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Mean and Gaussian curvatures of randomly decorated Voronoi and cubic tesselations

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It is now generally accepted that some midrange microemulsions are bicontinuous, i.e., continuous in both oil and water simultaneously. The first model of the microstructure of microemulsion that could account for a progression from discrete to bicontinuous was the Talmon–Prager or "randomly decorated Voronoi" model. Space is tessellated into Voronoi polyhedra and the polyhedra are randomly decorated with oil and water. In variations of the model DeGennes and Taupin and Widom decorate a cubic tesselation of space. At first glance it might appear that the decorated Voronoi and cubic tessellations are zero-mean-curvature models, since they are constructed from polyhedra with planar faces. However, the edges of the polyhedra are concentrations of mean curvature, and the vertices are concentrations of Gaussian curvature. The area-averaged mean and Gaussian curvatures of the oil–water interface in the randomly decorated Voronoi and cubic models are calculated. The area-averaged mean curvatures of the two models are linear functions of oil volume fraction, change sign at a volume fraction of 0.5, and are within 0.2% of one another in magnitude. The area-averaged Gaussian curvature of the Voronoi model varies quadratically with volume fraction, and is negative for oil volume fractions from 0.18 to 0.82 (oil and water are bicontinuous for volume fractions ranging from 0.135 to 0.865). The area-averaged Gaussian curvature of the randomly decorated cubic model is a sixth-order polynomial function of oil volume fraction and is negative for volume fractions ranging from 0.23 to 0.77 (oil and water are bicontinuous over the volume fraction range 0.25 to 0.75). As an additional application, the model results are used to interpret curvature aspects of the bilayer theory of the L_3 phase of surfactant solutions presented recently by Cates *et al.* [Europhys. Lett. **5**, 733 (1988)].

INTRODUCTION

A microemulsion can be defined as a thermodynamically stable, optically isotropic liquid phase containing hydrocarbon, water and surfactant.[1] Microemulsions have received a great deal of attention, motivated in part by their intrinsic scientific interest but also by their commercial importance, their demonstrated ability to recover oil trapped in reservoirs by capillary forces,[2] and their potential use for controlled enzymatical catalysis.[3]

Since the first description of their properties by Hoar and Schulman,[4] an important problem not yet fully resolved has been the relationship between the morphology of microemulsions and their observed physical properties. A traditional view of microemulsion microstructure is that of water-continuous phases containing oil-swollen micelles, or oil-continuous phases containing water-swollen inverted micelles. An alternative hypothesis[5] is that at certain oil/water ratios the microemulsion is bicontinuous, possessing continuity in both water-rich and oil-rich regions. Compelling experimental evidence has recently come forth supporting the existence of bicontinuous microemulsions.[6–12]

In such a bicontinuous structure, water-rich and oil-rich regions form interpenetrating, sample-spanning networks separated by a surfactant-rich film, which can be identified by a highly connected dividing surface characterized by its local mean curvature H and Gaussian curvature K. In terms of the local principal curvatures κ_1 and κ_2, of which the radii of curvature are reciprocals, these quantities are $H = (\kappa_1 + \kappa_2)/2$ and $K = \kappa_1\kappa_2$. The mean curvature of the surface can be toward the water or the oil, or it can be zero and therefore toward neither oil nor water. In the current view of microemulsion structure, the change in the oil/water ratio is accompanied by, or driven by, a change in the mean curvature of the surfactant-rich interfacial film.

The first microemulsion model that could account for a progression from singly continuous to bicontinuous was the Talmon–Prager or "randomly decorated Voronoi" model.[13] The model is constructed by tessellating (dividing) space into random polyhedra[14] and then randomly decorating the polyhedra with oil and water (see Fig. 1). In variations of the theory of Talmon and Prager, DeGennes and Taupin[15] and Widom[16] randomly decorate a cubic tessellation with oil and water. Although the faces of polyhedra have zero principal curvatures, differential geometry teaches us that edges are concentrations of mean curvature and the vertices are concentrations of Gaussian curvature. Thus the oil–water interface in the Voronoi and cubic models of microemulsion is not a zero curvature surface. Although the representation of the interfacial mean curvature as having been swept into edges and Gaussian curvature into the vertices is not physi-

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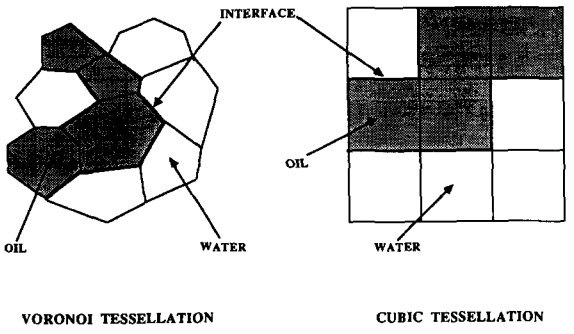

FIG. 1. Illustration of cross section of polyhedra of the Voronoi and cubic tessellations randomly decorated with oil and water separated by oil–water interfaces.

cally realistic, it does provide a simple qualitative model for analyzing the dependence of curvature on oil/water ratio.

The Gaussian curvature at a given point of a smooth surface can be positive, in which case the surface is locally concave or convex, or negative, so that the surface is locally saddle-shaped, or it can be zero. The surface integral of the Gaussian curvature over a surface S (also called the "total curvature") is related to the Euler characteristic χ of S by the Gauss–Bonnet theorem: $\int\int_S K dA = 2\pi\chi - \Sigma_i \int \kappa_g ds$ where κ_g is the geodesic curvature along the ith component of the boundary of S. The Euler characteristic of a closed body, whether smooth or not, is positive only if the surface is topologically equivalent to a sphere; it is zero for a torus; a bicontinuous structure is determined by a surface of highly negative Euler characteristic (or high positive genus, where the genus $g = 1 - \chi/2$ gives the number of "holes"), and therefore significantly negative integral Gaussian curvature (this has been discussed in detail in Anderson[17]).

There is a connection between low mean curvature and bicontinuity that has not been explicitly brought out in the literature. If the mean curvature is approximately zero due to cancellation of oppositely signed principal curvatures, then the Gaussian curvature is negative, being the product of a positive and a negative number. As just discussed, simple closed structures have positive integral Gaussian curvatures, whereas bicontinuous structures have negative total curvature. Thus the observation[6] that bicontinuous structures are often associated with a surfactant-rich zone of approximately zero mean curvature is explained by the Gauss–Bonnet theorem.

In the next section, the area-weighted average mean curvature of the randomly decorated Voronoi model is calculated analytically as a function of the oil volume fraction, and of the concentration c of Poisson points per unit volume (c^{-1} is the average volume of a polyhedron in the Voronoi model and is the volume of a cubic cell in the cubic model). In the subsequent section is calculated the area-averaged Gaussian curvature, which has implications as to the topology of the microemulsion.

CALCULATION OF THE MEAN CURVATURE

The area-weighted average mean curvature $\langle H \rangle$ of the oil–water interface is a function of two variables, namely the volumetric concentration c of Poisson points (and so of polyhedra), and the volume fraction f of oil, i.e., f is the probability that a given polyhedron is of identity "A" (e.g., oil) and $1 - f$ is the probability that it is of identity "B" (e.g., water). Since f is dimensionless and c has dimensions of inverse length cubed, dimensional analysis shows that the area-averaged mean curvature $\langle H \rangle$ must vary as $c^{1/3}$ and the area-averaged Gaussian curvature $\langle K \rangle$ must vary as $c^{2/3}$. These dependencies will be proven in what follows.

The Voronoi tessellation in three dimensions[14] is accomplished by distributing points—called Poisson points—randomly in space with number concentration c, and using perpendicular bisecting planes between pairs of Poisson points to determine the Dirichlet cell of each. Statistics of the Voronoi tessellation were worked out by Meijering[18] and extended to the randomly decorated Voronoi by Winterfeld[19] and by Jerauld.[20]

The values given by Meijering for the expected surface area, total edge length, number of vertices, edges, and faces per unit volume, etc., must in the decorated Voronoi case be multiplied by the probability that a given vertex, edge or face belongs to the A/B interface. We will use the qualifier "true" to indicate that an edge, vertex or face belongs to the true A/B interface; in the case of a face this requires that the two polyhedra sharing that face have opposite identities, one A and one B; in the case of an edge, which is determined by three polyhedra (an edge consists of points equidistant from three Poisson points), the identities must not be all three the same, so the two cases are A–A–B and A–B–B; and in the case of a vertex, which is determined by four polyhedra, not all four polyhedra can have the same identity. The probability that a given face is a true face is then $2f(1-f)$; the probabilty that a given edge is a true edge is $3f^2(1-f) + 3f(1-f)^2$; and the probability that a given vertex is a true vertex is $4f^3(1-f) + 6f^2(1-f)^2 + 4f(1-f)^3$. The area-averaged mean curvature $\langle H \rangle$ is the integral mean curvature $\mathbf{H}$ divided by the area, in the limit of infinite sample size:

$$\langle H \rangle = \text{the large sample limit of } \{\mathbf{H}/\mathrm{A}\}. \quad (1)$$

The integral mean curvature is concentrated in the dihedral angles along the true edges. We choose to measure the dihedral angle through the A phase, and so positive mean curvature will correspond to curvature toward A. If the dihedral angle along an edge of length L is α, then the contribution to the integral mean curvature from this dihedral angle is $(\pi - \alpha)L/2$. The length L and the dihedral angle α are statistically independent, so that the expected sum over the true edges per unit volume $\Sigma(\pi - \alpha)L/2$ is simply the expected value of $(\pi - \alpha)$, multiplied by the expected total true edge length per unit volume. The latter quantity is the expected total edge length per unit volume times the probability $3[f^2(1-f) + f(1-f)^2]$ that a given edge is a true edge. Meijering has calculated the expected total edge length p.u.v. as $(4\pi)^{5/3}\Gamma(4/3)/(3^{2/3}5)c^{2/3} \simeq 5.83c^{2/3}$. Similarly the expected true surface area per unit volume is $2f(1-f)$ times the expected area per unit volume, given by Meijering as $(256\pi/3)^{1/3}\Gamma(5/3)c^{1/3} \simeq 2.9105c^{1/3}$. It remains to calculate the expected value of $(\pi - \alpha)$.

Since an edge is shared by three polyhedra, which are statistically equivalent, the expected dihedral angle *before decoration*, measured through a *single* polyhedron, is of course $2\pi/3 = 120°$ by symmetry. After decoration, the edge is a true edge if and only if the three polyhedra are either A–A–B, or A–B–B; in the first case the total dihedral angle measured (as per our convention) through the A phase will be the sum of two such angles, one through each A polyhedron, while in the second case only one such angle will contribute. The size of each angle contributing is of course independent on the A/B decoration, so the expected dihedral angle is $4\pi/3$ (240°) times the probability of A–A–B identities, plus $2\pi/3$ (120°) times the probability A–B–B identities. The first probability is

$$3f^2(1-f)/3[f^2(1-f)+f(1-f)^2],$$

and the second is

$$3f(1-f)^2/3[f^2(1-f)+f(1-f)^2],$$

where these are conditional probabilities that assume the edge is already a true edge. Upon simplification, the expected value of $(\pi-\alpha)$ for a true edge is

$$\langle(\pi-\alpha)\rangle = (1-2f)\pi/3. \tag{2}$$

The final result is this expected value times the expected value of half the total true edge length per unit volume, divided by the expected true area per unit volume:

$$\begin{aligned}\langle H\rangle &= [(1-2f)\pi/3]\times(5.83c^{2/3}/2)\\ &\quad\times\frac{3[f^2(1-f)+f(1-f)^2]}{[2.9105c^{1/3}\times 2f(1-f)]}\\ &= (\pi^7/48)^{1/3}\Gamma(4/3)/[5\Gamma(5/3)]c^{1/3}(1-2f)\\ &= 1.574c^{1/3}(1-2f).\end{aligned} \tag{3}$$

Thus, *the area-averaged mean curvature varies linearly with the oil volume fraction, from positive toward oil for $f<0.5$, to zero at $f=0.5$, to negative, i.e., positive toward water, for $f>0.5$.*

By arguments similar to those presented above, the area-averaged mean curvature of the oil–water interface in the randomly decorated cubic model is found to be

$$\langle H\rangle = (\pi/2)c^{1/3}(1-2f) = 1.571c^{1/3}(1-2f), \tag{4}$$

almost exactly the same as the Voronoi result!

That the mean curvature of cubic models is proportional to $1-2f$ has been given without proof by previous investigators, e.g., Jouffroy *et al.*[21] and Widom,[16] in connection with the Bancroft parameter in the free energy of curvature. Recently, Auvray *et al.*[22] used the relation $\delta A = 2\langle H\rangle\delta V$ to estimate $\langle H\rangle$ for the cubes model. Unfortunately, however, this relation holds for smooth surfaces only, and one of the present authors[17] has derived a correction factor for this relation for surfaces with dihedral angles, which then yields the correct value for $\langle H\rangle$. Specifically, the correct value of the contribution to the integral mean curvature from a dihedral angle α, is obtained by multiplying the contribution to $\delta A/\delta V$ by the correction factor $(\pi-\alpha)\tan(\alpha/2)/2$. This correction factor is only equal to unity in the limit as $\alpha\to\pi$. Thus, although the relation $\delta A = 2\langle H\rangle\delta V$ leads to the correct functional form for $\langle H\rangle$, namely $\langle H\rangle \propto 1-2f$, the constant prefactor derived is not correct.

CALCULATION OF THE GAUSSIAN CURVATURE

The calculation of the area-averaged Gaussian curvature is similar. Again we need the expected true area p.u.v., and in the numerator the expected integral Gaussian curvature of the true A/B interface. The integral Gaussian curvature is concentrated in the vertices of the true interface. The contribution to the integral Gaussian curvature of a vertex is $2\pi - \Sigma\beta_i$ where the β_i are the angles between consecutive edges around the vertex. There are four polyhedra involved, and the three cases A–A–A–B, A–A,B–B, and A–B–B–B are the cases in which the vertex is a true vertex (corresponding to the three terms listed above in the expression for the probability that the vertex is real).

The expected value of β_i was calculated by Winterfeld as $\langle\beta\rangle = 2/3\pi - 35/(72\pi) \simeq 1.939\,66 \simeq 111.134°$. In the case A–A–B–B four angles will contribute, while in the other two cases only three will contribute. Note that with Gaussian curvature, in contrast to mean curvature, the sign convention does not matter. The expected value of $2\pi - \Sigma\beta_i$ for a true vertex is then:

$$\begin{aligned}\left\langle 2\pi - \sum\beta_i\right\rangle &= [4f(1-f)^3 + 4f^3(1-f)]\\ &\quad\times\{2\pi - 3[2/3\pi - 35/(72\pi)]\}\\ &\quad + 6f^2(1-f)^2\{2\pi - 4[2/3\pi - 35/(72\pi)]\}.\end{aligned} \tag{5}$$

The number of vertices p.u.v. was given by Meijering to be $(96\pi^2/35)c/4 \simeq 27.07c/4$, and the probability that a given vertex is true is $4f^3(1-f) + 6f^2(1-f)^2 + 4f(1-f)^3$ as given above. Combining these results with the expected true area used in the calculation of $\langle H\rangle$, and simplifying, yields the final result:

$$\langle K\rangle = [a_1(f-\tfrac{1}{2})^2 - a_2]c^{2/3}, \tag{6}$$

where

$$a_1 = 96\pi^{8/3}(3/256)^{1/3}\,[35\Gamma(5/3)] \simeq 14.612\,176,$$

and

$$a_2 = [6\pi^2/35 - 1]\pi^{2/3}/[\Gamma(5/3)(4/3)^{1/3}] \simeq 1.493\,742\,7.$$

The two values of f at which $\langle K\rangle = 0$ are $f = 1/2 \pm \sqrt{a_2/a_1} \simeq 0.819\,727\,8$ and $0.180\,272\,2$.

Thus, *the area-averaged Gaussian curvature varies quadratically with oil volume fraction, is symmetric about $f=0.5$, and is negative for $0.18 < f < 0.82$.* (See Fig. 1.)

The same result can be derived another way. The Euler characteristic χ of a surface is, by a well-known formula due to Euler, equal to $F - E + V$ for a surface with F faces, E edges, and V vertices (it is related to the genus by $\chi = 2 - 2g$). By the Gauss–Bonnet theorem, the integral Gaussian curvature $\mathbf{K}$ is related to the Euler characteristic by $\mathbf{K} = 2\pi\chi$, or

$$\mathbf{K} = 2\pi(F - E + V). \tag{7}$$

The expected values for the number of faces, edges, and vertices per polyhedron (for the undecorated Voronoi) were

given by Meijering: $2+48\pi^2/35\simeq 15.54$ faces, $144\pi^2/35\simeq 40.61$ edges, and $96\pi^2/35\simeq 27.07$ vertices. Note that $f-e+v=2$ for these numbers, since the Euler characteristic is 2 for a body homeomorphic to a sphere. For the undecorated Voronoi, Meijering noted that these numbers should be multiplied by $c/2$, $c/3$, and $c/4$, respectively. For the decorated Voronoi, these are then multiplied by the probabilities given above, yielding the expected values of F, E, and V for the number of faces, edges, and vertices in the true A/B interface. The formula:

$$\langle K\rangle = \text{the large sample limit of } \{\mathbf{K}/A\}$$
$$= \text{the large sample limit of } \{2\pi(F-E+V)/A\} \quad (8)$$

then yields the result given above.

The two terms in the expression for $\langle 2\pi-\Sigma\beta_i\rangle$ above can be separated out to evaluate the contributions to $\mathbf{K}$ form synclastic (concave or convex) and form anticlastic (saddle-shaped) vertices. The contribution per unit volume from synclastic vertices is $+12.566\,[f(1-f)^3+f^3(1-f)]c$, and anticlastic vertices contribute $-59.911f^2(1-f)^2c$. At $f=0.819\,727\,8$ and $0.180\,272\,2$, where $\langle K\rangle=0$, the magnitude of either contribution is $1.3083c$. At $f=0.5$, the contributions are $+1.5708c$ and $-3.7444c$.

Similarly, the contributions to the integral mean curvature per unit volume from edges of positive and negative mean curvature can be separated. The positive contributions amount to $9.16f(1-f)^2c^{2/3}$, and the negative contributions are $-9.16f^2(1-f)c^{2/3}$. At $f=0.5$, for example, the magnitude of either contribution is $1.145c^{2/3}$.

The area-averaged Gaussian curvature for the cubic model is

$$\langle K\rangle = (2\pi c^{2/3}/3)\{-3+3f-3f^2 + [4(1-f)^6+14f(1-f)^5 + 28f^2(1-f)^4+35f^3(1-f)^3+28f^4(1-f)^2 + 14f^5(1-f)+4f^6]\}. \quad (9)$$

Here f is again the volume fraction of the oil phase which is randomly dispersed in cubes of volume c^{-1}.

The area-averaged Gaussian curvature of the cubic model is symmetric about $f=0.5$, is negative for $0.233<f<0.767$, and is positive outside that range.

Thus, the area-averaged Gaussian curvature behaves similarly for the cubic and the Voronoi tessellations. However, as is seen in Fig. 2, the area-averaged Gaussian curvature of the cubic tessellation at $f=0.5$ is only about 38% of the value for the Voronoi tessellation, indicating a much lower genus per unit volume for the cubic tessellation, with coordination number $z=6$, than for the Voronoi, with average coordination number $z=15.54$.

DISCUSSION

The area-weighted average mean and Gaussian curvatures of the oil/water interfacial surface in the randomly decorated Voronoi microemulsion model have been calculated analytically, as functions of the oil volume fraction f and the concentration of polyhedra, where the latter is simply related to the radius of gyration of the structure[23] via $R_g=0.571c^{-1/3}$. The primary result is that the area-averaged mean curvature varies linearly with f, from significantly positive toward oil at $f\ll 0.5$, to zero at $f=0.5$, to negative (or positive toward water) for $f\gg 0.5$. The limiting value as f approaches zero is $1.57c^{1/3}$; note that a sphere with the same volume, $1/c$, as the average polyhedron volume would have mean curvature $(4\pi/3)^{1/3}c^{1/3}\simeq 1.612c^{1/3}$. This reflects the fact that for very small f, the structure consists of dilute isolated oil polyhedra in a water-continuous medium.

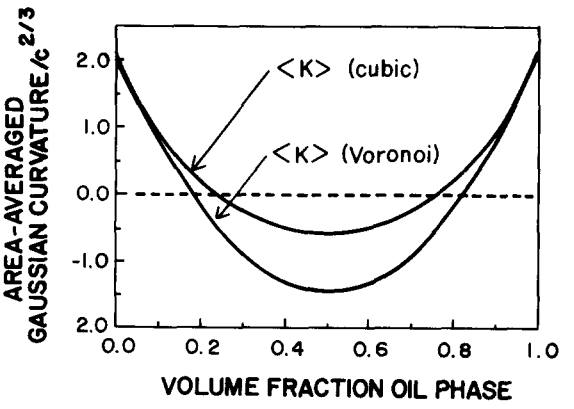

FIG. 2. The area-averaged Gaussian curvature vs the volume fraction of the oil phase for the Voronoi and the cubic tessellations.

The area-averaged Gaussian curvature of the Voronoi model is negative for $0.18<f<0.82$, over which range the randomly decorated Voronoi is bicontinuous (see Fig. 2). The range over which the model structure is bicontinuous is estimated[20] to be $0.135\ll f<0.865$ (below a percolation threshold at 0.135 the oil is discontinuous and above a percolation threshold at 0.865 the water is discontinuous). Therefore there is a small concentration range over which the structure is bicontinuous even though the area-averaged Gaussian curvature is positive. When considering this, one must remember that bicontinuity only requires that sample-spanning paths exist in both oil and water, and not that every oil polyhedra be accessible to every other through oil channels, for example. Over the concentration range $0.135<f<0.18$ $(0.82<f<0.865)$, the majority of oil (water) polyhedra do not belong to a sample-spanning path of oil (water) even though one exists. For the cubic tessellation the percolation threshold is 0.25 for oil and 0.75 for the water[24] and so there are in this case small concentration ranges, namely $0.233<f<0.25$ and $0.75<f<0.767$, over which the Gaussian curvature is negative but the structure is not bicontinuous. The implication is that in the concentration range 0.233 to 0.25 (0.75 to 0.767) the clusters of oil (water) phase while not sample spanning are large and highly ramified.

Randomly decorated Voronoi polyhedra and cubes are crude models in some respects, in that it neglects longer-ranged interactions and lacks microscopic detail in terms of the exact interfacial shape. However, the Voronoi model in particular has proved valuable in understanding the trends in small-angle x-ray and neutron scattering measurements over wide concentration ranges[6,10,22,23] in cases where other models fail. Combining these results with the present calcu-

lations will show that continuous variations in mean curvature, from positive toward oil to positive toward water, occur with concentration variations concomittently with progressions from water continuous, to bicontinuous, to oil continuous.

Another interesting application of the theory developed above is the calculation of the area-averaged mean curvature for a model in which a *bilayer* is draped over the A/B dividing surface, for either the Voronoi or the cubic model. Such a model, using the cubic tessellation, has recently been proposed as a description of the so-called "L_3" phase occurring in various surfactant systems. In this model, both the A and B cubes are envisioned as containing the same component which we will refer to here as the "solvent" (taken as oil in the work of Cates *et al.*[25]). A bilayer of constant width $2L$ is envisioned as being draped over the A/B dividing surface, thus creating vesicles at low ratios of A/B, and at moderate ratios, "sheetlike" phase at moderate ratios, which is bilayer continuous.

There is a general formula[26] for the area-averaged mean curvature, evaluated over the two surfaces lying at a distance L from a base surface S, in terms of the area-averaged Gaussian curvature of S. Let the mean and Gaussian curvatures of S be denoted by H_0 and K. The sign of H_0 will depend on which side of the surface we are viewing from. The mean curvature on the surface displaced a distance L will be denoted as H_L. From differential geometry it follows that the area element and the mean curvature on a displaced surface are given by

$$dA_L = (1 - 2H_0L + KL^2)\, dA_0 \tag{10}$$

$$H_L = (H_0 - KL)/(1 - 2H_0L + KL^2). \tag{11}$$

When averaging over the two displaced surfaces in our model bilayer, it must be taken into account that these two surfaces see the surface S from opposite sides, and thus the H_0 in the above formulae is oppositely signed for the two. If we make the sign convention that H_L is positive when the mean curvature is toward the solvent, then we get the following expression for the total integral mean curvature over both displaced surfaces, taking advantage of the cancellation of the denominator in Eq. (11) upon multiplication with the area element in Eq. (10):

$$\begin{aligned}\langle H_L\rangle dA_l &= \int\int (H_0 - KL)dA_0 \\ &\quad + \int\int (-H_0 - KL)dA_0 \\ &= -2L\int\int K dA_0 \equiv -2L\,\langle K\rangle A_0. \end{aligned} \tag{12}$$

One can rewrite this to express the area-averaged mean curvature $\langle H\rangle$ over the two displaced surfaces:

$$\langle H_L\rangle = -L\,\langle K\rangle/(1 + L^2\langle K\rangle). \tag{13}$$

(Note that if $\langle H_L\rangle$ is calculated by dividing by twice the area of S, rather than by the actual area of the displaced surfaces, the formula becomes simpler: $\langle H_L\rangle = -L\,\langle K\rangle$.) Thus (for physically realistic values of L), *the area-averaged mean curvature over the bilayer surfaces is toward the solvent when the area-averaged Gaussian curvature $\langle K\rangle$ of the base surface S is negative, and is away from the solvent when $\langle K\rangle$ is positive.* Furthermore, the Gauss–Bonnet theorem shows that the integral mean curvature over the bilayer surfaces depends solely on the topological type of the base surface S, and of course on L.

Formula (13) is exact for smooth surfaces S, but the A/B surface in the Voronoi and cubic tessellations are not smooth, and one can in fact check that for a single unit cube, for example, the formula yields $\langle H_L\rangle = -L\pi(3/2 + \pi L^2)$, whereas the exact value is $\langle H_L\rangle = -L\pi(1 + 4L^2)$. However, in the context of fluid microstructures it is of course more realistic to imagine the curvature to be smoothly distributed, as is envisioned in the model of Cates *et al.*,[25] rather than concentrated into singularities. When this is done without changing the topology of the surface, i.e., without tearing or fusing the surface, the formula then applies to the smoothed surface with the *same* value of the integral Gaussian curvature. In other words, formula (13) gives the area-averaged mean curvature for a bilayer draped over the *smooth* surface with the same topological type (and same A_0) as the original (possibly unsmooth) surface.

Thus for the case of a bilayer draped over the dividing surface in the randomly decorated Voronoi tessellation, where this surface is smoothed without topological change, formula (13) holds and the result given by Eq. (6), shown graphically in Fig. 1, shows that the area-averaged mean curvature over the displaced (parallel) surfaces is significantly *toward the solvent* for $0.18 < f < 0.82$. In applying formula (13) to the randomly decorated cubic tesselation, however, there is a complication due to the fact that the A/B dividing surface has self-intersections. This occurs when the identities of the cubes, proceeding in a circuit around a given edge, are in the order A–B–A–B, so that "vertical" and calculations described above, offsetting structures without self-intersections were assumed, but in the present case it is possible to ascribe a bilayer to this situaiton in which four monolayers, each with a 90° bend toward the solvent, meet along this edge. Clearly, this introduces very strong mean curvature toward the solvent. Thus, the mean curvature in the model of Cates *et al.*[25] is *even more strongly toward the solvent* than as given by formula (13) using the result in Eq. (9).

The results for $\langle K\rangle$ in Fig. 1 can now be applied to the model of Cates *et al.* Thus we see that when the A/B ratio is close to unity (= 0.5 in their notation), there is significant net mean curvature toward the solvent. Then for A less than 0.233, the net mean curvature is away from the solvent.

The physical significance of these results in the case of L_3 phase will be discussed in a forthcoming publication.

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[1] I. Danielsson and B. Lindman, Colloids Surf. **3**, 391 (1981).
[2] R. N. Healy, R. L. Reed, and D. G. Stenmark, Soc. Pet. Eng. J. **16**, 147 (1976).

[3]P. L. Louisi and L. J. Magid, CRC Crit. Rev. Biochem. (in press).
[4]T. P. Hoar and J. H. Schulman, Nature **152**, 102 (1943).
[5]L. E. Scriven, in *Micellization, Solubilization and Microemulsions*, edited by K. L. Mittal (Plenum, New York, 1977), Vol. 2, 877.
[6]L. Auvray, J. P. Cotton, R. Ober, and C. Taupin, J. Phys. Chem. **88**, 4586 (1984); also J. Phys. (Paris) **45**, 913 (1984).
[7]K. E. Bennett, J. C. Hatfield, H. T. Davis, C. W. Macosko, and L. E. Scriven, *Microemulsions*, edited by I. D. Robb (Plenum, New York, 1982), pp. 65–84.
[8]J.-F. Bodet, J. R. Bellare, H. T. Davis, L. E. Scriven, and W. G. Miller, J. Phys. Chem. (in press).
[9]M. T. Clarkson, D. Beaglehole, and P. T. Callaghan, Phys. Rev. Lett. **54**, 1722 (1985).
[10]M. Kahlweit, R. Strey, D. Haase, H. Kunieda, T. Schmeling, B. Faulhaber, M. J. Bokovec, H. F. Eicke, G. Busse, F. Eggers, Th. Bunck, H. Richmann, L. J. Magid, O. Soderman, P. Stilbs, J. Winkler, A. Dittrich, and W. Jahn (submitted).
[11]M. Sanchez-Rubio, L. M. Santos-Vidals, D. S. Rushforth, and J. E. Puig, J. Phys. Chem. (submitted).
[12]B. Lagourette, J. Peyrelasse, C. Bonel, and M. Clausse, Nature **281**, 60 (1979).
[13]Y. Talmon and S. Prager, Nature **267**, 333 (1977); J. Chem. Phys. **69**, 2984 (1978).
[14]G. Voronoi, J. Reine Angew. Math. **134**, 198 (1908).
[15]P.-G. DeGennes and C. Taupin, J. Phys. Chem. **86**, 2294 (1982).
[16]B. Widom, J. Chem. Phys. **81**, 1030 (1984).
[17]D. M. Anderson, Ph.D. thesis, University of Minnesota, Minneapolis, 1986; see also D. M. Anderson, H. T. Davis, J. C. C. Nitsche, and L. E. Scriven (to be submitted).
[18]J. L. Meijering, Phil. Res. Rep. **8**, 270 (1953).
[19]P. Winterfeld, Ph.D. thesis, University of Minnesota, Minneapolis, 1981.
[20]G. R. Jerauld, Ph.D. thesis, University of Minnesota, Minneapolis, 1985.
[21]J. Jouffray, P. Levinson, and P. G. de Gennes, J. Phys. (Paris) **43**, 1241 (1982).
[22]L. Auvray, J. P. Cotton, R. Ober, and C. Taupin, in *Physics of Complex and Supermolecular Fluids*, edited by S. A. Safran and N. A. Clark (Wiley, New York, 1987), pp. 449–462.
[23]E. W. Kaler and S. Prager, J. Colloid and Interface Science **86**, 359 (1982).
[24]K. K. Mohanty, J. M. Ottino, and H. T. Davis, Chem. Eng. Sci. **37**, 905 (1982).
[25]M. E. Cates, D. Roux, D. Andelman, S. T. Milner, and S. A. Safran, Europhys. Lett. **5**, 733 (1988)
[26]A. G. Petrov, M. D. Mitov, and A. Derzhanski, Phys. Lett. A **65**, 374 (1978).