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To cite this version:

D. Anderson. A NEW TECHNIQUE FOR STUDYING MICROSTRUCTURES: 2H NMR BANDSHAPES OF POLYMERIZED SURFACTANTS AND COUNTERIONS IN MICROSTRUCTURES DESCRIBED BY MINIMAL SURFACES. Journal de Physique Colloques, 1990, 51 (C7), pp.C7-1-C7-18. <10.1051/jphyscol:1990701>. <jpa-00231100>

HAL Id: jpa-00231100

https://hal.archives-ouvertes.fr/jpa-00231100

Submitted on 1 Jan 1990

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A NEW TECHNIQUE FOR STUDYING MICROSTRUCTURES: $^2$H NMR BANDSHAPES OF POLYMERIZED SURFACTANTS AND COUNTERIONS IN MICROSTRUCTURES DESCRIBED BY MINIMAL SURFACES

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Abstract - The polymerization of bicontinuous cubic and, in particular, aligned intermediate phases provides a new way to use NMR to study and characterize these microstructures. The computation of the $^2$H NMR bandshape for a polymerized, deuterated surfactant or counterion in an aligned cubic or intermediate phase is given here for many model microstructures. The calculation applies over the whole volume fraction range defined by the family of parallel surfaces. The polymerization of the surfactant (which has been performed in a cubic phase without inducing change in the SAXS pattern or optical isotropy) prevents the self-diffusion of the surfactant and, since the distribution of normal directions over a surface parallel to a minimal surface does not cover the sphere uniformly, the NMR bandshape will not be a delta function nor a Pake pattern. Instead, this bandshape will be a distinctive signature of the structure. Using the expressions for the Gauss map and Gaussian curvature of the underlying minimal surface in the isothermal coordinates of the usual Weierstrass representation, the expected bandshape can be computed in terms of elliptic integrals. The computation of this bandshape is demonstrated in the case of the family of minimal surfaces which includes the CLP, Scherk, G, D, and P minimal surfaces, and for rhombohedral and tetragonal relatives of the P and D surfaces. The latter surfaces would seem to provide particularly good models for the intermediate phases of rhombohedral and tetragonal symmetry.

1 - Introduction.
To date, the only experimental technique which has provided detailed information on the microstructures of cubic and intermediate phases has been small-angle X-ray scattering (SAXS). Structural determination in the case of a 'bicontinuous' phase, in which hydrophilic and hydrophobic moieties are simultaneously continuous and the notion of particles is inappropriate, is in general a difficult problem and the structures of many of the so-called 'intermediate phases' are still open questions. SAXS becomes a more difficult undertaking in the intermediate phases where symmetries are lower, and in contrast with the cubic phases which have been studied by thorough SAXS investigations /1/, many of the intermediate phases are by comparison virtually
unstudied. Firm structural assignments in these lower symmetry cases may call for experimental techniques complementary to SAXS, techniques providing detailed structural information capable of distinguishing various microstructures. Such a technique is described in this paper.

As evidenced by the papers in this proceedings, the description of the bicontinuous microstructures is facilitated by reference to triply-periodic minimal surfaces. For each of the bilayer-bicontinuous cubic phase structures, for example, there is a minimal surface (called a minimal 'balance' surface by Koch and Fischer) with the same topology and symmetry as the phase. These minimal surfaces are now the subject of intense study, and it has been observed that a complete parameterization of each triply-periodic minimal surface is uniquely determined, up to a Bonnet transformation, by the normal direction and order of the flat points where the Gaussian curvature vanishes. One important feature of the experimental technique introduced in this paper is that it provides data which can be directly related to the underlying minimal surface and, in particular, to the normal direction at the flat points.

NMR bandshape analysis provides direct information on the distribution of normals to the mathematical surface describing the locus of surfactant polar groups in a liquid crystal. As discussed in more detail in section 3, this is due to the fact that the molecular director of the surfactant molecule, or the dipole of a bound water molecule or counterion, is on the average in the direction of this surface normal. However, in a monomeric system the self-diffusion of these components averages out this orientation, resulting in a loss of information.

The polymerization of bicontinuous cubic phases has now been accomplished, making it possible to study the distribution of normals without interference from this averaging effect. In particular, the distribution function itself can be obtained if three experimental conditions are satisfied:

A) a surface-active component, such as the surfactant or its counterion, which displays a preferential orientation with respect to the interface, must be labelled with a quadrupolar nucleus such as deuterium;

B) this component must be polymerized (to form a crosslinked polymer) so as to prevent its diffusion; during the timescale of the experiment, it cannot diffuse so as to change its location with respect to the interface significantly, which typically means less than about 10Å to obtain the best resolution;

C) at the time of polymerization the liquid crystal must be aligned, so that the optic axis (or principle axis in the case of a cubic phase) of every microcrystallite makes the same angle with the NMR magnetic field.

With respect to point C), if the polymerization does not fix the structure, as for example in the case of the polymerization of the counterion or of only a fraction of the surfactant, then the alignment must be maintained throughout the experiment.

In the last section some of the experimental considerations for satisfying these requirements are briefly discussed. Most of the paper focuses on the computation of the theoretical bandshapes from models determined by minimal surfaces and surfaces parallel to minimal surfaces. The next section is a short introduction to models which have been used to described intermediate phases, and a proposal of minimal surface models which provide the basis for the calculations.

2 - Models of intermediate phase microstructures.

The normal intermediate phases in sodium and potassium salts, and in sodium sulfonates, were classified by Rendall and coworkers as 'int(1)' and 'int(2)', where int(1) phases occurred at lower surfactant concentration than the cubic phase, adjacent to the hexagonal phase, and int(2) at higher concentration than the
cubic phase, adjacent to the lamellar phase. The authors argued that in the int(1) phase, the structure of int(1) phases comprises rods with non-circular cross-sections packed on a rectangular or distorted hexagonal lattice. There is much evidence that some phases, which could be called 'intermediate', indeed have this structure. Important information on this structure is obtained by $^2$H NMR, where the absence of three-fold (or higher) symmetry means that the powder-averaged bandshape is no longer the usual Pake pattern. The bandshape expected for this structure has been computed and shown to compare well with experimental NMR data in the int(1) phase /6,7/.

The structure of the int(2) phase is still unknown. One class of models describes the structure in terms of disconnected layers, of surfactant in the normal case and water in the reversed case, in which each layer is in turn composed of a periodic network of rods. Many years ago Luzzati and coworkers /8/ proposed this type of model for the reversed intermediate phase in the lecithin - water system, with the rods in a given layer forming a hexagonal net of coordination number $z=3$. More recently, Kekichef and Tiddy /9/ proposed a similar structure for a normal intermediate phase of tetragonal symmetry in the lithium perfluorooctanoate system, with the rods in each layer forming a square net with $z=4$.

In the latter paper, however, the self-diffusion rate of water perpendicular to the layers (i.e., in the direction of the optic axis) would seem to be too high to be consistent with this model. The thickness of the primitive unit cell of the tetragonal phase is almost identical to the d-spacing in the lamellar phase, in which all of the water is between layers. Thus the aqueous 'holes' in the layers of their intermediate phase model would constitute a small area fraction and consequently a large obstruction to diffusion, since diffusion normal to the layers requires at every step a passage through such a hole. In particular, if instead of calculating a volume fraction as was done in ref. /9/, one calculates an area fraction corresponding to these holes, this comes out to be 0.29. This fraction would be even smaller if the true shape of the rods were accounted for rather than the square cross-section of ref. /9/. This low area fraction for passage would imply a relative diffusion constant $D/D_0$ which is much smaller than the observed value; indeed, the ratio of diffusion rates perpendicular to, and parallel to, the layers was about 0.5 for the counterion and 0.8 for the water, much higher than what should be expected for their model. For a solution of the diffusion equation in bicontinuous cubic geometries see ref. /10/, where it is shown that such restrictions have a strong effect on self-diffusion rates.

Another inadequacy of the model of Kekichef and Tiddy has to do with an apparent contradiction between their interpretations of the triple-periodicity and the NMR splittings. On the one hand, the registry between adjacent layers, giving rise to a three-dimensional (body-centered) space group, was argued to be the result of steric interactions between rods of adjacent layers, which led those authors to conjecture that the rods were elliptical in cross-section with the major axis normal to the layers. This same effect was argued to be responsible for the very high viscosity of the phase relative to the lamellar phase. On the other hand, in order to explain the NMR splittings with this model, a local anisotropy was assumed in which the major axes of the rods were taken to be perpendicular to the director, i.e., parallel to the layers.

A reference to triply-periodic minimal surfaces -- which have been so successful in the description of the very closely related cubic phases -- suggests alternative structural models which are in fact bicontinuous. For example, putting connections between neighboring layers in the $z=3$ structure proposed by Luzzati et al. gives rise to the $H'$ -- T minimal surface beautifully illustrated in figure 13 of Schoen's monograph /11/. These minimal surface models might be more in accord with the properties of the int(2) phases:
1) the triple-periodicity is directly incorporated into the model starting at the underlying minimal surface itself;

2) the water self-diffusion rate in the direction of the optic axis can be understood in terms of diffusion through the connections;

3) the high viscosity relative to the lamellar phase is also explained by these connections;

4) the close proximity of the int(2) and bicontinuous cubic phases in composition space is mimicked by the very close relationship between the underlying minimal surfaces;

5) perhaps most significantly, the mean curvature of the polar-apolar interface can be very homogeneous (for computations of families of model surfaces with exactly constant mean curvature see ref. /12/), in contrast to the layer model in which non-circular cross-sections and "... thick junction zones..." of negative mean curvature require very large variations in mean curvature;

6) the NMR splittings are consistent with these models without invoking local anisotropy, as is demonstrated in this paper.

It should be pointed out that there can be no minimal surface underlying the structures proposed by Luzzati et al. in the sense that the P, D and Gyroid minimal surfaces underlie the well-known cubic phases. This is because there can be no minimal surface, except for a plane, which lies between two fixed parallel planes (D. Hoffman, this proceedings). Particularly for the int(2) phase lying between the bicontinuous cubic and the lamellar phase and thus having low mean curvature, one would expect there to exist an underlying minimal surface.

An examination of the literature, in particular Schoen's now-celebrated monograph /11/, reveals several minimal surfaces which might provide useful models for intermediate phases. Many of these are treated in the calculations of section 5. In addition, there are a few other surfaces not treated here which could be important in this respect. We have mentioned the H'-T surface of Schoen, which to this author's knowledge has not been assigned a Weierstrass representation. The S'-S" surface also of Schoen, and computed in ref. /12/, has only been computed numerically, and will be treated at a later occasion.

Another question which seems unresolved is whether the int(1) phase is the same as the deformed hexagonal phase, as proposed in reference /5/, or is another separate phase with possibly a bicontinuous structure or one such as that proposed by Luzzati. In the phase diagram of reference /9b/, there is a phase of monoclinic symmetry which is presumably composed of discrete (possibly deformed) rods, with apparently no sign of a two-phase region between it and the hexagonal phase. Then, in addition there are two intermediate phases on either side of the cubic phase, one with rhombohedral symmetry and the other tetragonal. The latter are three-dimensional space groups and the triply-periodic structures proposed herein -- in particular the rhombohedral distortions of the cubic P and D structures -- may apply to these two phases, with the deformed hexagonal being entirely separate from these.

It is also worth mentioning that elsewhere in this proceedings, a recently-discovered minimal surface -- a 'Karcher tower' -- has been used to model the transformation from a hexagonal phase to a cubic phase. The same calculation performed herein for equilibrium phases are also possible in structures of this sort, and may prove useful in the analysis of transitory states in phase transitions, and in the study of liquid crystalline defects /13/. Thus, the calculation in section 5 for the rPD family may find application in the transitory states in the D (Pn3m) to P (Im3m) transformation, and the Scherk surface calculation could apply in the analysis of twist defect regions in lamellar phases of surfactant and block copolymer systems /13/.
The theory of the NMR bandshape for polymerized liquid crystals with 3-fold symmetry.

The $^2$H NMR bandshape which is obtained from a deuterated surfactant, counterion, or less reliably from heavy water bound to the surfactant head group, gives information on the distribution function of the C-D (or O-D, N-D, etc.) bond direction with respect to the static field of the NMR experiment/14/. We will restrict the present discussion to the case where both of the following conditions are satisfied:

Condition 1: There is three-fold or higher local symmetry around the axis described by the time-averaged surfactant molecular director, within the surfactant film; and

Condition 2: There is three-fold or higher crystallographic symmetry to the periodic liquid crystalline structure; i.e., to the unit cell, the labelled molecules are not free to diffuse.

If Condition 1 is satisfied, as is the case with liquid crystals composed of non-chiral ($C_{3v}$ symmetry) or chiral ($D_{3d}$ symmetry) molecules, then only the projection of the C-D bond onto the normal to this surface is relevant. Thus, the NMR bandshape problem is transformed into the mathematical problem of finding the distribution function of $x=(3\cos^2\theta_{nB}-1)/2$, where $\theta_{nB}$ is the angle between the normal to the surface describing locus of the head groups, with the static NMR magnetic field direction $B$. If the deuterated component is executing self-diffusion so as to sample the different possible orientations during the timescale of the experiment, as is normally the case with an unpolymerized system, then the molecules are statistically indistinguishable and the distribution function is averaged by this diffusion. If on the other hand, the labelled molecules are polymerized, then they are distinguishable by their position and the normal direction at that position, and this motional averaging is not in effect.

If we focus attention for the moment on a given microcrystallite with the optic axis having a direction $S$, then we consider the two cases:

1. The labelled species is unpolymerized and diffusing. In this case the NMR signal from this microcrystallite will consist of two delta functions, located at the two shift frequencies $x=\pm v_0 < (3\cos^2\theta_{nS}-1)/2 > (3\cos^2\theta_{SB}-1)/2$, where $\theta_{nS}$ is the angle between the surface normal $n$ and the optic axis $S$, and $\theta_{SB}$ is the angle between $S$ and $B$. This is because under Conditions 1 and 2 the interaction with the magnetic field can be performed in two steps, first by projecting the surface normal direction onto the optic axis $S$ because of the motional averaging, and then considering the residual interaction as having an orientation given by $S$ and thus an angle $\theta_{SB}$ with respect to the magnetic field. The constant of proportionality $v_0$ is discussed in the next paragraph.

2. The labelled species is polymerized and not diffusing. In this case one cannot use motional averaging to project onto $S$, but rather the intensity at each shift frequency $v_0x$ is simply proportional to the value of the distribution function $f(x)$ where $x=(3\cos^2\theta_{nB}-1)/2$, or more precisely, to the sum $f(x)+f(-x)$, since NMR cannot distinguish between $x$ and $-x$. This distribution will in general be different for relative orientations $S - B$ which are not crystallographically equivalent.

In all cases the proportionality constant $v_0$ must be determined by the use of a reference sample, which is typically a lamellar phase, where care is taken to assure that the local motions of the labelled molecule are the same in the reference sample and the sample of interest; in particular, if the sample of interest is (un)polymerized then the reference sample must also be (un)polymerized. If the powder lamellar phase is used as the reference, then $v_0$ is the half-bandwidth of the spectrum in Hertz; by half-bandwidth is meant one-half the distance between the edges of the spectrum, which correspond to the 0 degree orientation. Alternatively, $v_0$ is half the distance between delta functions (again a half-bandwidth) in an aligned lamellar phase with the optic
axis $\mathbf{S}$ parallel to $\mathbf{B}$. If the hexagonal phase is used, then $v_0$ is twice the observed half-bandwidth (i.e., the full width) in either the powder or the $\mathbf{S} \parallel \mathbf{B}$ case.

We next consider these two cases in a powder sample (polycrystalline with $\mathbf{S}$ uniformly distributed over the sphere).

case 1: the labelled species is unpolymerized and diffusing. This is the situation normally encountered in NMR of liquid crystals. Each microcrystallite contributes two delta functions as just described, and the superposition of these delta functions -- weighted by the distribution

$$g(\theta_{SB}) = \frac{1}{\sqrt{2}} \sin(\theta_{SB})$$

corresponding to the uniform distribution over the sphere of $\mathbf{S}$ -- gives rise to the so-called 'Pake' pattern, shown in figure 1.

![Fig. 1](image-url)  

Fig. 1 - The classical 'Pake pattern' bandshape, obtained from a superposition of delta functions for a uniform covering of the sphere. The x-axis has been made dimensionless and would have dimensions of Hertz in an NMR experiment. The y-axis is also dimensionless and normalized. This is the bandshape which results for any structure with a three-fold or higher axis in the powder-averaged, diffusional averaged (unpolymerized) case.

The half-width of this bandshape is $v_0 < (3\cos^2\theta_{NS}-1)/2>$, which gives information on the unit cell. It has the value $v_0$ for lamellar phase, $v_0/2$ for the hexagonal, 0 for a cubic phase, and values are given in this paper for various intermediate phase models.

case 2: the labelled species is polymerized and not diffusing. The superposition of the patterns discussed above, with the vector $\mathbf{S}$ distributed uniformly over the sphere, must result in a Pake pattern with half-bandwidth $v_0$, under Condition 1; there is no translational diffusion that could induce asymmetry. This in turn means that the bandshape contains no structural information.

We thus see that only in the case of a polymerized, aligned intermediate phase does the NMR bandshape provide a distinctive signature of the structure, giving essentially the distribution function of the normal directions over the head group surface. Furthermore, this bandshape is different for different (non-equivalent)
relative orientations $S - B$, and thus the set of curves for different values can be checked, in principle, against the experimental NMR curves over a selection of orientations of the optic axis with respect to the magnetic field. In section 5 are results showing how the curve can change quite dramatically with change in orientation. This provides for a very strong and discriminating test of a model structure.

An additional bonus from the calculation of these bandshapes for the polymerized, oriented case is that the bandwidth, commonly called the splitting, computed by integrating the first moment of the distribution function $f(x)$:

$$\text{splitting} = \int x f(x) \, dx,$$

is the same as the bandwidth for the unpolymerized powder case, which is much more routine experimentally.

The distribution function $f(x)$ for the variable $x = (3 \cos^2 \theta - 1)/2$ is easily obtained from the distribution function $F(\theta_B)$ via $f = F/(\sin \theta_B \cos \theta_B)$.

4 - General case of a head group surface parallel to a minimal surface.

We now focus on the case where the surface describing the locus of the labelled groups is a parallel surface to a minimal surface; we focus on the case of a triply-periodic surface but note that, for example, the Scherk minimal surface is a limit of one of the families of minimal surfaces treated in the next section and the results apply also for this doubly-periodic surface.

The parallel surface is obtained by moving a fixed distance $L$ along the normal to the minimal surface at each point, thus arriving at a point on the new surface. This construction leads to a well-defined surface as long as $L$ is less than $\sqrt{-K_{\text{min}}}$, where $K_{\text{min}}$ is the most negative value of Gaussian curvature over the minimal surface. Formulae for the volume fractions, surface areas, mean curvatures, etc. of the parallel surface are given in ref. /15/. Typically $L$ will represent the half-width of the bilayer, converted to dimensionless units using (one of) the lattice parameters.

This work is done under the assumption that the probability density of finding a labelled group is constant over the surface area of the parallel surface. Thus the weighting of angles $\theta_B$ is done by the area element $dA$ of the parallel surface.

It is necessary to derive the distribution function of the angle $\theta_B$ where $\mathbf{n}$ is on the parallel surface. One elementary property of parallel surfaces is that the normal direction is the same as that on the original surface (at the corresponding point, of course). However, the area element $dA_L$ is not the same, but related by:

$$dA_L = (1 + KL^2) \, dA_0,$$

where $dA_0$ is the area element on the minimal surface.

The key to the computation is the use of the Gauss mapping. The normal directions $(x,y,z)$ at a point $(X,Y,Z)$ on the surface are mapped to the unit sphere, and then via stereographic projection to the $(u,v)$ complex plane:

$$u = x/(1-z), \quad v = y/(1-z).$$

It will be expedient to write the complex plane in polar coordinates:

$$u = r e^{i\psi},$$

and by the properties of the stereographic projection, the angle $\psi$ is the same for the complex plane and the Gauss sphere: e.g., $\tan \psi = y/x$. The differential area elements in the three representations, with $dO$ representing area on the sphere, are (wherever $K \neq 0$):

$$dA_0 = dO/|K| = [r/(1+r^2)^2] \, dr \, d\psi/|K|.$$
Here as everywhere, $K$ will refer to the Gaussian curvature not on the sphere but on the corresponding point on the minimal surface.

The importance of the Gauss map lies in the following observation: if we parameterize the surface so that the $z$-direction is parallel to the magnetic field direction $B$, then the locus of points on the parallel surface whose normals lie at a constant angle $\theta_{nB}$ with respect to the magnetic field are circles -- lines of constant $r$ -- in the complex plane, since they are circles at constant $z=\cos(\theta_{nB})$ on the Gauss sphere; here the fact that the parallel surface and minimal surface have the same normal has been used. Thus the problem is transformed into finding the distribution function $F(r)$, weighted by the area element $d\alpha_L$ of $r$. One can compute that:

$$\cos \theta_{nB} = \frac{(r^2-1)}{(r^2+1)}$$

so that:

$$x=(3 \cos^2 \theta_{nB}-1)/2 = \frac{(r^4 - 4r^2 +1)(1+r^2)^2}{2}$$

and by differentiation of this:

$$f(x) = F(r) \left(1+r^2\right)^2/[12r(r^2-1)]$$

To obtain this weighting, we begin by writing the expression for the area of a patch of parallel surface:

$$A = \int_P d\alpha_L = \int_C \left((1+K L^2)/|K|\right) \left[r/(1+r^2)^2\right] d\psi dr$$

the subscript $P$ on the integral sign will refer to integration over the parallel surface, while $C$ refers to integration over the complex plane.

But examination of this nested integral reveals that the distribution function in question is given by:

$$F(r) = \int_C \left((1+K L^2)/|K|\right) \left[r/(1+r^2)^2\right] d\psi$$

$$= \left[r/(1+r^2)^2\right] \left\{ \int_C i|K|^{-1} d\psi - L^2 \right\}$$

where the minus sign in the second term comes from the fact that $K/|K|=-1$ for a minimal surface, since the Gaussian curvature is negative except at isolated points (except for a plane). In all the minimal surfaces treated herein, the integration on the top half sphere -- where $r>1$ -- gives the same value as that on the bottom half, so we consider only $r<1$ and integrate over the unit circle in the complex plane. Furthermore, in the cases treated here, by symmetry we need only take $0<\psi<\pi/4$. Therefore the integration to be performed is:

$$F(r) = 16 \left[r/(1+r^2)^2\right] \left\{ \int_A i|K|^{-1} d\psi - L^2 \pi/4 \right\}$$

where the domain of integration $A$ is the circular arc of radius $r$ from $\psi=0$ to $\pi/4$ in the $(u,v)$ complex plane.

The Weierstrass representation of the minimal surface provides the expression for the Gaussian curvature -- without the need to explicitly integrate the Weierstrass equations to get $X,Y,$ and $Z$ coordinates! Explicitly:

$$K = -4 \Re(\omega)^2 / (1+r^2)^4$$

Thus, the mathematical problem comes down to evaluating the integral:

$$I = \int_A \Re(\omega e^{i\psi}) |^2 \ d\psi$$

The formula for $\Re(\omega)$ is:

$$\Re(\omega) = \Pi (\omega - \omega_m)^{1/b_m}$$

where the $\omega_m$, with $m=1,\ldots,M$ represent the normals to the flat points of the lattice-fundamental region of the minimal surface (this lattice-fundamental region is obtained by taking the periodic surface modulo the
orientation-preserving isometries of the surface; many mistakes in the literature can be traced to misinterpretation of this criterion), and $b_m$ is the degree of the Gauss map at the $m$th flat point. In most of the cases treated here, the number of flat points is $M=8$.

In the general case, the integration is very difficult to reduce to elliptic integrals. In the cases treated here, the situation is better in that the $b_m$ are all equal, say $b_m=b$. The attempt then begins by writing the reciprocal of the integrand as:

$$\int R(e^{i\psi})^2 = \left[ R(e^{i\psi}) R(e^{-i\psi}) \right]^{1/b},$$

using the fact that the complex conjugate of a polynomial $P(\omega)$ is $P^*(\omega^*)$, where the $P^*$ means that any complex coefficients in $P$ must be conjugated. Using the relations $\cos n\psi = (e^{in\psi} + e^{-in\psi})/2$ and $\sin n\psi = (e^{in\psi} - e^{-in\psi})/2$, this expression is converted to an expression of the form:

$$\int R(e^{i\psi})^2 = \left[ \Sigma P_n(r) \cos(n\psi) + Q_n(r) \sin(n\psi) \right]^{1/b},$$

where the highest degree of $r$ in $P_n$ and $Q_n$, and the highest value of $n$, is no greater than $M$. Notice that although the coefficients of the cosine and sine terms are polynomials, this does not cause any complications since along the integration path $A$, $r$ is constant and thus so are the coefficients. One can then use trigonometric identities to convert from terms of the form $\cos(n\psi)$ to terms of the form $\cos^m\psi$. For example:

$$\cos(8\psi) = 1 - 32 \cos^2\psi + 160 \cos^4\psi - 256 \cos^6\psi + 128 \cos^8\psi.$$ 

Then the substitution $s=\cos\psi$ yields a polynomial of eighth degree in $s$ or less if the sine occurs only to even powers; this appears in the denominator raised to the $1/b$ power, together with the Jacobian $\sqrt{1-s^2}$ from the substitution.

If the $b_m$ are all equal and the polynomial $T(\omega) = \Pi (\omega - \omega_m)$ has only real coefficients, then the sine terms all vanish. If in addition the only nonzero terms have powers which are all divisible by 3 (4), then the substitution $\sigma=3\psi$ ($\sigma=4\psi$) reduces the degree of the highest cosine term, to two in the cases treated here. In this case the resulting integral can be evaluated with complete elliptic integrals.

The derivation has been done under the assumption that the $z$-direction of the surface corresponds to the direction of the magnetic field. Thus, in order to obtain the theoretical NMR curve for an arbitrary orientation of the optic axis with respect to the magnetic field, it is necessary to rotate the minimal surface so that the optic axis is in the desired direction. This is equivalent in the present problem to rotating the sphere so that the flat points $\omega_m$ change correspondingly. In the surfaces treated in this paper, the order $b_m$ of each flat point is the same, and in fact $b_m=2$. This means that $R(\omega)$ is the square root of a polynomial with coefficients that are in general complex for an arbitrary orientation.

In this paper, the only orientations which are treated are those which result in a polynomial $R(\omega)$ with only even powers, and with real coefficients. In these cases it is possible to reduce the problem to complete elliptic integrals. The more general problem will be treated elsewhere, and will probably require numerical integration. Fortunately however, the computation for a single orientation is sufficient to yield the value of the splitting for the unpolymerized, powder case.

Note concerning associate surfaces. Since the Gauss map and Gaussian curvature distributions of two minimal surfaces related by a Bonnet transformation are identical, the equations above are formally the same and it would appear that one could never distinguish between associate surfaces via this technique -- for example between the Schwarz P, D, and the Gyroid structures. However, there are several important factors which make this less of a complication in actual experimental situations:
A) one common process for creating aligned intermediate phases consists of starting from an aligned lamellar or hexagonal phase and changing temperature, in which case there may be reasonably predictable epitaxial relationships which would be different in general for different members of the Bonnet family; this might rule out possible members because the NMR bandshape does change significantly for different orientations of the same surface, as we see in the next section.

B) in most actual applications of this method the space group of the structure will be known from SAXS, and the different Bonnet members are usually easily distinguishable by the space group; also, from the lattice parameter the K and L (usually known from chemical information) can be made dimensionless, and the relationship between volume fraction and dimensionless \( L/\sqrt{15} \) as well as the change of \( P(r) \) with \( L \) could be used to distinguish between different Bonnet members.

5 - Calculation for several families.

The first class of examples comprises the case where the flat point orders \( b_m=2 \) for \( m=1,...,8 \), and the polynomial \( T(\omega) \) has in fact only powers divisible by four:

\[
T(\omega) = 1 - c_4 \omega^4 + c_8 \omega^8 .
\]

This case includes with \( c_8=1 \):
- the CLP surface, when \( 0 < c_4 < 2 \);
- the Scherk surface, when \( c_4 = 2 \); and
- the Schwarz P and D surfaces and their tetragonal distortions, when \( c_4 > 2 \) (P and D when \( c_4 = 14 \)).

These properties which make the polynomial \( T(\omega) \) easy to work with only hold for special orientations of the surface, and we will treat here only the case where the 4-fold axis is vertical.

Using the method outlined above one can easily compute that:

\[
| R(r e^{i\psi}) |^2 = (1+\alpha^2+\beta^2) - 2\alpha(1+\beta) \cos \mu + 2\beta \cos 2\mu
\]

where \( \alpha = r^4 c_4 \) and \( \beta = r^8 c_8 \), and the substitution \( \mu = 4\psi \) has been used. The integral \( I \) becomes, after factoring the quadratic and recalling that the exponent \( 1/\beta = 1/2 \):

\[
I = (4\beta)^{-1/2} \int [(\varepsilon_1 - \cos \mu)(\varepsilon_2 - \cos \mu)]^{-1/2} d\mu ,
\]

where the integration is from \( \mu = 0 \) to \( \pi \). The values of \( \varepsilon_1 \) and \( \varepsilon_2 \) (< \( \varepsilon_1 \)) are given by:

\[
\varepsilon_1 = (a_1 + a_2 r^8)/r^4, \quad \varepsilon_2 = (a_2 + a_1 r^8)/r^4 ,
\]

where for \( c_4 \geq 2 \):

\[
a_1 = [c_4 + \sqrt{(c_4^2 - 4)}]/4 \quad \text{and} \quad a_2 = [c_4 - \sqrt{(c_4^2 - 4)}]/4 ,
\]

with appropriate changes for the CLP case where \( c_4 < 2 \). Upon the substitution \( t = \cos \mu \) we obtain:

\[
I = (4b)^{-1/2} \int [(1-r^2)(\varepsilon_1 - t)(\varepsilon_2 - t)]^{-1/2} dt .
\]

This can be evaluated in terms of elliptic integrals via, e.g., equation 252.00 of Byrd and Friedman’s handbook. The integrals are complete elliptic integrals (ultimately because of the integration range from 0 to \( \pi \)), and were evaluated with a canned routine on the Macintosh software program "MatLab". The formulae for these cases are:

i) \( P_1 \) and its associate \( D_{10} \), tetragonal distortions of \( P \) and \( D \) (including \( P \) and \( D \) themselves), four-fold axis parallel to the magnetic field:

\[
f(x) = \left[ \frac{4}{3}(1+r^2)/(1-r^2) \right] \left\{ \left[ (1+r^2)^4/(16r^4) \right] K(k)[(\varepsilon_1 - 1)(\varepsilon_2 + 1)]^{-1/2} - L^2 \pi /4 \right\} ,
\]
where the modulus $k$ of the complete elliptic integral of the first kind is given by:

$$k^2 = 2(e_1 - e_2)/[(e_1 - 1)(e_2 + 1)]$$

ii) The CLP surface (including the Scherk surfaces), four-fold axis parallel to the magnetic field:

$$f(x) = \left\{ \frac{4/3(1+r^2)/(1-r^2)}{[(1+r^2)^4/8] K(k)(1+(2-c_4^2)r^8 + r^{16})^{-1/2} - L^2\pi/4} \right\},$$

where the modulus $k$ is given by:

$$k^2 = (4-c_4^2)r^8/[1+(2-c_4^2)r^8 + r^{16}]$$

It should be emphasized that the evaluation of the dimensionless number $L$ in this formula, the unit cell will not in general have unit length because the normalization constant in the Weierstrass representation has been left out. Thus, for the D surface, for example, the $Pn3m$ unit cell will have edge length $a=\kappa^{1/2}$ where $\kappa=0.8389222985$....

iii) The "rPD" family, rhombohedral distortions of D (including P and D):

In this family, a slightly different approach will be used, because the appropriate orientation for evaluating the splitting is with the (highest symmetry) three-fold axis in the direction of the magnetic field $B$, which puts one of the flat points is at infinity. This is accounted for by leaving the term corresponding to this flat point out of the polynomial $T$ (since in the limit of $\omega \to 0$ as $\omega \to \infty$, the $\omega$ dependence disappears).

The positions of the flat points are given in reference 17/ for this orientation, but the rotation used in that paper to eliminate the flat point at infinity will not be used here. Therefore it is easy to see that the two triplets of variable flat points, when projected onto the complex plane, are cube roots of $\omega=-\mu/(1-E)$ and of $\omega=-1/a$, respectively. The downward pointing flat point gives a factor of $\omega-0$, and the polynomial is simply:

$$T(\omega) = \omega(\omega^3+a^3)(\omega^3-b^3) = \omega^7 - (b^3-a^3) \omega^4 - \omega$$

Following the normal procedure:

$$\Re(r e^{i\psi})^2 = (r^2 + g^2 + r^{14}) - 2g(r-r7) \cos \mu - 2r^8 \cos 2\mu$$

where $g=r^4(b^3-a^3)$, and the substitution $\mu=3\psi$ has been used. Very much as before, we obtain:

$$f(x) = \left\{ \frac{4/3(1+r^2)/(1-r^2)}{[(1+r^2)^4/(12r^4)] K(k)((e_1 + 1)(e_2 + 1))^{-1/2} - L^2\pi/4} \right\},$$

where the modulus $k$ of the complete elliptic integral of the first kind is given by:

$$k^2 = 2(e_1 + e_2)/[(e_1 + 1)(e_2 + 1)]$$

here

$$e_1 = \sqrt{((8+8p^2+q^2)/16)} + q/4 \quad \text{and} \quad e_2 = \sqrt{((8+8p^2+q^2)/16)} - q/4 \quad ,$$

where

$$p^2 = (r^2 + g^2 + r^{14})/(2r^8) \quad \text{and} \quad q = g(r-r7)/r^8 \quad .$$

In order to account for instrumental broadening, some of the curves shown were convoluted with a Lorenzian function, chosen to have a width which would be representative of a typical NMR setup. This
convolution was performed after the flipping and adding, corresponding to $f(x) + f(-x)$. The convoluted curves have the practical advantage that they do not diverge at $x = \pm 1/2$, in addition to being more directly comparable to experiment. The curves have been normalized by setting the highest intensity to 100.

6 - **Selected results.**

To begin with, from the derivation it is clear that the integral under the curve $f(x)$ should give the surface area of the unit cell -- actually of half the unit cell since only $r \leq 1$ has been used. This is a bit more difficult to make use of than one might suspect, because in order to make the unit cell of the surface come out to have unit edge length, one must know the appropriate normalization constant in the Weierstrass representation. In the case of the cubic D surface, this value was mentioned above, and indeed the surface area computed by direct numerical integration of $f(x)$ was within 0.03% of the correct value. In addition, varying $L$ in the program resulted in a change in surface area which also checked within 0.03% of the value for the parallel surface. Thus, this provides a check on the numerical method. However, although the ratio $c/a$ for the tetragonal and rhombohedral surfaces has been graphed in reference /17/, the values of $c$ and $a$ themselves were not, and thus the normalization of the surface areas will not be performed here, but will appear in a more comprehensive publication at a later date.

**Results for the tetragonal surfaces.** The parameter $E$ used in reference /17/ will be used rather than the value of $c_4$ in the presentation of these results. They are related by

$$c_4 = 2 + \frac{4E}{(1-E^2)^2}.$$

The bandshape for the cubic D and its associates, the P and Gyroid surfaces, is found by taking $E = 1/\sqrt{3}$. The computed splitting was, within the numerical error of about 0.005, equal to zero, as it must be for a cubic structure. The bandshape, with $L = 0$, is shown in figure 2. One notices immediately that there is a strong peak at $x = 0$. This is not due to the isotropy of the cubic phase, as will become clear; rather it is due to the presence of flat points with normals in the $(111)$ directions, which lie at the 'magic angle' ($\cos^{-1}(1/\sqrt{3}) = 54.735\ldots$) at which $x = (3\cos^2 \Theta - 1)/2 = 0$.

![Fig. 2](image-url)

Fig. 2 - Calculated bandshape for a polymerized Schwarz P or D cubic phase with one crystallographic axis parallel to the static field of the NMR spectrometer. The width $L = 0$. The axes are as in fig.1. The peak at $x = 0$ results from the flat points with normals in the $(111)$ directions, giving rise to a high concentration of normals near these directions, in the distribution function $F(\theta_{nB})$. 
Indeed, for each tetragonal surface, peaks are found at \( x = \pm (3E^2 - 1)/2 \). Changing the value of \( L \) did not cause significant changes in any of the curves investigated. This is a fortunate situation from the point of view of interpreting experimental data. For instance, the bandshape for \( L = 0.25 \) is shown in figure 3.

For \( E = 0.3 \), the value of \( x \) corresponding to the flat point normal direction is \(-0.365\), and indeed peaks are seen at \( x = \pm 0.365 \).

---

**Fig. 3** - Calculated bandshape for the same structure as in fig. 2 but with the width parameter \( L = 0.25 \).

**Fig. 4** - Calculated bandshape for tetragonal distortion of P or of D with \( E = 0.3, L = 0 \).
Thus it is possible, in principle at least, to determine the value of $E$ directly from experimental NMR data. Since each value of $E$ corresponds to a different value of the $c/a$ ratio, then agreement between the $c/a$ ratios from the two experimental techniques would provide very strong evidence in favor of the model structure. One would then of course go further by comparing the full bandshape with these calculated curves, and computing structural lengths such as $L$, etc.

The calculation also yielded values for the NMR splittings for the normal, unpolymerized powder experiment. These are given in the following table. Here, the value is normalized as usual, by taking the lamellar phase splitting equal to unity; the value for the hexagonal phase for example would be $1/2$.

Table 1. Calculated splittings for tetragonal surfaces, $L=0$.

<table>
<thead>
<tr>
<th>$E$</th>
<th>Splitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5774</td>
<td>0.0</td>
</tr>
<tr>
<td>0.5</td>
<td>0.078</td>
</tr>
<tr>
<td>0.4</td>
<td>0.161</td>
</tr>
<tr>
<td>0.3</td>
<td>0.229</td>
</tr>
<tr>
<td>0.15</td>
<td>0.315</td>
</tr>
</tbody>
</table>

Results for the CLP family. All of the CLP surfaces have all of their flat points horizontal with respect to the (vertical) optic axis; that is, at $\theta_{HS} = \pi/2$. We take the four-fold axis to be vertical of course, for the evaluation of the splitting as well as for making the integrations analytically tractable. With this in mind it is clear that the peak position should be at $x=\pm0.5$. What is surprising is the extent to which these two peaks dominate the bandshape. In all cases the bandshape is very similar to that in figure 5, which is for the CLP surface with $c_4=1.975$.

Fig. 5 - Calculated bandshape for CLP structure with $c_4=1.975$ and $L=0$. 
The splitting is also relatively constant. In the limit as $c_4$ goes to 2, which corresponds to the Scherk surface where the fraction of surface with non-horizontal normal directions is vanishingly small, the splitting of course approaches 0.5. For most of the CLP surfaces, the value is closer to 0.3, and approaches 0.5 only when $c_4$ is extremely close to 2.

Table 2. Calculated splittings for CLP surfaces, L=0.

<table>
<thead>
<tr>
<th>$c_4$</th>
<th>Splitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.316</td>
<td>0.303</td>
</tr>
<tr>
<td>1.0</td>
<td>0.310</td>
</tr>
<tr>
<td>1.975</td>
<td>0.376</td>
</tr>
</tbody>
</table>

Experimentally, the CLP bandshape for the polymerized oriented structure may be very hard to distinguish from the two-delta-function pattern for an oriented, unpolymerized structure. Care must be taken to insure that the phase is indeed polymerized. One important difference between these two cases is that the two-delta-function pattern will remain as the unpolymerized sample is tilted with respect to the magnetic field, whereas the bandshape for a polymerized CLP structure will not remain as two delta functions but rather the flat points will become non-horizontal and the curve will take on features.

Results for the rhombohedral surfaces. These curves are similar to those for the tetragonal surface but with one important difference. Once again the parameter $E$ gives the location of the flat point normals through $x=\pm(3E^2-1)/2$. However, in addition there are peaks at the edges of the curve where $x=\pm1$. These are due to the fact that two of the flat points lie in the vertical directions. As always, there are peaks at $x=\pm0.5$. Figures 6-8 show the evolution of the curves as $E$ is varied from 0.2, to 0.375, to 0.59. The last value is very close to the limit of existence of the minimal surface 1171.

Fig. 6 - Calculated bandshape for the rhombohedral structure with $E=0.2$, L=0.
The range of splittings for these rhombohedral surfaces is smaller than that for the tetragonal distortions.

Table 1. Calculated splittings for rhombohedral surfaces, L=0.

<table>
<thead>
<tr>
<th>E</th>
<th>Splitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.59</td>
<td>0.196</td>
</tr>
<tr>
<td>0.5</td>
<td>0.112</td>
</tr>
<tr>
<td>0.375</td>
<td>0.019</td>
</tr>
<tr>
<td>0.3333</td>
<td>0.0</td>
</tr>
<tr>
<td>0.2</td>
<td>0.068</td>
</tr>
<tr>
<td>0.1</td>
<td>0.095</td>
</tr>
<tr>
<td>0.0</td>
<td>0.103</td>
</tr>
</tbody>
</table>
Polymerization of surfactants and counterions in bicontinuous liquid crystals.

A future publication will deal much more comprehensively with the experimental side of this technique, but it is important here to make some comments about the experimental feasibility. In particular, work in this research group has demonstrated that polymerizable ionic monomers can be successfully ion-exchanged for the counterion of a surfactant in a bicontinuous liquid crystal, and subsequently polymerized. For example, an ion-exchange column was charged with vinylbenzoic acid, and the cationic surfactant cetylpyridinium chloride run through the column, producing cetylpyridinium vinylbenzoate. A cubic phase was formed with the addition of water, and the vinyl monomer was polymerized by UV light. Similarly, with a variety of surfactants it has been possible to add significant quantities of styrenesulfonic acid to the aqueous phase, together with other monomers such as acrylamide, methylene-bis-acrylamide, etc. In many cases the amount of styrenesulfonic acid added corresponds to the solubility limit in water, and presumably even higher concentrations could be added without destroying the equilibrium cubic phase. We have also been able to add 15% styrenesulfonic acid to the aqueous phase of rhombohedral phase in the SDS-water system, and polymerize; work is under way to establish that the microstructure is maintained. With an anionic surfactant, however, there is question as to whether the monomer has a preferred orientation with respect to the surfactant film. Presently work is under way to perform counterion substitution in the intermediate phase which occurs in the cetyltrimethylammonium chloride-water system, using deuterated vinylbenzoic, styrenesulfonic, or acrylic acid.

Another method is to polymerize the surfactant itself, which must then be labelled. Many polymerizable surfactants can now be found in the recent literature. The present author has succeeded in polymerizing a cubic phase made with unsaturated sunflower oil monoglycerides, water, and the activators cobalt naphthanate and aluminum isopropoxide. The polymerization, which was done over a period of months at 40°C, is believed to have occurred by the absorbance of atmospheric oxygen and the formation of oxygen bridges across neighboring double bonds, much as in the vulcanization of rubber with sulfur. The polymerized sample was clear, non-birefringent, and had a good, rubbery elastic feel (indeed, polymerized fatty acids are of interest as rubber substitutes). A SANS scan of the polymerized cubic phase is seen in figure 9a; the theoretical peak positions for an Ia3d (Gyroid) structure of lattice parameter 110Å is included in the figure. In figure 9b is shown a profile for an unpolymerized Ia3d phase (data to be published), for a comparison of the form factors; these are seen to be very similar in the polymerized and unpolymerized samples.

Figure 9 - a) SANS profile from a polymerized monoglyceride-water cubic phase, indexed to the Ia3d space group with lattice parameter 110Å. b) SANS profile from unpolymerized lecithin-decanol-water Ia3d cubic phase, showing that the form factor is very similar in the polymerized and unpolymerized samples.
With this approach it is necessary to obtain, or synthesize, a surfactant which is not only polymerizable, but also labelled with deuterium. This will almost certainly be expensive on a weight basis but it is not necessary to have all of the surfactant labelled. A small portion, even a few percent, could be labelled; however, the surfactant should all be polymerizable, in order to insure that no diffusion of the labelled surfactant occurs.

Concerning alignment, there are an increasing number of techniques available for creating liquid crystals with a high degree of alignment:

1) it was discussed above that aligned phases can be created by cooling or heating from an aligned lamellar (or hexagonal) phase, where many techniques, including simple shearing between glass plates, are known for obtaining well-aligned lamellar phases;
2) magnetic or electric fields, including the NMR static field itself, have been used to align liquid crystals;
3) certain liquid crystals align spontaneously when confined within certain geometries, as in ref. [16];
4) thermal gradient techniques, as used in growing single crystals, are now being successfully applied to liquid crystals including even cubic phases, as described by Toprakcioglu and coworkers elsewhere in this proceedings.

REFERENCES

/2/ Koch, E. and Fischer, W. this book.