Gaussian curvature in an Ising model of microemulsions

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We extend Widom's Ising-like model of microemulsions on a simple cubic lattice by a new term which accounts for the Gaussian curvature energy of the oil–water interfaces. The new term distinguishes between different topologies of the interfaces and plays an important role in determining the microstructure of microemulsions on a scale larger or comparable to the persistence length provided that the microemulsion is dominated at all by curvature energies. We also speculate on its possible role for the breakdown of curvature energies in microemulsions.

Recently, Widom[1,2] has proposed a model of microemulsions which consists of an Ising model with additional next-nearest neighbor and three-spin interactions. These interactions are introduced in order to describe the curvature energies of the surfactant film. Since the work of de Gennes and others,[3] these are believed to be responsible for the occurence of three-phase equilibria and the low interfacial tensions in the model. The purpose of this letter is to draw attention to the fact that Widom's energy is a lattice version of only the mean curvature energies. Since a surface possesses, in general, a further material constant[4] which determines the cost of energy due to Gaussian curvature, we derive the Ising model form for this energy. In addition, we comment on its role in microemulsions.

Widom employs a simple cubic lattice whose links carry oil (AA), water (BB), and amphiphile (AB) molecules. The A and B end points of the molecules meet at the sites and the condition is that each site is occupied either by six A or six B end points (see Fig. 1). Hence the variables $\sigma = +1$, $\sigma = -1$ allow us to parametrize all configurations, just as in an Ising model. In order to account for three-phase equilibria and low interfacial tensions, Widom introduces an extra energy $\kappa(1 - \lambda)$ if the A end points of *two* amphiphile molecules come together and an energy $\kappa(1 + \lambda)$ if the B end points come together. This assignment gives an extra energy to curved amphiphile sheets [Figs. 2(a), 2(b)]. It also does so to flat, amphiphile bilayers [Fig. 2(c)], a shortcoming of the assignment which must eventually be corrected.

As the curvature is concentrated at the lattice edges of the surfactant film, the effect upon continuous amphiphilic layers is nontrivial to evaluate and requires the inclusion of surface fluctuations. A representative example is a sheet which forms a staircase of elementary lattice steps. Averaged over a few lattice spacings, this is flat, but the unrenormalized lattice Hamiltonian renders an energy proportional to its area. The analogous problem for line ensembles is well understood where the entropy leads to isotropy between staircase-like diagonal lines and those along the coordinate directions. One has to solve the difficult problem of a continuum limit of lattice curvature. First, perturbative insights in this direction have only recently become available.[5,6]

It is therefore not possible to compare Widom's curvature energies directly with the quadratic continuum form which was introduced by Helfrich in the form[4]

$$F = \int dA \left[\frac{\kappa}{2}(C_1 + C_2 - C_0)^2 + \bar{\kappa}C_1C_2 \right] = F_M + F_G. \quad (1)$$

Here, dA is the invariant area element, $\kappa, \bar{\kappa}$ are elastic moduli, $(C_1 + C_2)/2$ is the mean, C_1C_2 the Gaussian, and C_0 the spontaneous curvature. In Widom's curvature energy the parameter λ sets a bias towards oil in water or water in oil curvatures just as C_0 does in the continuum form [Eq. (1)], implying that his energy corresponds to the first term in Eq. (1). Indeed, we shall now show that the second term in Eq. (2) involving the Gaussian curvature is not contained in Widom's model: By the Gauss–Bonnet theorem, the integral of C_1C_2 over a closed surface is a topological quantity which only depends on the genus g (= number of handles) of the surface ($g = 0$ for a sphere, $g = 1$ for a torus, etc.), namely,

$$F_G = \bar{\kappa} \int C_1C_2 \, dA = 4\pi\bar{\kappa}(1 - g). \quad (2)$$

Consider two lattice surfaces shown in Figs. 3(a) and 3(b) homeomorphic to a sphere and Fig. 3(c) homeomorphic to a torus. For the first two surfaces, F_G should have the same energy whereas it should vanish for the toroidal surface. In Widom's lattice model, the energy depends on the number of edges on the surfaces and is $36\kappa(1 - \lambda)$ for the cube of Fig. 3(a) and $32\kappa(1 - \lambda) + 4\kappa(1 = \lambda)$ for both the distorted curbe and the torus of Figs. 3(b), and 3(c) (assuming the surfaces to contain oil surrounded by water). This demonstrates that Widom's curvature energy shows no genus de-
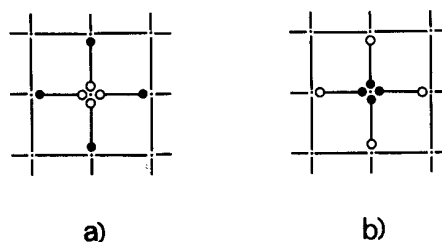

a)   b)

FIG. 1. (a) *A* end points, (b) *B* end points of molecules meeting at a lattice site (Fig. 1 of Ref. 2).

FIG. 4. Four plaquettes carrying amphiphilic molecules which meet at one link to form a singular line. Also shown are the corresponding AB molecules in Widom's graphical scheme.
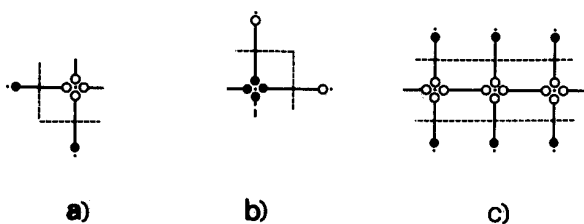
FIG. 2. AB molecules and associated surfactant film (dashed line). Film bent in opposite senses in (a), (b), three pairs of interacting amphiles in a bilayer (c) (Figs. 2 and 4 of Ref. 2).

pendence and cannot account for the Gaussian term in Eq. (1). Now, from several works,[7] it is known that the interplay of mean and Gaussian curvature is relevant for determining the microstructure of the microemulsion. Equilibrium configurations of closed surfaces will tend to "sphere up", form saddle-like configurations, or produce handles called "pores" or "necks" depending on the relative magnitudes of κ and $\bar{\kappa}$. As the Gaussian curvature energy controls the genus of single surfaces as well as the number of surfaces in an ensemble we expect $\bar{\kappa}$ to play an important role in deciding whether the microstructure of the ensemble is layered, bicontinuous (sponge-like) or consists of spheres cylinders, or disks of oil or water immersed in the other liquid.

We are thus motivated to turn to the main purpose of this letter and formulate the Gaussian curvature energy on the simple cubic lattice in terms of Ising variables. Our problem is simplified by the topological nature of this energy. There is no need to know the local curvature $C_1 C_2$ on the lattice. We only have to count the number of surfaces and their geni for each configuration. In contrast with the mean curvature energy, there will be no uncertainty as to the proper continuum limit of our lattice energy due to the purely topological nature of the Gaussian curvature.

For a single closed surface it is well known how to calculate the genus on a simple cubic lattice[8]: Let a connected surface consist of n_2 plaquettes, n_1 distinct links, and n_0 distinct sites. Then the genus of the surface is[11]

$$g = 1 - \tfrac{1}{2}(n_2 - n_1 + n_0 + b). \tag{3}$$

Here, b is the number of singular lines plus boundary lines of the surface. As the Ising model admits only closed surfaces, no boundaries occur and b reduces to the number of singular lines. In the Ising model on a simple cubic lattice only one type of singular line element can occur: if four plaquettes carrying amphiphilic molecules meet at one link (Fig. 4). We can now use rule (3) and count the plaquettes, links, and sites on the surfaces of Fig. 3. This gives $g = 0$ for Figs. 3(a)
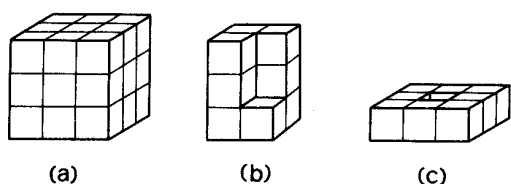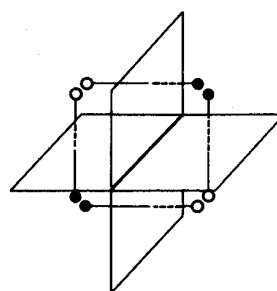
and 3(b) and $g = 1$ for Fig. 3(c), which are the correct geni of these surfaces. The Gaussian curvature energy for an ensemble of surfaces is therefore

$$F_G = 4\pi\bar{\kappa} \sum (1 - g)$$

$$= 2\pi\bar{\kappa} \sum (n_2 - n_1 + n_0 + b)$$

$$= 2\pi\bar{\kappa}(N_2 - N_1 + N_0 + B) \tag{4}$$

with $N_i = \sum n_i, B = \sum b$ being the total number of plaquettes, links, sites, and singular lines on the surfaces of the ensemble configuration.

The counting of the number of sites and of singular lines needs some additional specifications: The definition [Eq. (3)] holds for a single "connected" surface. Two surfaces having contact along links, as shown in Fig. 5(a), have to be counted as a single connected surface. Two surfaces which merely touch at a site as in Fig. 5(b) are counted as disconnected. Accordingly, the genus of the surface in Fig. 5(a) may be calculated using Eq. (3) with each plaquette, link, and site being counted once and $b = 1$ for the singular line, resulting in $g = -1$. For the two disconnected surfaces in Fig. 5(b), on the other hand, the genus has to be calculated for each surface separately via Eq. (3). As the common site is contained in each of the two surfaces, it also has to be included in the calculation of each genus and is thus effectively counted twice in the ensemble formula [Eq. (4)]. This results in $g = 0$ for each of the surfaces of Fig. 5(b). So Figs. 5(a) and 5(b) both contribute $8\pi\bar{\kappa}$ to the Gaussian curvature energy [Eq. (4)] which agrees with the intuitive picture that in a microemulsion both configurations represent two spherical ($g = 0$) surfaces.[12] There is yet another rule for the counting of singular lines in the energy [Eq. (4)]: Singular lines which form closed loops are no longer considered as singular: (i.e., they do not contribute to either the sum b or B). This is demonstrated using Fig. 6, which shows a torus capped with an elementary cube, thus forming a connected

FIG. 3. Two spherical surfaces (a) and (b) and a torus (c) each having 36 bents contributing to Widom's curvature energy.
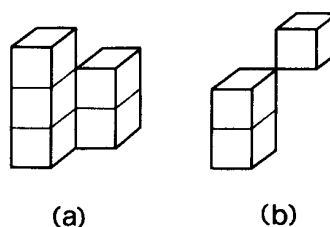

FIG. 5. A surface which is connected because its two parts share common links (a) and two disconnected surfaces sharing only a common site (b).

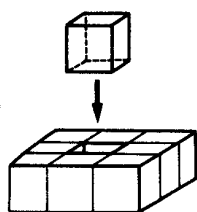FIG. 6. A torus capped with a cube (which has been lifted up for graphical clearness).

a)   b)

FIG. 7. A site (marked ⊗) of the amphiphile sheet and the surrounding eight sites of the original lattice carrying A(O) and B (●) (a). The spin configurations of the lower and upper four sites as defined in Eq. (9) and as used in Tables I and II.

surface with a closed singular line. If we were to count this line in Eq. (3) we would obtain $1 - g = 3/2$, whereas intuitively we expect that the $1 - g = 0$ of the torus and the $1 - g = 1$ of the cube should add to give the total $\Sigma(1 - g) = 1$. This is achieved if the closed singular line is considered as nonsingular.

After having specified the counting rules let us now turn to specifying the Gaussian curvature energy in terms of Ising variables $\sigma = \pm 1$. For this purpose it is convenient to split Eq. (4) into two contributions:

$$F_G = F_G^R + F_G^E. \tag{5}$$

The regular part F_G^R is defined as

$$F_G^R = 2\pi\bar{\kappa}(N_2 - N_1 + N_0^R). \tag{6}$$

With N_0^R being the sum of all distinct sites on the surfaces, each site contributing 1. The remainder is the excess Gaussian curvature

$$F_G^E = 2\pi\bar{\kappa}(N_0^E + B) \tag{7}$$

which includes the number B of open singular lines and the excess number N_0^E of sites which contribute more than the 1 already accounted for in Eq. (6). [For example Fig. 5(b) contributes 1 to N_0^E.]

The regular part [Eq. (6)] is easily expressed in terms of Ising variables in the following way: The number N_2 of occupied plaquettes is simply the number N_{AB} of amphiphile "molecules" in Widom's notation,

$$N_2 = \sum_{x,i} \frac{1 - \sigma(x)\sigma(x + e_i)}{2}, \tag{8a}$$

where $c = (x_1, x_2, x_3)$ are the lattice sites and $i = 1,2,3$ labels the basic lattice vectors e_i: (1,0,0), (0,1,0), (0,0,1). Similarly, the number N_1 of links on the amphiphilic surface is calculated by considering the four A,B carrying sites which encircle this link (see Fig. 4): An amphiphile sheet passes through the link if the four sites have different A,B assignments and the link is surface-free if all the sites are either of A type or of B type:

$$N_1 = \sum_{x,i<j} \left\{ 1 - \frac{1 + \sigma(x)}{2} \frac{1 + \sigma(x + e_i)}{2} \frac{1 + \sigma(x + e_j)}{2} \right.$$
$$\cdot \frac{1 + \sigma(x + e_i + g_j)}{2} - \frac{1 - \sigma(x)}{2} \frac{1 - \sigma(x + e_i)}{2}$$
$$\left. \times \frac{1 - \sigma(x + e_i + e_j)}{2} \frac{1 - \sigma(x + e_j)}{2} \right\}. \tag{8b}$$

The number N_0^R of distinct sites (each counted once) on the amphiphile surface may be calculated from the A,B content of the eight sites on the original lattice which surround the dual site on the surface (see Fig. 7 for an example). Only if
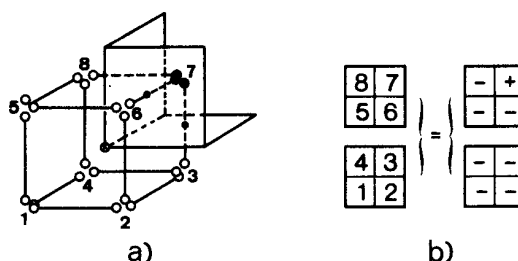
all eight sites are of A type or if all are of B type no surface passes through the central site. In all other cases N_0^R gets a contribution 1:

$$N_0^R = \sum_x \left\{ 1 - \prod_{v=1}^{8} \frac{1 + \sigma_v}{2} - \prod_{v=1}^{8} \frac{1 - \sigma_v}{2} \right\}, \tag{8c}$$

where we introduced the shorthand notation

$$\sigma_1 = \sigma(x), \sigma_2 = \sigma(x + e_1), \sigma_3 = \sigma(x + e_1 + e_2),$$
$$\sigma_4 = \sigma(x + e_2), \sigma_5 = \sigma(x + e_3), \sigma_6 = \sigma(x + e_3 + e_1),$$
$$\sigma_7 = \sigma(x + e_3 + e_1 + e_2), \sigma_8 = \sigma(x + e_3 + e_2). \tag{9}$$

We shall now consider the excess part F_G^E [Eq. (7)] which is much more involved.

We note that Eq. (7) may be rewritten as a sum of contributions coming purely from the sites on the amphiphile surface. As far as the counting of the excess site number N_0^E is concerned, this is obvious. With respect to the singular line-number B the statement is true for the following reason: As the contributing singular lines must be open, each such line has two end points which are located at the surface sites, each such site contributing 1/2 to B. To calculate the energy at each site we take the eight surrounding sites [Eq. (9)] on the original lattice and write the excess part as

$$F_G^E = 2\pi\bar{\kappa} \sum_x \left(n_0^E + \frac{b}{2} \right) \tag{10}$$

with n_0^E and $b/2$ being the contributions at the dual site $x + \frac{1}{2}(e_1 + e_2 + e_3)$. At each site the configuration is specified by the values of the eight $\sigma_v = \pm 1(v = 1,...,8)$. The resulting $2^8 = 256$ configurations give rise to 14 different surface structures. Table I records the spin values of the lower and upper four spins as defined in Fig. 7(b). It also shows a graphic representation of the resulting surface and gives the associated n_0^E and b as well as the degeneracy number of the configuration. Configuration 1 contains no surface and hence contributes nothing to F_G. Configurations 2–7 have a single surface passing through the site and contribute to the regular part of F_G only. Configuration 8 shows two disconnected surfaces as discussed in the context of Fig. 5(b). The site has to be counted twice, so the excess number n_0^E is 1. Configurations 9, 10, 11 have an odd number of singular lines running into the central site. Hence a singular line terminates at this site and $b = 1$. The number n_0^E vanishes for these as well as for all other remaining surfaces, as they are

TABLE I. The 14 possible surface configurations at a site. See the text for the definition of the entries.

Graph	4 3 / 1 2	8 7 / 5 6	surface	n_0^E	b	degen. Number
1	+ + / + +	+ + / + +	∅	0	0	2
2	+ + / + −	+ + / + +		0	0	16
3	− − / + +	− − / + +		0	0	6
4	+ + / + +	+ + / − +		0	0	24
5	+ + / + −	− − / − −		0	0	48
6	+ + / + −	+ + / − −		0	0	8
7	+ − / + +	− − / − +		0	0	24
8	− − / + −	− + / − +		1	0	48
9	+ + / + +	+ − / − +		0	1	16
10	+ − / + −	− + / − −		0	1	48
11	+ − / − +	− + / + +		0	1	16
12	+ + / + −	− − / − +		0	0	24
13	− + / + −	− + / + −		0	0	6
14	+ − / − +	− + / + −		0	0	2

all connected at links. The configurations 12, 13, 14 finally have an even number of singular lines and so $b = 0$ for these graphs.

To facilitate the construction of the energy F_G^E in terms of Ising variables, we present, in Table II, the spin configurations of the upper and lower four spins [see Eq. (9) and Fig.

7(b)]. To the recorded configurations one has to add those with upper and lower spins interchanged and to the resulting expression one has to add the exchange $\sigma_v \to -\sigma_v$ to obtain the complete set of configurations contributing the values n_0^E and b recorded in Table I.

We do not bother to write down the full expression in terms of Ising spins. The reason is that we expect the regular part of the Gaussian curvature energy to be sufficient to describe the overall influence of the topological curvature: From the definition of the regular and excess parts [Eqs. (6) and (7)], it is obvious that the excess part vanishes for strictly self-avoiding surface configurations (no contact at links nor at sites). Consequently, n_0^E and b vanish for the configurations 1–7 in Table I. Since the only microemulsions of practical importance are those which have a low content of amphiphiles the restriction to self-avoiding surfaces should be a good approximation. Moreover, Table I shows that the excess term also vanishes for the configurations 12, 13, 14 which contain surface contacts. As a result only 96 out of the possible 256 configurations at each site contribute to the excess energy. These configurations will occur sparsely as long as the amphiphile concentration is not too large.

Therefore we should be allowed to proceed with the regular part of the Gaussian energy only. Replacing $\sigma(\mathbf{x})$ by its expectation value σ in a simple mean field approximation in Eq. (8) leads to the Gaussian curvature energy per site:

$$\frac{F_G}{N} \approx \frac{F_G^R}{N}$$

$$= 2\pi\bar{\kappa}\left\{\frac{17}{32}\sigma^2 - \frac{11}{64}\sigma^4 - \frac{7}{32}\sigma^6 - \frac{1}{128}\sigma^8\right\} + \text{const.} \tag{11}$$

Not much information can be gained from this mean field expression except that the sign of $\bar{\kappa}$ helps to stabilize the occurence of three-phase regions ($\bar{\kappa} > 0$) or tends to destabilize it ($\bar{\kappa} < 0$). In fact, the influence of the Gaussian curvature energy cannot be judged by mean field methods as it concerns the detailed microstructure of the system such as the occurence of bicontinuous surfaces (sponge-like structures of high genus) the immersion of simple spherical, rod, or disk-like droplets of one component in the other, or the formation of flat bilayers. None of these structures may be obtained by a simple mean field analysis but they require the investigation of more complicated ground states such as the lamellar states investigated by Widom.[2]

Here, we shall not attempt such an investigation but end this letter by a general more speculative discussion of the possible role of the Gaussian curvature energy for microemulsions: Let us first investigate what would happen, if Gaussian curvature energies were the only relevant ones: Recall from the discussion between Eqs. (4) and (5) that each surface contributes $4\pi\bar{\kappa}(1 - g)$ to the energy as if it were completely disconnected from all other surfaces. Assuming that the parameter $\bar{\kappa}$ can take any value between -10^{-13} and $+10^{-13}$ erg, the Boltzmann factor of each surface at room temperature,

$$\exp\{-4\pi\bar{\kappa}(1 - g)\}, \tag{12}$$

can vary between $e^{-20(1-g)}$ and $e^{20(1-g)}$. We now observe

TABLE II. The configurations contributing to surfaces 8, 9, 10, 11 of Table I.

Surface 8 of Table I

| 8 7 | | + + | | + − |
| 5 6 | | + − | | + + |

| 4 3 | | − + | | + + |
| 1 2 | | + + | | − + |

Surface 9 of Table I

| 8 7 | | − + | + − | + + | + + | + + | + − |
| 5 6 | | + − | − + | − + | + − | + − | + + |

| 4 3 | | + + | + + | − + | + − | + + | − + |
| 1 2 | | + + | + + | + + | + + | − + | + + |

Surface 10 of Table I

| 8 7 | | + − | + − | − + | − + | − − | − − | + + | + + | − + | + + | + + | + − |
| 5 6 | | + − | + − | − + | − + | + + | + + | − − | − − | + + | − + | + − | + + |

| 4 3 | | − + | + + | + + | + − | + + | + + | − + | + − | − + | + − | − + | + − |
| 1 2 | | + + | − + | + − | + + | + − | − + | + + | + + | + − | − + | + − | − + |

Surface 11 of Table I

| 8 7 | | + − | + − | + + | + − |
| 5 6 | | − + | − + | − + | + + |

| 4 3 | | − + | + + | − + | − + |
| 1 2 | | + + | + − | + − | + − |

that the same type of weight per (self-avoiding) surface is obtained in $U(n)$ lattice gauge theories $(n^{-2(1-g)})$ if we identify n with $n = e^{-10}$ to e^{10}. In this wide range, the phases change drastically. For small n, the configurations consist mainly of a single surface with high genus, for large n there are many surfaces of low genus (planar or spherical). In contrast to gauge theories, the total area in a microemulsion is essentially fixed experimentally by the concentration of the surfactant. For $\bar{\kappa} > 0$ the Boltzmann factors [Eq. (12)] suppress spherical surfaces of genus 0 and favor configurations with high genus. They are not sensitive to the number of surfaces over which the total available area is distributed. It is then essentially the entropy of mixing which will bias the system towards many surfaces with moderate geni or towards a few high genus surfaces, reminiscent of the bicontinuous phase proposed by Scriven.[9] For $\bar{\kappa} < 0$ on the other hand, spherical surfaces are the favored ones and energy is released if the total available area is distributed over many small spherical surfaces. The entropy of mixing plays a much weaker role in this case and it is the short distance cutoff which prevents the system from subdividing into more and more spheres of ever smaller radius.

Consider now the effect of the mean curvature energy. As $\kappa > 0$ the amphiphile sheets are stiff, on a scale of the

persistence length[3] ξ (= a few hundred angstroms). They are flexible on scales much larger than ξ. If we assume $\kappa > |\bar{\kappa}|$ for the bare constants, then Widom's curvature energy will dominate at small scales. On larger scales, κ is softened by thermal fluctuations while $\bar{\kappa}$ receives an additional *positive* contribution, independent of its initial sign.[5] Suppose now
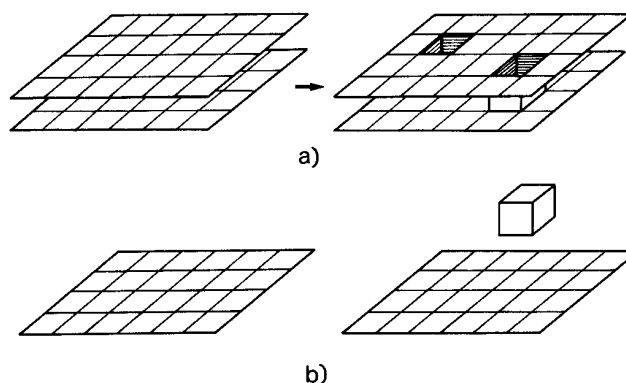

FIG. 8. Elementary surface fluctuations which may cause a collapse of curvature energy for $\kappa \approx \bar{\kappa}$ (a) and $\kappa - \bar{\kappa}$ (b).

the initial $\bar{\kappa}$ is positive and of the same order as κ, i.e., $\kappa_0 > \bar{\kappa}_0 > 0$. Then κ and $\bar{\kappa}$ can crossover on a scale which is of the order of the persistence length. It is at this scale at which the aforementioned effects of the Gaussian curvature energy will take over and play an important role for the microstructure of microemulsions.[13]

Let us end our letter with some speculation concerning a possibly more dramatic effect of the Gaussian term. From light scattering data it appears that the curvature energy in microemulsions is much smaller than one might estimate for a single amphiphilic layer using liquid crystal elastic constants. Some fluctuation effects may be active, leading to a collapse of curvature stiffness. The perturbative renormalization of κ cannot be carried into this regime. The interplay of κ and $\bar{\kappa}$ terms, on the other hand, may explain this collapse. If κ and $\bar{\kappa}$ are of the same order of magnitude (either on Widom's lattice scale or at some larger scale with a κ softened by perturbative effects), topological fluctuations may become abundant. As a topological fluctuation costs some units of κ, it has to be such that a similar amount of energy is saved by the corresponding change in the Gaussian term. For $\bar{\kappa} > 0$ this may be achieved by drilling holes into bilayer sheets as visualized in Fig. 8(a). Such configurations have been seen in lecithin layers.[10] For $\bar{\kappa} \approx -\kappa$, a similar balance may take place if small spherical surfaces are emitted from a larger surface, as in Fig. 8(b).

[1]B. Widom, J. Phys. Chem. **88**, 6508 (1984).

[2]B. Widom, J. Chem. Phys. **84**, 6943 (1986).

[3]P. G. de Gennes and C. Taupin, J. Chem. Phys. **86**, 2294 (1982); S. A. Safran, D. Roux, M. E. Cates, and D. Andelman (Exxon preprint, 1986).

[4]W. Helfrich, Z. Naturforsch. Teil B **103**, 67 (1975).

[5]W. Helfrich, J. Phys. (Paris) **46**, 1262 (1985); **47**, 321 (1985); L. Peliti and S. Leibler, Phys. Rev. Lett. **54**, 1690 (1985); D. Förster (unpublished); H. Kleinert, Phys. Lett. A **114**, 263 (1986), **116**, 59 (1986);

[6]W. Janke and H. Kleinert, Phys. Lett. A117, 353 (1986); Phys. Rev. Lett. **58**, 144 (1986).

[7]W. Helfrich, *Amphiphilic Mesophases Made of Defects, Les Houches, Session XXXV, 1980*, edited by R. Balian, M. Kléman, and J.-P. Poirier (North-Holland, Amsterdam, 1981), and references therein; S. A. Safran, L. A. Turkevich, and P. Pinkus, J. Phys. Lett. **45**, L69 (1984).

[8]See, for example, J.-M. Drouffe and J.-B. Zuber, Phys. Rep. **102**, 1 (1983).

[9]L. E. Scriven, Nature **123**, 263 (1976); F. Lichterfeld, T. Schmeling, and R. Strey, J. Phys. Chem. (submitted).

[10]W. Harbich, R. M. Servuss, and W. Helfrich, Z. Naturforsch. Teil A **33**, 1013 (1978).

[11]Notice that plaquettes, links, and sites on the surface are located on the lattice dual to that of Widom, because the amphiphile sheets are defined on the plaquettes dual to the *AB* links of Widom.

[12]Of course, the full energies of Figs. 5(a) and 5(b) will also have different contact energies which will, however, not be considered here.

[13]This is, of course, only true if other energies such as, for example, electrostatic interactions do not drown these effects.