Chapter 3

Geometric models of microemulsions

In this chapter I describe in detail two new models for microemulsions which fall under the general framework set out in the introduction. That is, they treat microemulsion behaviour as a purely geometric question by assuming that the cost of deviations from the optimal volume fractions, interfacial area and curvature is sufficient to justify treating these as constraints. Systems are thus defined by their polar volume fraction \( \phi \), internal surface per unit volume \( \Sigma \) and average value of the effective surfactant packing parameter \( v/\alpha \).

The DOC\(^1\) cylinders and spheres model describes systems in which the interface is strongly curved—that is, for which \( v/\alpha \) is quite different from one. The structure is a random network of cylinders with spheres at the points of intersection. The connectivity can vary, giving a transition to isolated spheres. The DOC lamellar model, a modified Talmon-Prager model, describes systems with very low interfacial curvature. The structure here is a random bilayer with no edges or seams. Both these structures contain unphysical cusps—sharp edges at which the surface suddenly changes direction. It is not imagined that these actually occur: rather they are introduced into the models for the purposes of tractability and are assumed to be details which lie below the resolution of any experiment.

Before going into the details of these new models, I first give a critical review of existing models for microemulsions. One novelty here is the presentation of the first three-dimensional perspective views of the random wave model of Berk [14]. In Section 3.2 I describe the DOC cylinders model and in Section 3.3 the DOC lamellar model. Determination of the curvature of the surface in this latter model requires the development of some geometric techniques which are used to in Section 3.4 to give the first rigorous calculation of the curvature of the cubic random cell model of Jouffroy, Levinson & De Gennes [69]. Finally the understanding of how to deal with cusps developed in the context of the lamellar model is applied to the more complicated circular cusps in the cylinders model to give an exact expression for the curvature

\(^1\)DOC stands for Disordered Open Connected. The name is a product of the French mania for acronyms. I don't know what the “open” refers to, although it presumably has something to do with bicontinuity; the other words speak for themselves.
3.1 Existing models

3.1.1 Spherical droplets

We assume that the system segregates into a dispersion of identical spherical droplets, either of oil in water or water in oil. The internal volume fraction $\phi$ and the total surface $\Sigma$ then determine the radius $r$ and density $n$ of the droplets are determined by the equations

$$\phi = \frac{4}{3} \pi R^3 n$$
$$\Sigma = 4 \pi R^2 n$$

which can be inverted to give

$$R = \frac{3}{\Sigma} \frac{\phi}{\Sigma^3}$$
$$n = \frac{\Sigma^3}{36 \pi \phi^2}.$$  \hspace{1cm} (3.2)

This places a severe restriction on the structure: the sphere radius, and hence the interfacial curvature, is completely determined by the composition, and is independent of everything else, including effective molecular shape of the surfactant. So if bending energy is important, one would expect this model to fail outside a restricted range of composition.

Using the factorisation

$$I(q) = P(q) S(q)$$ \hspace{1cm} (3.3)

Hayter & Penfold [53,54,55,56] showed that for identical spherical objects interacting through a screened electrostatic potential, the full scattering curve can be predicted analytically using only knowledge of the composition, the molecular volumes and three physical parameters: the effective charge per micelle (mainly related to the value of the repulsive potential at contact), the aggregation number and the hydration. This method is now widely used and there exist a number of reviews describing its use and range of applicability [53,54,24,89]. It has been extended using the work of Sharma & Sharma [119] to include some types of attractive interactions.

This is a structural model, and it succeeds in explaining the behaviour of a great number of systems. The simplicity of the geometry involved allows the interactions to be treated with a greater sophistication than in any other model. But the extremely restricted geometric options available to the structure mean that it is incompatible with many observations, for example the bicontinuity convincingly demonstrated in many microemulsions by electrical conductivity or NMR self-diffusion measurements.
3.1.2 Parametric models

A totally different approach to microemulsions is embodied in the parametric models. On the basis of general thermodynamic arguments, Teubner & Strey [126], propose that the scattering should be of the form

$$I(q) = \frac{(8\pi/\xi) \eta^2 c_2}{a_2 + c_1 q^2 + c_2 q^4}.$$  \hspace{1cm} (3.4)

where $a_2$, $c_1$ and $c_2$ are parameters with $c_1 < 0$, $a_2, c_2 > 0$. This expression has been extremely successful at fitting a large number of scattering curves even on absolute scale. From the damped periodic correlation function which gives this scattering, one can derive values for the “spatial periodicity” $d$ ($D^*$ in our notation) and the correlation distance $\xi$ from the equations

$$\xi = \left( \frac{1}{2} \left( \frac{a_2}{c_2} \right)^{\frac{1}{2}} + \frac{c_1}{4c_2} \right)^{-\frac{1}{2}}$$

$$d = 2\pi \left( \frac{1}{2} \left( \frac{a_2}{c_2} \right)^{\frac{1}{2}} - \frac{c_1}{4c_2} \right)^{-\frac{1}{2}}$$  \hspace{1cm} (3.5)

as well as the internal surface

$$\Sigma = \frac{4\phi(1 - \phi)}{\xi}.$$  \hspace{1cm} (3.6)

Another general expression has been derived by Vonk, Billman & Kaler [128]. For an ideal lamellar structure with periodicity $D$, water fraction $\phi$ and thickness polydispersity $\sigma$, they derive a correlation function $\gamma^0(r)$. They then introduce distortions—described as resulting from twisting or bending of the lamellar structure—which cause the correlation function to become

$$\gamma(r) = \gamma^0(r)e^{-2r/d}$$  \hspace{1cm} (3.7)

where $d$ is the “distortion length”. This results in a very similar expression to that of Teubner & Strey. This form is slightly more general in that it is also able to fit scattering curves with no peak.

However there is no guarantee that a given set of $d$, $\xi$ and $\Sigma$ or of $D$, $d$ and $\sigma$ lead to a geometrically possible microstructure. Teubner & Strey do not even suggest a microstructure, while that of Vonk et al. is extremely vague, giving no information about bicontinuity for example. Furthermore both expressions depend on three parameters and hence cannot be tested as they will fit virtually any scattering curve [137].

3.1.3 The random wave model

This model was proposed by Berk [14] using an algorithm of Cahn [19]. The idea is to produce a random structure of typical size $D^*$ by superposing waves of wavelength $D^*$
with random phases and directions. Space is then divided into polar and nonpolar regions by cutting the resulting random field at some threshold value—the polar region is that in which the total amplitude exceeds the threshold.

This "random" structure produces a scattering peak in the desired position but it is sharp rather than broad as observed. To rectify this, a polydispersity in the magnitudes of the wavevectors needs to be introduced. This has been done in two dimensions by Welberry [130] and in three dimensions by Berk and by Chen et al. [25].

With a suitable choice of the functional form for the polydispersity, this formalism allows control over the total interface Σ and the morphology of the structure, but in a rather non-intuitive way. A better solution is to remove the long-range order implied by infinite propagation of waves, and to introduce local correlations which allow the interfacial area and curvature to be controlled. The first step is to give each wave a limited spatial extent. Such a change does not alter the generality of this framework: damped or "localised" waves are a complete basis for all structures. This version produces scattering curves which fit experiment at least as well as the expression of Teubner & Strey [91]. The next step is relate local correlations between the phases to the total interface and the curvature. Work along these lines suggests that, given the simplicity of the formalism, this may lead to the first of the next generation of models: those which are compatible with both geometric and thermodynamic requirements.

Figure 3.1 gives a three-dimensional view of a sample structure produced by Berk's original model and Figure 3.2 one of the localised random wave model of Marcelja. Both structures appear to be bicontinuous. The loss of long-range correlations in the localised random wave model shows up extremely clearly even in the small regions shown.

### 3.1.4 The Talmon-Prager model

This was the first structural model to offer a continuous transition from water droplets to oil droplets via a bicontinuous network [124]. The structure is constructed from the Voronoi cells of a random distribution of points in space with density n by filling them with water or oil at random in the proportions φ and 1 − φ. A surfactant monolayer is then imagined to separate cells with different contents.

This structure is bicontinuous for polar volume fractions between 18% and 82%. It predicts a monotonic increase in electrical conductivity with polar volume fraction, with a percolation threshold at 18%. Observed electrical conductivity behaviour is often much more complicated than this. In particular, the systems studied in Chapter 4 show the opposite behaviour, a decrease in conductivity with increasing water content.

The scattering from the Talmon-Prager model has been calculated analytically [72]
Figure 3.1: Three-dimensional view of the structure given by Berk's random wave model. The region shown is a cube 950Å on a side and the wavelength is approximately 680Å.
Figure 3.2: Three-dimensional view of the structure given by the localised random wave model of Marcelja. The region shown is a cube 950Å on a side and the wavelength is approximately 680Å. The difference here is the finite correlation length $\xi = 227$Å.
and gives no peak. Modification of the model by the imposition of a distance of closest approach on the cell centres [1,3] has the effect of producing a characteristic distance in the structure and hence a peak in the scattering at $D^* \approx n^{1/3}$.

Both versions of this model predict that the correlation length $l_c$ should be equal to the periodicity $D^*$. While this reasoning is based on the problematic identification of $l_c$ with the mean chord (see Section 2.1.4), it is still the case that when $l_c$ is much smaller than $D^*$, there must exist some local structure within the Voronoi cells. This is one of the ideas behind the development of the DOC models: a successful model needs to have two independent length scales.

3.1.5 The cubic random cell model

This model was introduced by De Gennes as a modified Talmon-Prager model [69], and the two are clearly closely related. The construction is exactly that of the Talmon-Prager model but with the Voronoi lattice replaced by a simple cubic lattice of repeat distance $\xi$. Again the cells are filled with water or oil at random, according to the volume fraction $\phi$. The edge length $\xi$ is fixed by

$$\xi = \frac{6\phi(1 - \phi)}{\Sigma} \quad (3.8)$$

and the peak position is given by $D^* = \xi$.

Calculation of the full scattering curve by the method described in Section 2.2 shows that this model gives no peak at all in scattering [8,10]: the zero of the form factor of the cubes exactly cancels the sharp Bragg peak due to the underlying lattice. This is an artefact of the exact calculation and the peak will reappear when a variation in the cube size—justified perhaps by the decoration with a surfactant monolayer—is taken into account.

As noted by Auvray et al. [7], the peak in scattering is usually observed at about $D^* = 2\xi$, twice the distance predicted by the model. This has been taken by some as confirmation of the validity of the CRC model, but the missing factor of 2 in the observed periodicity is instead proof of the existence of correlations between nearby cells, such as could be imposed for example by bending energy considerations [3,113]. If the cells are really filled at random, the peak must be at $D^* = \xi$. This is an alternative way to introduce a second length scale into the system: producing microstructure within the cells leaves $D^*$ unchanged but reduces the correlation length, while introducing correlations between cells leaves the correlation length equal to the cell size but increases the repeat distance.

If correlations are to be introduced on the basis of curvature energy, it is important that the curvature of this model be known. This has until recently only been guessed at. A rigorous calculation is presented in Section 3.4, which shows that the results are rather different to what has been previously envisaged.
3.1.6 "Bicontinuous" models

These models derive from a proposition originally made by Scriven [118] and revived more recently [106,64]. The idea is to "melt" or disorder the structures of bicontinuous cubic liquid crystal phases to obtain a structure with the same properties but which does not give Bragg peaks in the scattering. Cubic phase structures have been shown in several cases to consist of a normal or reversed bilayer centred on a periodic minimal (zero mean curvature) surface which separates two distinct external subvolumes [64]; when "melted" this is believed to give rise to the structure of the isotropic "sponge" or L3 phase [107]. This has been proposed as a possible general model for microemulsion microstructure [106].

Unfortunately, there is no known algorithm for generating a zero or other constant mean curvature surface on a random network. So this model is a qualitative one which cannot yet be tested by experiment. Moreover, if we are going to go to such mathematical lengths to obtain smooth surfaces of prescribed curvature, it is not clear that it is best to go for constant mean curvature. If the modulus of Gaussian curvature is zero and $g_{\text{bend}} = \frac{1}{2}k_c(H-H_0)^2$ then a surface with constant mean curvature $H = H_0$ is clearly an energy minimiser. But it is not necessarily a free-energy minimiser, and if the curvature energy differs from this most simple form, then there is no particular reason why a constant mean curvature surface should be especially favoured, unless for example $H = \text{constant}$ minimises $K$ variations.

None of these models does what we want, except over extremely limited ranges of composition. They are either incompatible with observed results, computationally intractable or simply do not attempt to describe microstructure. From the experience of these attempts it is possible to draw some general conclusions. Firstly there needs to be a repulsion or excluded volume effect in order for there to be a peak in the scattering. More than that, structures require two different length scales: models like CRC and the repulsive version of Talmon-Prager consistently get the peak position wrong because they only have one.

3.2 The DOC cylinders model

We construct a random connected surface with variable connectivity as suggested by Ninham et al. [27]. Instead of requiring that the surface be smooth, as one would undoubtedly imagine, we construct it from spheres and cylinders with cusps at the joins, and assume that these details lie below the experimental resolution. The exact construction is as follows.

1. Begin with a lattice of points of density $n$ which interact via a hard core repulsion. As for the modified version of the Talmon-Prager model this introduces a
natural length scale and ensures the existence of a peak in scattering at around $n^{-\frac{1}{3}}$. The details of exactly what the distance of closest approach should be are discussed further below.

2. Place a sphere of radius $R$ centered on each of these points.

3. Connect pairs of neighbouring spheres with cylinders of radius $r < R$, until there are an average of $Z$ cylinders issuing from each sphere. Thus there are a total of $\frac{1}{2}nZ$ cylinders per unit volume.

This gives us a model structure which depends on the four parameters: the sphere density $n$, the average co-ordination number $Z$, the sphere radius $R$ and the cylinder radius $r$. Figure 3.3 illustrates this construction schematically in two dimensions.

For a reversed ($v/a > 1$) phase, the water (along with the counterions and surfactant head groups) is imagined to lie inside this structure and the oil and tails outside, with the surfactant film coating the surface with a layer whose thickness is the length of the tails. In this case the physically obvious value for the hard-sphere radius is $R + \ell$ where $\ell$ is the surfactant tail-length. In some cases this value gives an impossibly high hard-sphere packing fraction and has to be reduced—effectively allowing the tails of molecules from neighbouring spheres to interdigitate. A three-dimensional view of a part of the structure so formed is shown in Figure 3.4. A direct DOC cylinder structure can be constructed similarly by putting the oil and tails inside and the rest outside. In this case it is presumably electrostatic repulsion that keeps the spheres apart.

The maximum value of $Z$ is the co-ordination number of the lattice. We define this as the number of faces on the Voronoi polyhedron: two cells are neighbours if they share a face. Meijering [92] has shown that for the Voronoi network with no restriction on the distance of closest approach, there are an average of 15.54 faces per cell. For dense random packings of spheres, however, Coxeter [29] finds a co-ordination number of only 13.4, while Finney [43] has 14.3 for “random close packing”. This suggests that there may be appreciable structural differences as the hard sphere density is changed. For safety we restrict ourselves to $Z < 13.4$ although in practice, co-ordination numbers greater than about 6 are rarely encountered.

If $Z$ is less than its maximum value then we have to choose which pairs of neighbouring spheres to connect. Originally this was imagined to occur at random. When the algorithm was computerised for the purpose of calculating scattering curves by the method of Section 2.2 this choice was performed by listing pairs in order of separation distance and just taking the closest ones until the required number was reached. This would presumably have little effect on the structure for moderate to high hard-sphere packing fractions, but might have an appreciable effect at low packing densities, when the spread of nearest-neighbour distances would be much larger.
Figure 3.3: Schematic two-dimensional view of the construction of the DOC cylinders model: (i) one generates a distribution of hard spheres with radius $R + \ell$; (ii) one places water spheres of radius $R$ at each centre; and (iii) neighbouring spheres are joined by cylinders of radius $r$ until the average co-ordination number is $Z$. 
3.2.1 Calculation of volume and surface

As long as the cylinders do not intersect with each other outside the spheres, the internal volume fraction $\phi$ is clearly given exactly by

$$\phi = n \left( \left( \frac{4}{3} \pi R^3 \right) - Z \text{ (volume of "cap")} \right) + \frac{1}{2} n Z \left( \pi r^2 \right) \left( \text{(average cylinder length)} - 2\sqrt{R^2 - r^2} \right)$$

and the internal surface similarly by

$$\phi = n \left( \left( 4\pi R^2 \right) - Z \text{ (area of "cap")} \right) + \frac{1}{2} n Z \left( 2\pi r \right) \left( \text{(average cylinder length)} - 2\sqrt{R^2 - r^2} \right).$$

The geometry of this situation is shown in Figure 3.5. By elementary integration we
Figure 3.5: A cylinder meeting a sphere. The cap which has to be removed from the sphere is shaded. The part of the cylinder which has to be cut off has length \( \sqrt{R^2 - r^2} \).

We have

\[
\text{Volume of cap} = \pi \int_{\sqrt{R^2 - r^2}}^R (R^2 - r^2) \, dx = \frac{1}{3} \pi r^3 \left( 2\rho^3 - (2\rho^2 + 1)\sqrt{\rho^2 - 1} \right)
\]

where \( \rho = R/r \), and similarly

\[
\text{Area of cap} = 2\pi \int_{\sqrt{R^2 - r^2}}^R R \, dx = 2\pi r^2 \rho \left( \rho - \sqrt{\rho^2 - 1} \right).
\]

Substituting these results gives

\[
\phi = \pi r^3 n \left( \frac{2}{3} \rho^3 (2 - Z) + \frac{2}{3} Z (\rho^2 - 1) \sqrt{\rho^2 - 1} + \frac{ZL}{2r} \right)
\]
\[
\Sigma = 2\pi r^2 n \left( \rho^2 (2 - Z) + Z (\rho - 1) \sqrt{\rho^2 - 1} + \frac{ZL}{2r} \right)
\]

Here \( L \) is the average cylinder length, which is equal to the average distance between the centres of neighbouring spheres in the hard-sphere packing used. Clearly one has as a first rough estimate that

\[
L \approx n^{-\frac{1}{2}}
\]

and hence is equal to the periodicity \( D^* \). It is hard to do much better than this. The co-ordination number for a liquid is notoriously ill-defined [93], and hence so is the average neighbour distance. A simple definition, and one which would eliminate the rather messy considerations involved in defining the co-ordination number, would
be to take the position of the peak in the sphere-sphere correlation function. Unfortunately this is wrong: it says that the neighbour distance is equal to twice the radius—contact in other words—for all but the least dense hard sphere packings.

An alternative estimate as to how far out this is can be obtained from the following reasoning. According to Williams [134] the closest regular packings to those of dense systems of hard spheres are the body-centered tetragonal packings of \( \alpha \)- or \( \beta \)-tetrakaidecahedra. The \( \alpha \)-tetrakaidecahedron or Kelvin body is the solid with the smallest surface to volume ratio which packs to fill space without any gaps. It is a slightly modified truncated octahedron, with faces and edges curved so that all vertex angles are equal to the tetrahedral angle 109°28'. The \( \beta \)-tetrakaidecahedron is a further modification with the distribution of number of edges per face closer to that found in foams and similar natural structures. The closest thing which is easy to compute with is the truncated octahedron, the Voronoi cell for the body-centered cubic lattice. This has fourteen faces: six squares and eight regular hexagons, all with the same edge length. For octahedra with edge length 1, the separation between neighbours which share a square face is \( 2\sqrt{2} \) and between those which share a hexagonal face \( \sqrt{6} \). Scaling to make the cell volume equal to \( n^{-1} \) gives an average distance between neighbours of \( L \approx 1.16n^{-\frac{1}{3}} \). This is presumably also a better approximation to the peak position \( D^* \).

### 3.2.2 Curvature

The simplest and most obvious way to calculate the average \( v/a\ell \) for this structure is simply to take

\[
\langle v/a\ell \rangle = \Delta \phi / \Sigma \ell
\]

(3.15)

where

\[
\Delta \phi = \phi(n, Z, R + \ell, r + \ell) - \phi(n, Z, R, r)
\]

(3.16)

is the volume fraction contained in a shell of thickness \( \ell \) around the structure. (This is correct for the reversed structure—water inside; for the direct version one has to change a few signs.) Unfortunately this expression is rather prone to errors caused by overlapping of the cylinders, especially for larger values of the co-ordination number \( Z \).

A second, more general method derives from the differential geometry of parallel surfaces. For a small element of surface, one has [51]

\[
A(x) = A(0) \left( 1 - 2Hx + Kx^2 \right)
\]

(3.17)

where \( A(0) = A \) is the area of the original surface, \( A(x) \) is the area of the parallel surface derived from it by displacing each point a (directed) distance \( x \) along its normal vector and \( H \) and \( K \) are the mean and Gaussian curvatures respectively. Integrating this over the whole of our structure and dividing the result by the total volume gives

\[
\Sigma_x = \Sigma \left( 1 - 2\langle H \rangle x + \langle K \rangle x^2 \right)
\]

(3.18)
where $\langle H \rangle$ and $\langle K \rangle$ are the area-averaged curvatures. This can be inverted to give the useful results

$$\langle H \rangle = \frac{\Sigma_{-\delta} - \Sigma_{+\delta}}{4\delta \Sigma_0}$$

$$\langle K \rangle = \frac{\Sigma_{+\delta} + \Sigma_{-\delta} - 2\Sigma_0}{2\delta^2 \Sigma_0}.$$  \hspace{1cm} (3.19)

where $\delta$ is any reasonably small distance. (Strictly $\delta$ can be any distance whatsoever, as long as we remember to count as negative any parts of the surface that are inverted—turned inside-out—by the displacement along the normal. This can only happen if $\delta$ is larger than one of the radii of curvature.) Now for our monolayer lying on the outside of the surface, and taking the normal vector as pointing towards the water, the total volume occupied by the tails is

$$v = \int_{-\ell}^{0} A(x) \, dx$$

$$= A(0) \ell \left( 1 + \langle H \rangle \ell + \frac{1}{3} \langle K \rangle \ell^2 \right) \hspace{1cm} (3.20)$$

and as the total headgroup area is just $A(0)$, the average value of the surfactant parameter is

$$v/a\ell = 1 + \langle H \rangle \ell + \frac{1}{3} \langle K \rangle \ell^2.$$  \hspace{1cm} (3.21)

Here the normal vector is taken as directed inwards, towards the water, so that a displacement by $+\delta$ decreases the radii and one of $-\delta$ increases them. This gives $H > 0$, meaning curvature towards the water, at low connectivities. So we can obtain the curvature numerically by calculating values of $\Sigma_0 = \Sigma(n, Z, R, r)$, $\Sigma_{+\delta} = \Sigma(n, Z, R-\delta, r-\delta)$ and $\Sigma_{-\delta} = \Sigma(n, Z, R+\delta, r+\delta)$ for any $\delta$, no matter how small. In particular $\delta$ can be chosen much smaller than $\ell$, thus reducing the overlap problems of the first method.

Unfortunately this method is only strictly valid when the surface is smooth. As our surface has cusps where the cylinders meet the spheres, the values obtained for $\langle H \rangle$ and $\langle K \rangle$ are not correct. As long as the angle along the cusp is not too sharp, this error is not too severe, and this method works well in practice. In Section 3.5 below we will return to this point in more detail, and use the tools developed for the DOC lamellar model to obtain an exact result for the curvature of this model.

### 3.2.3 Ratio between sphere and cylinder radii

As it stands, this model has four parameters, $n$, $Z$, $R$ and $r$, which are to be fitted to the three quantities calculated above, $\phi$, $\Sigma$ and $v/a\ell$. In order to reduce the freedom and give a unique match between parameter values and the physical constraints, it is desirable to eliminate one of these parameters. The simplest and physically the most reasonable way to do this is to require some fixed relationship between $R$ and $r$. 

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One possible scheme is to require that surfactant molecules pack with the same \( v/\alpha \) on the cylinders and on the spheres. This gives the condition

\[
\rho = 2 \left( 1 + \frac{\ell}{3R} \right)
\]  

(3.22)

Unless \( \ell \) is much greater than \( R \), this gives values of \( \rho \) between 2 and 3. Unfortunately this reasoning ignores the cusps, and so makes little sense. These make a very significant difference to the curvature of the surface (changing the Gaussian curvature from positive to negative for large enough \( Z \)).

A simpler condition, although one which suffers from the same problem, is to require that the mean curvature be the same on the spheres and the cylinders. This gives the simple condition \( \rho = 2 \), which agrees to zeroth order with Equation (3.22).

As this is a detail without very much real physical motivation—we imagine that the surface is actually smooth after all, and that this structure only approximates it—there does not seem much point in worrying too hard about what value to give to \( \rho \). The simplest thing, and one which cannot be too wrong, is to simply set \( \rho = 2 \) and leave it at that.

### 3.2.4 Calculation of parameters from constraints

The equations relating \( n \), \( Z \) and \( r \) to \( \phi \), \( \Sigma \) and \( v/\alpha \) are too complicated to invert analytically. For a given value of \( Z \), a simple interval-halving algorithm can be employed to zero in on values of \( n \) and \( r \) which give the correct \( \phi \) and \( \Sigma \). The curvature can then be calculated, along with the peak position. Repeating this for a number of values of \( Z \) gives a table from which one can choose that value of \( Z \) which gives the best value of \( v/\alpha \). Alternatively, if it is difficult to obtain an experimental value for \( v/\alpha \), one can choose the value of \( Z \) which gives the closest value of \( D^* \) to the experiment. The usual situation in the experiments of Chapter 4 is that a value for \( v/\alpha \) can be obtained from a fit to spheres in that region of the phase diagram for which this is unequivocally the correct description.

### 3.2.5 Predictions of the model

This simple model is surprisingly rich. Consider first what happens if one fixes the surfactant/oil ratio and follows a dilution path towards the water corner of the phase diagram (assuming as usual that the “internal” phase is water, with the oil and tails on the outside). This amounts to increasing \( \phi \), while at the same time decreasing \( \Sigma \). Below a certain minimum value of \( \phi \), the curvature demanded by the structure will be too high, irrespective of \( Z \), and the surfactant molecules will be unable to pack on it. At some minimum water content the structure will be able to form. Initially the co-ordination number \( Z \) will be high, but it will drop steadily as water is added. This
is essentially because spheres have a smaller surface to volume ratio than cylinders of the same curvature—when you have too much surface you can get rid of it by wrapping the water "inefficiently" with cylinders, but when the amount of water increases, you have to use a greater proportion of spheres. Eventually a limit is reached at which the structure consists only of isolated spheres, that is, $Z = 0$. Any further dilution requires that the spheres grow in size, violating the condition on the curvature, so instead the mixture phase separates expelling excess water. This is precisely the behaviour observed for the DDAB systems with penetrating oils examined in Chapter 4.

The predicted variation of electrical conductivity with water content is opposite to that of the Talmon-Prager and cubic random cell models. While those models predict a monotonic increase in conductivity with water content, the DOC cylinders model predicts a decrease, as the structure changes from a highly connected network of cylinders at low water content to a dispersion of water spheres in oil at high water content. Studies of percolation in Voronoi networks [68], give a value of $\approx 0.08$ for the critical bond percolation probability. Assuming, as discussed above, that the maximum possible co-ordination number is 13.4 [29], this yields a percolation transition—breaking of the last water path—at a connectivity of $Z \approx 1.1$.

Once a value has been deduced for $v/a\ell$, it is possible, using the reasoning given above, to predict the extent of the region in the phase diagram over which this structure can form [63]. From the co-ordinates of any point in the phase diagram one can easily calculate $\phi$ and $\Sigma$, modulo a few assumptions as to molecular volumes and headgroup area. These values are then fed into the numerical routine which determines parameter values, and the results accepted or rejected on the basis of whether $v/a\ell$ lies within the chosen range. Such a calculation clearly says nothing about the possible formation of other competing structures with lower free energy or of the possibility of two- or three-phase equilibria. Nonetheless, the predicted phase boundaries at maximum and minimum water content are in good agreement with those observed experimentally in DDAB systems with penetrating oils [9,34]. Lines of constant $Z$ run in gentle curves down from the oil corner. As the oil is changed from strongly to weakly penetrating, reducing the value of $v/a\ell$, the predicted single phase region—a teardrop hanging from the oil corner—swings from close to the surfactant-oil edge of the phase diagram to a more vertical position.

The final prediction is that of the full scattering curve for any given sample composition. This is calculated using the method expounded in Section 2.2. A modification of the same Monte-Carlo procedure as was used for generating the spectra for systems of hard spheres is used to produce a list of positions of sphere centres. Pairs of spheres are listed in order of increasing separation, and are allocated cylinders in this order until the desired connectivity is reached. It is then a tedious but relatively straightforward calculation to "fill" all of the little cubes whose centres lie inside a sphere or a cylinder. The resulting array is fed to the scattering program as described before. The only subtlety in this is the implementation of the periodic boundary conditions which are needed to avoid edge effects. Calculated spectra are compared with
experimental data and the predictions of other models in Chapter 4.

3.3 The DOC lamellae model

When \( v/\ell \) is close to one, the DOC cylinders model gives way to a random lamellar structure. The construction used here is identical to that used for the repulsive or "hard sphere" version of the Talmon-Prager model, except that the water and oil separated by a monolayer are replaced by two fictitious "different" types of water separated by a normal bilayer or two types of oil separated by a reversed bilayer [129]. This is closely related to the model of Cates et al. [20] for the flow-birefringent L3 phase, but with the cubic lattice replaced by the more reasonable hard sphere Voronoï.

The model is constructed as follows.

1. Start with a distribution of points with density \( n \), which are the positions of centres of a liquid of hard spheres. From this construct a "hard core" Voronoï tessellation. Each centre generates a polyhedral cell, bounded by portions of bisecting planes, which consists of all those points in space which lie closer to that particular centre than any other.

2. Label the cells \( A \) or \( B \) at random, with probabilities (and thus volume fractions) \( \psi \) and \( 1 - \psi \). This "pseudo volume fraction" is a free parameter, like \( Z \) for the DOC cylinders model, which will be fixed later by the interfacial curvature.

3. Whenever two adjacent polyhedra have different labels, set a bilayer on the polygon between the two polyhedra. For the direct DOC lamellar model, this is a normal oil-swollen bilayer with thickness \( 2\ell + 2t \) separating water \( A \) from water \( B \); for the reversed model it is a reversed bilayer with water thickness \( 2t \), separating oil \( A \) from oil \( B \).

This process is illustrated schematically in Figure 3.6.

When \( \psi \) is close to \( \frac{1}{2} \) this gives an infinite film which is connected throughout space, as are the two bulk regions "A" and "B"; the structure is thus "tricontinuous". When \( \psi \) is close to 0 (or to 1, although as the two regions are indistinguishable we may as well restrict ourselves to \( \psi \leq \frac{1}{2} \)) the structure is that of single-walled vesicles. This variation of the structure with \( \psi \) is shown in two dimensions in Figure 3.7, although this is a little misleading as bicontinuous structures are topologically impossible in two dimensions. As for the DOC cylinders model, it is not envisaged that the surfactant bilayer actually lies on a series of flat polygonal facets with sharp angled joins; as always we assume that it is smooth and that this is a convenient approximation which is valid at the resolution of our scattering experiments.

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Figure 3.6: Schematic two-dimensional view of the construction of the DOC lamellar model: (i) one generates a moderately dense distribution of hard spheres; (ii) one constructs a Voronoi tessellation from the bisecting planes and labels the cells A or B at random in the proportions $\psi$ and $1 - \psi$; and finally (iii) a bilayer is placed on all faces which separate A from B.
Figure 3.7: Two-dimensional illustration of the evolution of the DOC lamellar structure with increasing values of the pseudo volume fraction $\psi$. When $\psi$ is small the structure consists of isolated vesicles, while for $\psi \approx \frac{1}{2}$ it is a random connected bilayer.
As for the DOC cylinders model, the specification that the cells should satisfy a condition of closest approach is necessary if this model is to give a peak in the scattering. While in that case it was easy enough to justify this on the grounds that there would certainly be a repulsion between neighbouring spheres in the construction, in the case of the lamellar model simply requiring that opposite bilayers not intersect is nowhere near a strong enough excluded volume effect to produce a peak in the scattering. Instead we postulate that this effect is produced by the rigidity of the bilayer. If the distribution of the centres is too random, then there will be places at which the bilayer is forced to bend too sharply, even after we have smoothed out the sharp joints where the faces meet. Excluding such configurations is achieved by imposing a minimum distance of approach of the order of $\frac{1}{2}n^{-\frac{1}{3}}$. This gives an excluded volume of approximately 50%. This causes the distribution of the centres to be quite regular.

When we want to calculate the volume fraction $\phi$ contained in the film, the area of surfactant interface per unit volume and the average value of the packing parameter $v/a\ell$, these edges and vertices are all-important. As all the curvature is concentrated there, ignoring them leaves us with nothing more than a flat bilayer. As the Talmon-Prager and CRC models are also constructed from flat facets joined along their edges, and as the differential geometry of these surfaces does not seem to be well-known, the following sections treat the subject in slightly more generality than is required for simply solving the DOC lamellar model.

### 3.3.1 Curvature of facetted surfaces

Consider a surface made up of flat pieces joined along straight lines. The mean curvature $H$ and the Gaussian curvature $K$ are both zero wherever they exist—that is, everywhere except at the edges and vertices, where they are undefined. Nonetheless, the integrated curvatures

$$\mathcal{H} = \int_S H \, dA$$

and

$$\mathcal{K} = \int_S K \, dA$$

are not in general equal to zero, and thus neither are the area-averaged curvatures

$$\langle H \rangle = \mathcal{H} / A$$

and

$$\langle K \rangle = \mathcal{K} / A.$$  

All the curvature is concentrated at the edges and vertices. To get at this, let us consider edges and vertices as the zero-radius limits of suitable pieces of cylinders, spheres or other surfaces, and thus calculate the correct contributions to $\mathcal{H}$ and $\mathcal{K}$ [34].

First consider an edge of length $L$ and dihedral angle $\alpha$. This angle must always be measured on the same side of the surface and will therefore be greater than or less
than \( \pi \) according as the bend is towards or away from the chosen side. We choose our normal vector to point in the direction of this chosen side, so that if the curvature is towards this side it will be counted as positive. Thus we expect that if \( \alpha < \pi \) then the contribution to \( \mathcal{H} \) will be positive and if \( \alpha > \pi \) then it will be negative. Let us now remove narrow strips from along each side of this edge and replace them by a piece of cylinder of radius \( r \) which joins smoothly to the remaining flat pieces. In order for this to happen, this piece must subtend an angle of \( |\pi - \alpha| \) and have length \( L \) (plus a small correction of order \( r \) which takes account of what happens at the ends). At every point of this piece, the mean curvature is \( 1/2r \) if \( \alpha < \pi \) and \(-1/2r \) if \( \alpha > \pi \). As for any cylinder, the Gaussian curvature is zero. So the surface integral of the Gaussian curvature is zero and that of the mean curvature is

\[
(\pi - \alpha)(L + \varepsilon r)/2
\]

(3.27)

Notice that the sign is always correct here: the absolute value and the change of sign have cancelled. Taking the limit as \( r \to 0 \) gives the mean curvature contribution for a single edge

\[
\mathcal{H} = (\pi - \alpha)L/2.
\]

(3.28)

The situation at a vertex is similar. Suppose that \( n \) faces meet at a point and that the face angles are \( \beta_i \). If \( \sum \beta_i < 2\pi \) then a small neighbourhood of this vertex may be replaced by a spherical polygon with radius \( r \), \( n \) sides and vertex angles \( \pi - \beta_i \). As this has area

\[
A = \left( \sum_{i=1}^{n} (\pi - \beta_i) - (2 - n)\pi \right)r^2
\]

\[
= (2\pi - \sum \beta_i)r^2
\]

(3.29)

and the mean and Gaussian curvatures at every point are \( 1/r \) and \( 1/r^2 \) respectively, the integrated mean curvature is \( (2\pi - \sum \beta_i)r \) and the integrated Gaussian curvature is \( 2\pi - \sum \beta_i \). Letting \( r \to 0 \) as before, we see that the vertex contributes nothing to \( \mathcal{H} \), and \( 2\pi - \sum \beta_i \) to \( \mathcal{K} \).

If \( \sum \beta_i > 2\pi \) then a piece of a sphere will not do; something saddle-shaped is needed. But clearly the mean curvature is always going to be zero: no matter what the details, the area must be proportional to \( r^2 \) while \( H \) goes like \( 1/r \). For the Gaussian curvature the correct approach is to use the Gauss map, which sends every point on the surface to that point on the unit sphere corresponding to the direction of the normal vector. The area of the image of a region under this map is its integrated Gaussian curvature (by definition!), with the proviso that the area should be counted as negative if the vertex order is reversed by the mapping. Careful application of this method gives the required result: regardless of whether the vertex angles sum to less or more than \( 2\pi \), the Gaussian curvature contribution of a vertex is

\[
\mathcal{K} = 2\pi - \sum \beta_i.
\]

(3.30)

So for any surface built up in this way, the total curvatures \( \mathcal{H} \) and \( \mathcal{K} \) are simply obtained by summing these contributions over all edges and vertices respectively. Dividing by the total surface area then gives the average curvatures.
3.3.2 Curvature of Voronoi models

We now turn to models in which the faceted surface is constructed as described above by random filling of a Voronoi tesselation and then the selection of those facets which separate differently filled cells. This general framework, with the surface decorated by a monolayer gives the Talmon-Prager model; with a normal or a reversed bilayer it gives the two versions of the DOC lamellar model.

For the analysis of this section, we are unfortunately forced to avoid any condition of closest approach—this is “true”, not “hard sphere” Voronoi—even though that is what really interests us. So the results of this section are only strictly valid for the original Talmon-Prager model, which uses the true Voronoi lattice. For the “repulsive” version of Talmon-Prager model and for the DOC lamellar model, the results are only correct in the limit of small $n$.

Statistics for the full Voronoi lattice have been calculated by Meijering [92]. The average number of vertices per cell is approximately 27.07, so as each vertex is at the common point of four cells, the total number of vertices per unit volume is 27.07$n/4$. The average total edge length per unit volume is $5.83n^{1/3}$ and the total surface area per unit volume is $2.91n^{1/3}$.

As we did before, we can get some idea of what the corresponding statistics might be like for the lattice of centres of hard spheres by considering the body-centered cubic packing of truncated octahedra. In this regular packing every cell has 24 vertices, compared with the 27.07 for the Voronoi packing. A truncated octahedron with edge length 1 has total edge length 36, surface area 26.78 and volume 11.31 [134]. Rescaling to make the cell volume equal to $n^{-1}$ gives total edge length and surface area per cell of $16.04n^{-1/3}$ and $5.32n^{-2/3}$ respectively. As each face is shared by two cells and each edge by three and there are $n$ cells per unit volume, the total edge length per unit volume is $5.35n^{1/3}$ and the total surface area per unit volume is $2.66n^{1/3}$. These values are all systematically less than the corresponding values for the totally random distribution, but always by less than 10%. So carrying the results of this section over to moderate densities of hard spheres is certainly no worse than many of the other approximations made in these models.

To calculate the average curvatures, we first have to know the total surface area by which to divide. Now a face is “real” if it separates cells of different type, that is, with probability $2\psi(1-\psi)$. So the “real” surface area per unit volume is

$$A/V = 2(2.91)\psi(1-\psi)n^{1/3}. \quad (3.31)$$

From the previous section,

$$\mathcal{H} = \sum_{\text{edges}} (\pi - \alpha)L/2. \quad (3.32)$$
and so as $\alpha$ and $L$ are independent random variables

$$\frac{\mathcal{H}}{V} = \frac{1}{2} (\pi - \alpha) \left( \frac{L_{\text{tot}}}{V} \right)$$

(3.33)

where $L_{\text{tot}}/V$ is the total edge length per unit volume. There are four possible edge configurations: $AAA$, $AAB$, $ABB$ and $BBB$. The first and last contribute nothing: there is no “real” edge. If we adopt the convention that dihedral angles are measured on the $A$ side of the surface (so that $H > 0$ corresponds to curvature towards medium $A$), then as the dihedral angles are $2\pi/3$ on average, $AAB$ has $\langle \alpha \rangle = 4\pi/3$, and $ABB$ has $\langle \alpha \rangle = 2\pi/3$. So

$$\langle \pi - \alpha \rangle = 3\psi^2 (1 - \psi) \left( \frac{-\pi}{3} \right) + 3\psi (1 - \psi)^2 \left( \frac{+\pi}{3} \right) = \pi \psi (1 - \psi) (1 - 2\psi).$$

(3.34)

Multiplying by one-half the edge length per unit volume and dividing by $A/V$ gives

$$\langle H \rangle = \frac{\pi}{2} \frac{(5.83)n^{\frac{2}{3}}n}{2(2.91)n^3} (1 - 2\psi)$$

$$\approx (1.57)n^{1/3}(1 - 2\psi).$$

(3.35)

It is no coincidence that the coefficients cancel leaving $1.57 \approx \pi/2$—this is a direct consequence of Euler’s theorem on the number of faces, edges and vertices of polyhedra, and the fact that we always have three cells meeting at an edge. Note that $\langle H \rangle = 0$ only when $\psi = \frac{1}{2}$.

We proceed similarly for vertices. According to Winterfield [135], the expected angle between two adjacent edges in the Voronoi tessellation is approximately

$$\langle \beta_i \rangle = \beta \approx 1.93966 \text{ radians} \approx 111^\circ 8'$$

(3.36)

which is slightly larger than the tetrahedral co-ordination angle of approximately $109^\circ 28'$. There are five possible vertex configurations, of which again the all-$A$ and all-$B$ contribute nothing. For the configurations $AAAB$ and $ABBB$, which occur with probabilities $4\psi^3 (1 - \psi)$ and $4\psi (1 - \psi)^3$ respectively, we expect $2\pi - \sum \beta_i = 2\pi - 3\beta$, while for $AABB$, which occurs with probability $4\psi^2 (1 - \psi)^2$ it is $2\pi - 4\beta$. So

$$\mathcal{K}/V = \frac{27.07n}{4} \langle 2\pi - \sum \beta_i \rangle$$

$$= \frac{27.07n}{4} \psi (1 - \psi) \left( (4\psi^2 - 4\psi + 8)\pi - 12\beta \right)$$

(3.37)

and dividing by $A/V$ gives

$$\langle K \rangle = \frac{27.07}{8 \times 2.91}n^{\frac{2}{3}} \left( (1 - 2\psi)^2 \pi + 7\pi - 12\beta \right)$$

$$= \left( (3.65) (1 - 2\psi)^2 - (1.49) \right)n^{\frac{2}{3}}.$$
3.3.3 Calculation of volume, surface and surfactant parameter

We have already seen in the discussion of the DOC cylinders model how to relate \( v/\alpha \ell \) to the average curvatures \( \langle H \rangle \) and \( \langle K \rangle \). Application of Equation (3.21) with the curvatures just calculated gives the molecular packing for the Talmon-Prager model. For bilayers we can proceed similarly.

Consider first a normal oil-swollen bilayer with total oil thickness \( 2t \) and surfactant tail length \( \ell \) decorating a surface of known \( H \) and \( K \). This geometry is shown in Figure 3.8(b). From the area-variation formula of Equation (3.17), the tail volume is

\[
v = \int_{-\ell-t}^{-t} A(x)\,dx + \int_{\ell}^{\ell+t} A(x)\,dx
= 2A(0)\ell \left(1 + \langle K \rangle \left(\ell^2 + \ell t + \frac{1}{3} \ell^2\right)\right)
\]

and the total headgroup area is

\[
a = A(-\ell - t) + A(\ell + t)
= 2A(0) \left(1 + \langle K \rangle (\ell + t)^2\right)
\]
so that
\[ v/a \ell = 1 - \left( \ell t + \frac{2}{3} \ell^2 \right) \frac{(K)}{1 + (K)(\ell + t)^2}. \]  
(3.41)

In the limit of no swelling this reduces to
\[ v/a \ell = 1 - \frac{2(K)\ell^2}{3(1 + (K)\ell^2)}. \]  
(3.42)

The “internal” volume fraction \( \phi \) is that of the tails plus the oil. Ignoring the curvature, one would have \( \phi = 2(\ell + t)(A/V) \). The full calculation gives
\[ \phi = \frac{1}{V} \int_{-\ell-t}^{\ell+t} A(x) \, dx \]
\[ = 2(\ell + t)(A/V) \left( 1 + \frac{1}{3}(K)(\ell + t)^2 \right) \]  
(3.43)

Similarly, for a flat bilayer, \( \Sigma = 2(A/V) \), but with curvature we have (using the headgroup area above)
\[ \Sigma = 2(A/V) \left( 1 + \langle K \rangle (\ell + t)^2 \right). \]  
(3.44)

For a reversed bilayer the total tail volume is the same as for the normal bilayer, but the headgroup area is
\[ a = A(-t) + A(t) \]
\[ = 2A(0) \left( 1 + \langle K \rangle t^2 \right) \]  
(3.45)

and so
\[ v/a \ell = 1 + \left( \ell t + \frac{1}{3} \ell^2 \right) \frac{(K)}{1 + (K)t^2}. \]  
(3.46)

The “internal” volume is now the water (plus heads and counterions), and so has thickness only \( 2\ell \), giving
\[ \phi = 2\ell(A/V) \left( 1 + \frac{1}{3}(K)\ell^2 \right), \]  
(3.47)

and the surface is
\[ \Sigma = 2(A/V) \left( 1 + \langle K \rangle \ell^2 \right). \]  
(3.48)

These formulae are completely general—they are correct for any surface decorated by a bilayer. Substituting the values for \( A/V, \langle H \rangle \) and \( \langle K \rangle \) derived above for the randomly filled Voronoi models gives the defining equations for the DOC lamellar models. For the reversed bilayer these are
\[ \phi = \left(11.64\ell\psi(1 - \psi)n^{\frac{1}{2}} \left( 1 + \frac{1}{3} \left( (3.65)(1 - 2\psi)^2 - (1.49) \right) n^{\frac{1}{2}} \ell^2 \right) \right) \]
\[ \Sigma = \left(11.64\psi(1 - \psi)n^{\frac{1}{2}} \left( 1 + \left( (3.65)(1 - 2\psi)^2 - (1.49) \right) n^{\frac{1}{2}} \ell^2 \right) \right). \]  
(3.49)

As for the DOC cylinders model, these equations are too complicated to invert analytically, but it is a simple matter to do so numerically, using the “flat” bilayer as a first approximation and obtain values of \( n, \psi \) and \( t \) which agree with the given values for \( \phi, \Sigma \) and \( v/a \ell \). As this model is really only suited to rather flat films, there is of course a chance that these values will be unphysical, or that no such values will exist.
3.3.4 Model predictions

For $0.18 < \psi < 0.82$, the average Gaussian curvature of these models is negative. As the Gaussian curvature is directly related to topology as defined by the Euler characteristic (via the Gauss-Bonnet theorem) one can deduce that the structure is bicontinuous whenever $\langle K \rangle < 0$. (In fact it is probably bicontinuous over an even greater range of values of $\psi$, as percolation theory is only concerned with the existence of a single connecting path, which is likely to exist even when most of the structure is composed of closed objects.) It is tempting to think about a smooth transition from bicontinuous films to closed vesicles, but this is extremely unlikely if the interface is rigid. This is the result of a second consequence of the change in sign of $\langle K \rangle$, namely that it causes the average value of $v/\alpha t$ to change from less than to greater than 1 (or vice versa) irrespective of the values of $n$ and $t$. No matter how the other parameters change, $v/\alpha t$ must change during this transition—if it must remain constant then this is impossible.

The calculated average values of $v/\alpha t$ are independent of the mean curvature $H$. This is potentially misleading, and rather an oversimplification. When $\psi \neq \frac{1}{2}$, and thus $\langle H \rangle \neq 0$, the two monolayers will have different values for $v/\alpha t$. On one side the film will suffer a frustration with the tails pushed together and the heads apart, while the other side suffers exactly the opposite. For real vesicles, this is overcome by having a higher salt concentration inside, thus screening the headgroup repulsion between molecules in the inner monolayer. Such effects seem rather unlikely while the structure remains bicontinuous—even though the bilayer does strictly separate the two distinct bulk regions. So one anticipates a bending energy cost beyond the scope of this model whenever $\psi$ moves away from $\frac{1}{2}$. It is for this reason that bilayer phases are generally assumed to be minimal surfaces, and that such “symmetry breaking” is regarded as unlikely, if not impossible. The problem with this line of argument is that it is entirely local. Certainly the best thing locally is to have $H = 0$ and $K$ equal to that value which gives the correct $v/\alpha t$. But in all minimal (i.e. $H = 0$) surfaces except planes, the Gaussian curvature varies greatly, and that variation increases with the complexity of the topology. So the desired local situation cannot be maintained over the whole of the surface. Given this, it may well be better from the point of view of global bending energy minimisation to allow $\langle H \rangle$ to move away from zero if, for instance, this reduced the total Gaussian curvature variation.

While it is always possible to calculate the full scattering curve using the method of Section 2.2, setting up the array of cubes is extremely cumbersome for Voronoï models like this. In order to compare this model with scattering experiments, the most simple thing is to guess the peak position. From what we know heuristically about true and hard sphere Voronoï tessellations, we can say with some confidence that the peak position lies somewhere in the range

$$n^{-\frac{1}{3}} \leq D^* \leq 1.16n^{-\frac{1}{3}}.$$  \hspace{1cm} (3.50)

This is not too bad, as the values for $\Sigma$ taken from an experiment and fed into the model equations are only known to about 10%.
Nonetheless, such a guess is open to the criticism that it assumes that the peak in $I(q)$ coincides with that in $S(q)$, something which we know from the experience of spheres is not always the case. A better approximation is to calculate the full $I(q)$ by multiplying the $S(q)$ of the underlying Voronoi lattice by the $P(q)$ of the average polygonal face [81]. The excluded volume is fixed as discussed above, but the results are not sensitive to the details as the position of the first peak in $S(q)$ does not change noticeably with the volume fraction. The form factor is obtained by approximating the polygonal faces by disks of thickness $2t$ for the reversed bilayer (or $2(\ell + t)$ for the direct bilayer) and radius one quarter the nearest neighbour distance. (This gives roughly the correct surface area for the cells.) This admittedly rough procedure neglects correlations between adjacent facets—in particular that the local facet-facet correlation function will certainly be anisotropic—but is otherwise reasonably sound. It has been checked against two-dimensional optical Fourier transforms of two-dimensional realisations of the DOC-lamellar model [131] and found to give fair agreement.

### 3.4 Curvature of the CRC model

We can use the techniques of the previous section to calculate the curvature of the Cubic Random Cell model of Jouffroy, Levinson and DeGennes [69]. As the bilayer version of this model is the subject of considerable current interest despite its lack of obvious physical motivation, it is desirable to know the mean and Gaussian curvatures as a function of the filling fraction $\psi$. Various authors have guessed at the answer. According to the original authors [69,31], the radii of curvature are of the order of the cell edge length $\xi$. Cates et al. agree with this [20], although in earlier papers [3,113] they appear to have had a more complicated expression. The existence of a rigorous calculation should put an end to such speculation.

Recall that in this model the cells of a cubic lattice with edge length $\xi$ are filled strictly at random with two different media $A$ and $B$. The boundaries between neighbouring cells with the same contents are forgotten, and we are left with an interface which everywhere separates $A$ from $B$, with no joins or ends, but with plenty of right-angle edges and corners. If $\psi$ is the fraction of cells filled with medium $A$ then the internal surface per unit volume is

$$
\Sigma = \frac{6\psi(1 - \psi)}{\xi}. \tag{3.51}
$$

If $A$ and $B$ are water and oil then the interface is thought of as a surfactant monolayer and we have the original CRC model. This is directly analogous to the Talmon-Prager model, with the cubic lattice replacing the Voronoi lattice. If $A$ and $B$ are two fictitious "different" types of water then the interface is covered with a normal bilayer [3], and if they are two different oil regions it is a reverse bilayer. These versions are clearly analogous to the direct and reversed DOC lamellar structures, again with only the replacement of the (hard sphere) Voronoi lattice by the simple cubic lattice.
Figure 3.9: An ambiguous configuration of four cells meeting along a shared edge. The interface in (a) is impossible and must be modified either to the $A$-continuous variant shown in (b) or the $B$-continuous variant shown in (c). These give opposite values for the mean curvature $H$. In the full calculation they are both counted, the first with probability $\alpha$ and the second with probability $\beta = 1 - \alpha$.

An important difference between the cubic and the Voronoï models, and one which introduces significant additional complications, is the existence of ambiguous configurations. This arises from the fact that there are four rather than three cells meeting along each edge, and eight rather than four meeting at each vertex. Consider for example, the situation pictured in Figure 3.9(a). Here we are looking directly down an edge separating four cells, two filled with each medium. As it stands, the surface has no meaning: such configurations make no sense when thought of as surfactant films. Basically we have to make a decision as to whether the $A$ region should be made continuous, resulting in the modified configuration of Figure 3.9(b), or whether the $B$ region should be, giving Figure 3.9(c). The problem is that these are very different from the point of view of curvature: in fact they yield equal but opposite contributions to the mean curvature. In the bilayer case the problem evaporates. By symmetry the interface cannot show a preference for either configuration, so the two possibilities must be given equal weight and will therefore cancel. But for the monolayer there may very well be a preference for curvature towards one medium or the other (or if you like, for connecting one medium or the other). This can be quantified by assigning a probability of $\alpha$ to the $A$-continuous configuration of Figure 3.9(b) and a probability of $\beta = 1 - \alpha$ to the $B$-continuous configuration of Figure 3.9(c).

### 3.4.1 Mean Curvature

We proceed as for the Voronoï models, considering the different configurations of $A$ and $B$ cells around an edge. These are listed (up to symmetry) in Table 3.1, along with the probability of each. That the list is complete is easily seen by summing the probabilities $p_i$. Only the fourth configuration, that shown in Figure 3.9, is
Table 3.1: Enumeration of all possible edge configurations in the CRC model, along with the probability $p_i$ of each and its contribution to the total mean curvature $H$.

<table>
<thead>
<tr>
<th>$i$</th>
<th>$p_i$</th>
<th>$w_i$</th>
<th>$H_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$A^A$</td>
<td>$\psi^4$</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>$A^A$</td>
<td>$4\psi^3(1 - \psi)$</td>
<td>$-\pi \xi/4$</td>
</tr>
<tr>
<td>3</td>
<td>$A^B$</td>
<td>$4\psi^2(1 - \psi)^2$</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>$A^D$</td>
<td>$2\psi^2(1 - \psi)^2$</td>
<td>$\alpha - \pi \xi/2$</td>
</tr>
<tr>
<td></td>
<td>$D^A$</td>
<td>$\nu$-continuous</td>
<td>$\beta + \pi \xi/2$</td>
</tr>
<tr>
<td>5</td>
<td>$A^B$</td>
<td>$4\psi(1 - \psi)^3$</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>$D^B$</td>
<td>$(1 - \psi)^4$</td>
<td>1</td>
</tr>
</tbody>
</table>

ambiguous. Note that in each of its two possible interpretations, the total edge length is $2\xi$, as the single edge has become two.

There are $3/\xi^3$ edges per unit volume, so the total mean curvature per unit volume is

$$\frac{\mathcal{H}}{V} = \frac{3}{\xi^3} \sum_{ij} p_i w_j H_{ij}$$

$$= \frac{3}{\xi^3} \left( 4\psi^3(1 - \psi) \left( -\frac{\pi \xi}{4} \right) + 2\psi^2(1 - \psi)^2 \alpha \left( -\frac{\pi \xi}{2} \right) 
+ 2\psi^2(1 - \psi)^2 \beta \left( \frac{\pi \xi}{2} \right) + 4\psi(1 - \psi)^3 \left( \frac{\pi \xi}{4} \right) \right)$$

$$= \frac{3\pi \psi(1 - \psi)}{\xi^2} \left( 1 + (\beta - \alpha - 2)\psi + (\alpha - \beta)\psi^2 \right), \quad (3.52)$$

and dividing by $\Sigma$ gives the area-averaged mean curvature

$$\langle H \rangle = \frac{\pi}{2\xi} \left( 1 + (\beta - \alpha - 2)\psi + (\alpha - \beta)\psi^2 \right). \quad (3.53)$$

Figure 3.10 shows $\langle H \rangle$ as a function of $\psi$ for $\alpha = 0$, $\frac{1}{2}$ and 1.

In the symmetric or bilayer case, for which $\alpha = \beta = \frac{1}{2}$, this reduces to

$$\langle H \rangle = \frac{\pi(1 - 2\psi)}{2\xi}. \quad (3.54)$$

As expected, this is zero when $\psi = \frac{1}{2}$. When $\psi = 0$, the mean curvature is given by this formula as $\pi/2\xi$, independently of $\alpha$ and $\beta$. This can be understood as follows, giving an independent check on the analysis. In the limit as $\psi \to 0$, the structure tends to one of isolated cubes of $A$ in a continuum of $B$. As the probability that two $A$ cubes will share an edge goes like $\psi^3$, it can be ignored explaining the lack of
dependence of the limit on $\alpha$ and $\beta$. Now for an isolated cube of $A$ surrounded by $B$, the total edge length is $12\xi$, all with dihedral angle $\theta = \pi/2$. So $H = 3\pi \xi$ and as the surface area is $6\xi^2$ we have immediately that $\langle H \rangle = \pi/2\xi$, in agreement with the general result.

### 3.4.2 Gaussian curvature

As for the Voronoï models, the Gaussian curvature is the sum of the contributions of all vertex configurations. Whereas in that case there were only three distinct possibilities after excluding the all-$A$ and all-$B$ configurations, in this case things are considerably more complicated. A complete analysis is given in Table 3.2. There are $2^8 = 256$ possible vertex configurations. This reduces to 20 after elimination of the all-$A$ and all-$B$ configurations, which clearly contribute nothing, and the identification of configurations which are congruent under some symmetry operation. The job is further reduced by noting that an exchange of $A$ for $B$ everywhere leaves the Gaussian curvature unchanged. So Table 3.2 only lists the 13 different configurations with four or less $As$; the results for the others follow by symmetry.
Table 3.2: Enumeration of all vertex configurations in the CRC model, each with probability $p_i$, weight $w_j$ associated with the different choices as to how the surface can be placed, and the contributions to the total mean curvature $\mathcal{H}$ and Gaussian curvature $\mathcal{K}$. The comment “$A$ in $2^r$” means that the $A$ subvolume is divided into two connected components by this surface. Configurations 14–20, with five or more As, are omitted as they can be obtained from 1–7 by exchanging $A$ and $B$ (and at the same time $\alpha$ and $\beta$). This operation changes the sign of $\mathcal{H}$ but leaves $\mathcal{K}$ unchanged.

<table>
<thead>
<tr>
<th>$i$</th>
<th>$p_i$</th>
<th>$w_j$</th>
<th>$\mathcal{H}_{ij}$</th>
<th>$\mathcal{K}_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>B B</td>
<td>8$\psi(1 - \psi)^7$</td>
<td>1</td>
<td>3$\pi\xi/8$</td>
</tr>
<tr>
<td>2</td>
<td>B B</td>
<td>12$\psi^2(1 - \psi)^6$</td>
<td>1</td>
<td>2$\pi\xi/8$</td>
</tr>
<tr>
<td>3</td>
<td>B A</td>
<td>12$\psi^2(1 - \psi)^6$</td>
<td>$A$ connected</td>
<td>$\alpha$</td>
</tr>
<tr>
<td></td>
<td>B B</td>
<td></td>
<td>$B$ connected</td>
<td>$\beta$</td>
</tr>
<tr>
<td>4</td>
<td>B B</td>
<td>4$\psi^2(1 - \psi)^6$</td>
<td>$A$ connected</td>
<td>$\alpha$</td>
</tr>
<tr>
<td></td>
<td>B A</td>
<td></td>
<td>$B$ connected</td>
<td>$\beta$</td>
</tr>
<tr>
<td>5</td>
<td>B B</td>
<td>24$\psi^3(1 - \psi)^5$</td>
<td>1</td>
<td>$\pi\xi/8$</td>
</tr>
<tr>
<td>6</td>
<td>B B</td>
<td>24$\psi^3(1 - \psi)^5$</td>
<td>$A$ connected</td>
<td>$\alpha$</td>
</tr>
<tr>
<td></td>
<td>B A</td>
<td></td>
<td>$B$ connected</td>
<td>$\beta$</td>
</tr>
<tr>
<td>7</td>
<td>B B</td>
<td>8$\psi^3(1 - \psi)^5$</td>
<td>$A$ in 1, $B$ in 2</td>
<td>$\alpha^3$</td>
</tr>
<tr>
<td></td>
<td>B A</td>
<td></td>
<td>Both connected</td>
<td>$3\alpha^2\beta$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$A$ in 2, $B$ in 1</td>
<td>$3\alpha^2\beta^2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$A$ in 3, $B$ in 1</td>
<td>$\beta^3$</td>
</tr>
<tr>
<td>8</td>
<td>B B</td>
<td>6$\psi^4(1 - \psi)^4$</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>B B</td>
<td>8$\psi^4(1 - \psi)^4$</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>B B</td>
<td>24$\psi^4(1 - \psi)^4$</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>B B</td>
<td>24$\psi^4(1 - \psi)^4$</td>
<td>$A$ in 1, $B$ in 2</td>
<td>$\alpha^2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Both connected</td>
<td>$2\alpha\beta$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$B$ in 1, $A$ in 2</td>
<td>$\beta^2$</td>
</tr>
<tr>
<td>12</td>
<td>B B</td>
<td>6$\psi^4(1 - \psi)^4$</td>
<td>$A$ in 1, $B$ in 2</td>
<td>$\alpha^2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Both connected</td>
<td>$2\alpha\beta$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$B$ in 1, $A$ in 2</td>
<td>$\beta^2$</td>
</tr>
<tr>
<td>13</td>
<td>B B</td>
<td>6$\psi^4(1 - \psi)^4$</td>
<td>$A$ in 1, $B$ in 4</td>
<td>$\alpha^6$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$A$ in 1, $B$ in 3</td>
<td>$6\alpha^5\beta$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$A$ in 1, $B$ in 2</td>
<td>$15\alpha^4\beta^2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$A$ in 2, $B$ in 2</td>
<td>$8\alpha^3\beta^3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$A$ in 1, $B$ in 1</td>
<td>$12\alpha^2\beta^3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$A$ in 2, $B$ in 1</td>
<td>$15\alpha\beta^4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$A$ in 3, $B$ in 1</td>
<td>$6\alpha\beta^5$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$A$ in 4, $B$ in 1</td>
<td>$\beta^6$</td>
</tr>
</tbody>
</table>
As a check on this rather messy calculation, it is also possible to recalculate the mean curvature using this enumeration. We assign to each vertex one-half of each edge that issues from it, and calculate the contribution of the vertex to $\mathcal{H}$ from these six half-edges as before. For the mean curvature the swap of $A$ for $B$ changes the sign.

For each ambiguous edge we again consider both the $A$- and $B$-continuous possibilities, with a factor of $\alpha$ or $\beta$ multiplying the probabilities. As some of the vertex configurations are at the meeting point of several such edges, this can give rise to a number of alternatives, as the probabilities for each edge must be taken as independent.

Equation (3.30) states that a vertex contributes $2\pi - \sum \beta_i$ to the Gaussian curvature, where the $\beta_i$ are the angles between successive edges meeting at the vertex. This is valid when the small piece of surface near the vertex has only one connected component. For the Voronoi models, with four cells meeting at each vertex, this was always the case. But for several vertex configurations in the cubic lattice, there are variants in which the imagined dividing surface has more than one component. For instance configuration 4 in Table 3.2, with two $A$ cubes at opposite corners, can be taken as a sort of tilted hourglass shape by connecting the $A$s. This is a saddle-shaped surface with only one component and the correct curvature is indeed given by counting that there are six angles each of $\pi/2$, giving $\mathcal{K} = -\pi$. But this could also be seen as two separate $A$ pieces—say two eighth-spheres. Each of these clearly has positive Gaussian curvature, and the original formula fails. The correct thing is to apply the formula to each component of the surface separately and add the results. This gives two contributions each of $+\pi/2$ (as one would expect for eighth-spheres), hence $\mathcal{K} = \pi$. This situation can be summarised by rewriting the Gaussian curvature contribution for a vertex as $2n\pi - \sum \beta_i$ where $n$ is the number of surface components at the vertex.

While assigning a factor of $\alpha$ or $\beta$ to each ambiguous edge depending on whether we make medium $A$ or $B$ continuous is a consistent way of dealing with most configurations, it fails for configuration 4, where there is only vertex contact. It is unclear what relation the probability of connection across such a configuration should bear to that of connection across an edge. As the mean curvature for the two variants is the same, this will only affect the Gaussian curvature. An argument could certainly be made that the $A$-continuous variant should only get $\alpha^2$ or perhaps even $\alpha^3$, rather than $\alpha$ as given in the table, and that as a result our Gaussian curvature estimate will be too low. Trial calculations show that this has only a very slight effect.

As before, we can now calculate the total curvatures per unit volume from the figures in the table. As the vertex density is only $1/\xi^3$, we have

$$\mathcal{H}/V = \frac{1}{\xi^3} \sum_{i,j} p_i w_j \mathcal{H}_{ij}$$  \hspace{1cm} (3.55)

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and

\[ \mathcal{K}/V = \frac{1}{\xi^2} \sum_{i,j} p_i w_j \mathcal{K}_{ij}. \quad (3.56) \]

Dividing the results by \( \Sigma \) gives the area-averaged curvatures. For the mean curvature this gives the same result as Equation (3.53). For the Gaussian curvature it gives the somewhat untidy result:

\[ \langle K \rangle = \frac{2\pi}{3\xi^2} \left( 1 - 2\psi(1 + 4\alpha) - 2\psi^2(1 - 8\alpha - 4\alpha^3) \right. \]
\[ + \psi^3(1 - 20\alpha + 30\alpha^2 - 16\alpha^3 - 18\alpha^4 + 12\alpha^5 - 4\alpha^6) \]
\[ + \psi^4(1 + 44\alpha - 66\alpha^2 - 8\alpha^3 + 54\alpha^4 - 36\alpha^5 + 12\alpha^6) \]
\[ + \psi^5(3 - 44\alpha + 42\alpha^2 + 32\alpha^3 - 54\alpha^4 + 36\alpha^5 - 12\alpha^6) \]
\[ \left. + \psi^6(1 - 12\alpha + 6\alpha^2 + 16\alpha^3 - 18\alpha^4 + 12\alpha^5 - 4\alpha^6) \right) \quad (3.57) \]

For the bilayer, with \( \alpha = \beta = \frac{1}{2} \), this reduces somewhat to give

\[ \langle K \rangle = \frac{\pi}{24\xi^2} \left( 16 - 96\psi + 112\psi^2 - 69\psi^3 + 127\psi^4 - 111\psi^5 + 37\psi^6 \right) \]
\[ = \frac{\pi}{1536\xi^2} \left( (1 - 2\psi)^2(592\psi^4 - 1184\psi^5 + 700\psi^2 - 108\psi + 1509) - 485 \right) \]
\[ \approx \frac{2\pi}{3\xi^2} \left( (1.4834)(1 - 2\psi)^2 - (0.4736) \right), \quad (3.58) \]

with the last approximate equation holding to better than 2.5% over the entire range \( 0 \leq \psi \leq 1 \). Figure 3.11 shows the variation of Gaussian curvature with \( \psi \) for \( \alpha = 0, \frac{1}{2} \) and 1.

The bilayer results of this section are quite similar to those obtained for the Voronoï lattice. For the mean curvature, the approximate coefficient in that case was 1.57, which agrees to three significant figures with the exact value \( \pi/2 \) obtained for the CRC model. For the Gaussian curvature there are slight differences: the Voronoï models go to a deeper minimum of \( \langle K \rangle \approx -1.49\xi^2 \) as opposed to \( \langle K \rangle \approx -0.99\xi^2 \) at \( \psi = \frac{1}{2} \), and the change in sign occurs at \( \psi \approx 18\% \) for the Voronoï models as opposed to \( \psi \approx 22\% \) for CRC. The limits at \( \psi = 0 \) are identical for both lattices—as one would hope, for in this limit the lattice becomes irrelevant and the structure is one of isolated droplets.

As mentioned above in the context of the DOC lamellar model, the change in sign of \( \langle K \rangle \) is a good indicator of bicontinuity. The finding here, that for the cube model this occurs at \( \approx 22\% \) is in considerable disagreement with the estimate of Cates et al. [20], that this occurs at \( \psi = 0.3 \). As discussed above, \( \langle K \rangle > 0 \) is a necessary but not sufficient condition for loss of bilayer continuity, so one would in fact expect \( \psi = 0.22 \) to be an upper bound for the location of the percolation transition.
3.5 Cusps in the DOC cylinders model

With only a minor extension of the methods developed in Section 3.3.1, it is not too difficult now to go on and derive an exact treatment of the cusps in the DOC cylinders model. The situation is again that pictured in Figure 3.5. For the sake of conciseness and simplicity we restrict ourselves to the case where \( \rho = R/r = 2 \). In this case the dihedral angle \( \alpha \) is equal to \( 4\pi/3 \). As before, we cut away a narrow strip around the cusp and replace it with a smoothly curved surface which joins smoothly along both edges: in this case it is a piece cut from a torus with major radius \( r + \varepsilon \) and minor axis \( \varepsilon \) and which spans an angle of \( \pi/3 \) away from the plane of the ring\(^2\).

As this surface is smooth, it is valid to use the parallel surface method to calculate its curvatures. Taking co-ordinates with the \( x \)-axis lying along the axis of the cylinder, this torus and its parallel surfaces are obtained by rotating the concentric circles \( x^2 + (y - (r + \varepsilon))^2 = (\varepsilon + \delta)^2 \) about the \( x \)-axis between \( x = 0 \) and \( x = (\varepsilon + \delta) \sin(\pi/3) \).

The area of the piece we want is

\[
S_\delta = 2\pi \int_0^{(\varepsilon + \delta) \sin(\pi/3)} y\sqrt{1 + (y')^2} \, dx
\]

\[
= 2\pi \int_0^{(\varepsilon + \delta) \sin(\pi/3)} \left( \frac{(\varepsilon + \delta)(r + \varepsilon)}{\sqrt{(\varepsilon + \delta)^2 - x^2}} - (\varepsilon + \delta) \right) \, dx
\]

\(^2\)For finite \( \varepsilon \) this angle will be reduced as a result of the curvature of the sphere, but we can neglect this as we are only interested in the limit \( \varepsilon \to 0 \).
\[ \begin{align*}
&= 2\pi(\varepsilon + \delta) \left( (r + \varepsilon) \frac{\pi}{3} - (\varepsilon + \delta) \left( \frac{\sqrt{3}}{2} \right) \right). \\
&= \frac{S_{-\delta} - S_{+\delta}}{4\delta}
&= -\frac{(r + \varepsilon)^2}{3\sqrt{3}\pi} + \sqrt{3}\pi\varepsilon
\end{align*} \]

(3.59)

Note that \( \delta \) is positive on the positive (water) side of the surface. The total mean curvature for this piece of torus is therefore,

\[ \mathcal{H} = \frac{S_{-\delta} - S_{+\delta}}{4\delta} \]

and so taking the limit as \( \varepsilon \to 0 \) gives the contribution of each cusp to the mean curvature

\[ \mathcal{H} = -\frac{\pi^2r}{3}. \]

(3.60)

The Gaussian curvature contribution is

\[ \mathcal{K} = \frac{S_{-\delta} + S_{+\delta} - 2S_0}{26\delta} \]

\[ = -\sqrt{3}\pi. \]

(3.62)

Note that the curvature of this cusp has not affected our original formula for the mean curvature contribution of an edge-like cusp derived in Section 3.3.1. Here we have \( \alpha = 4\pi/3 \) and the length of the cusp \( L = 2\pi r \), which in that formula gives \( \mathcal{H} = (\pi - \alpha)L/2 = -\pi^2r/3 \).

We can now calculate the total curvatures per unit volume for the DOC model, for the mean curvature on the whole of the smooth part (assuming \( \rho = 2 \)) is \(-1/2r = -1/R\) and the Gaussian curvature is \(1/R^2\) on the spherical parts and 0 on the cylindrical parts. This gives

\[ \mathcal{H}/V = -\frac{\Sigma}{2r} + \frac{nZ\pi^2r}{3} \]

\[ = \pi rn \left( \frac{\pi}{3} + 4 - \sqrt{3} - \frac{L}{2r} \right)Z - 8 \]

(3.63)

for the mean curvature. Now \( L \geq 2R + 2\ell = 4r + 2\ell \). If we assume dense packing, so that we have approximate equality, then in the limit of large structures \( r \gg \ell \), this gives zero mean curvature at \( Z \approx 6 \). This is the co-ordination number of the standard periodic minimal surface proposed as a model for bicontinuous phases, the P-surface of Schwarz. As \( r \) gets smaller relative to \( \ell \), this threshold climbs quickly, and for \( r \) less than about \( 2\ell \) we have mean curvature toward the water for all possible coordination numbers. For less dense packing, \( L \) will be even larger and it will be correspondingly less likely that the mean curvature changes sign.

The total Gaussian curvature per unit volume has the particularly simple form

\[ \mathcal{K}/V = 2n\pi(2 - Z). \]

(3.64)
This is interesting in the light of the earlier discussion of the percolation transition from disconnected to bicontinuous structures. If we were to take the sign of $K$ as the condition for bicontinuity, we would say that the transition took place at $Z = 2$, whereas the percolation studies of Jerauld et al. [68] give the transition at $Z \approx 1.1$ at which point the structure has quite strong positive Gaussian curvature.