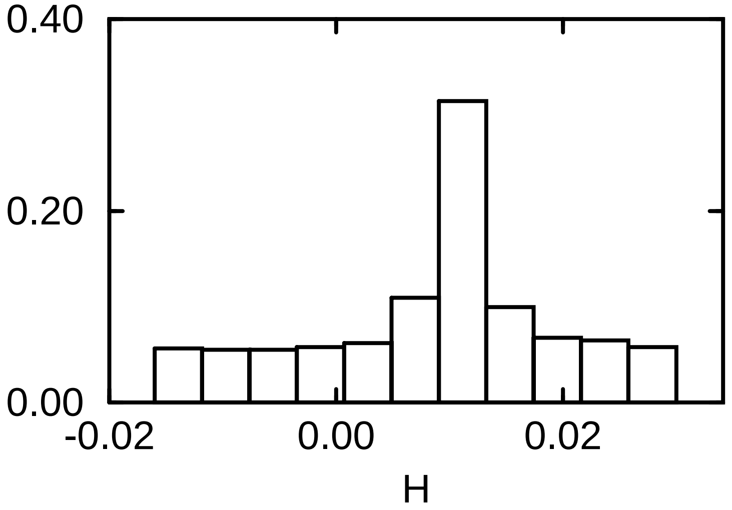

Figure 4.18: The histogram of the mean curvature for the surface I-WP

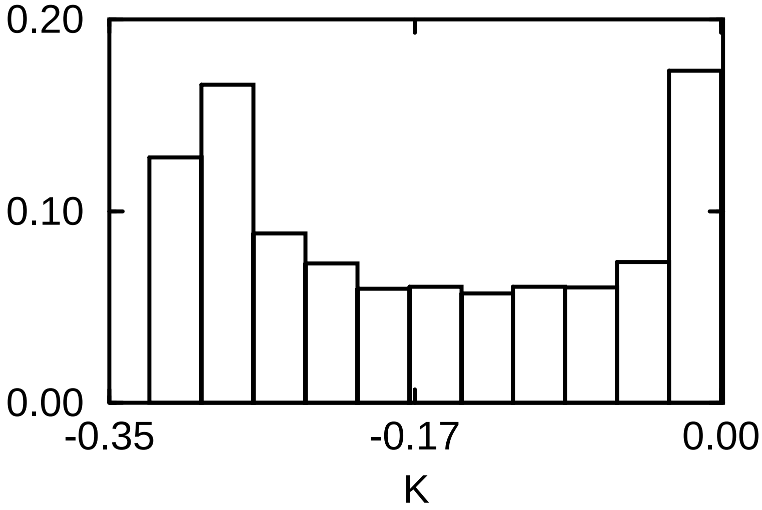

Figure 4.19: The histogram of the Gaussian curvature for the surface I-WP

the functional (2.9) is in minimum. The O,C-TO structure collapses to I-WP when the cell length is varied. Such a behavior suggests that this structure is very unstable and finding it in real systems is problematic.

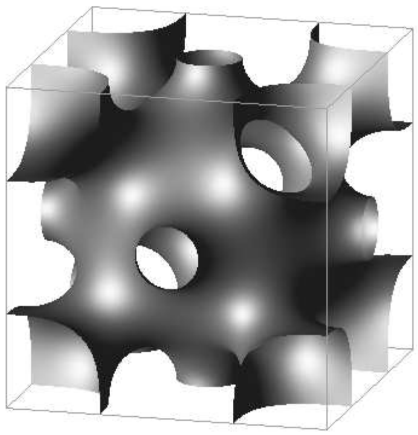

Figure 4.20: Schoen surface O,C-TO generated from the functional (2.9) The unit cell. Off front view.

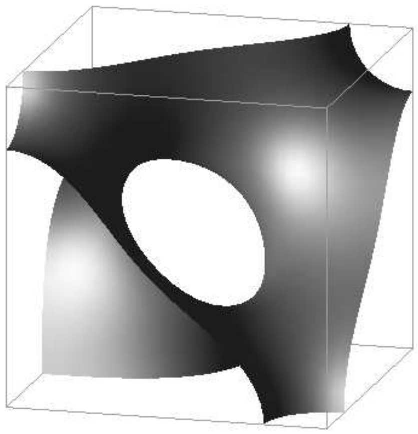

Figure 4.21: Schoen surface O,C-TO generated from the functional (2.9) 1/8 of the unit cell. Off front view.

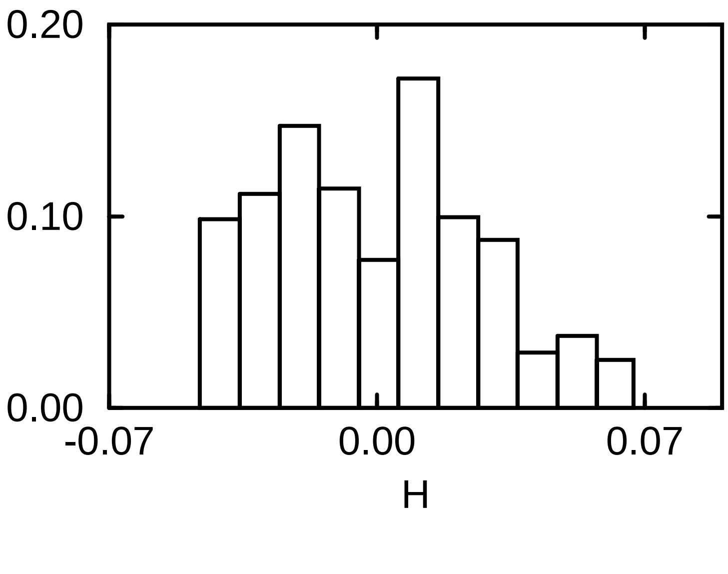

Figure 4.22: The histogram of the mean curvature for the surface O,C-TO

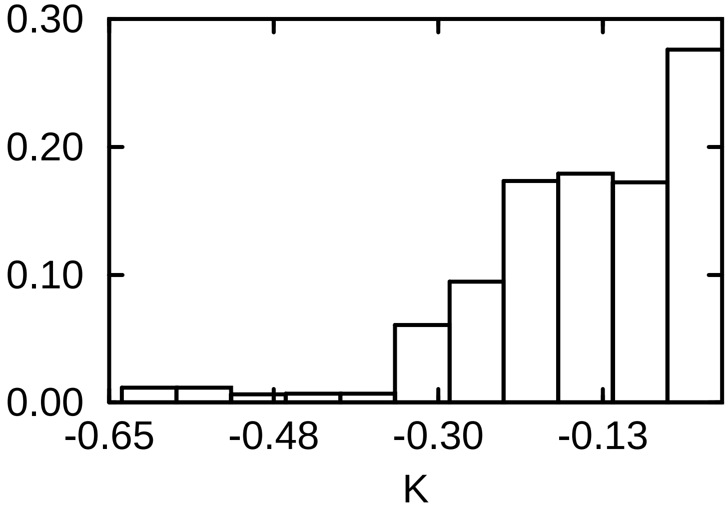

Figure 4.23: The histogram of the Gaussian curvature for the surface O,C-TO

Name	**Cell Length**	**Energy**	**Surface Area**	**Genus**	**Volume Fraction**
P	7.88	-0.181	2.3453 [2.3451068]	3	0.5
D	12.56	-0.188	3.8387 [3.8377862]	9	0.5
I-WP	11.78	-0.180	3.4640 [3.4646016]	7	0.533
G	10.08	-0.190	3.0919	5	0.5
O,C-TO	14.68	-0.162	3.6805	10	0.535

Table 4.1: The geometrical properties of the known minimal surfaces obtained from the functional (2.9), for the parameters $f_0 = 0.0$, $g_0 = -3.0$. In the square brackets are given the exact values found in the literature. Surface area $\tilde{S}$, in the table, is the normalized per face of the unit cube L^2 surface area S of the interface in the unit cell, $\tilde{S} = S/L^2$, $L = (N-1)h$. The energy is given per unit volume.