Statistical morphology of random interfaces in microemulsions

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We introduce a phenomenological lattice model of interacting surfaces to relate the phase behavior of microemulsions with the random geometry and topology of microstructures formed by the self-assembling surfactants. The model rests upon an effective Hamiltonian whose morphological character is manifest. In contrast to earlier membrane models, we focus attention on energy parameters favoring multiply connected microstructures. By employing mean-field and related approximations supported by Monte Carlo simulations, we study phase diagrams, liquid structure factors, and macroscopic surface tensions to demonstrate that the model reflects prominent features of microemulsions. © 1995 American Institute of Physics.

I. INTRODUCTION

Amphiphilic surfactants added to oil and water tend to assemble spontaneously at the interface of the immiscible solvents and are capable to form polymorphic aggregates by separating oil-rich from water-rich domains. Apparently, the complex phase diagrams observed in these mixtures originate from the variety of sizes, shapes, and topologies displayed by the interfacial patterns. Globular and bicontinuous microemulsions are particular examples among the structured liquid phases occurring at low surfactant concentration.1

The attempt to work out the phase diagram of such mixtures by starting at the microscopic level with realistic molecular forces and covering the full range of compositions is still a problem for the future. However, considerable progress has already been made with idealized models constructed to explain salient features in the phase behavior of microemulsions.2–5

In this paper we pursue a similar purpose by tying the thermodynamics of such composite media with the statistical morphology of their supramolecular structures. In order to simplify the statistics we adopt a lattice model of random interfaces whose Hamiltonian is taken to be a linear combination of the geometric invariants volume, area, integral mean curvature, and Euler characteristic. These invariants constitute the distinguished family of Minkowski functionals, and provide a complete class of additive morphological measures for characterizing size, shape and connectivity of spatial patterns. Thus, the statistical averages of these functionals qualify as extensive thermodynamic variables which may be interpreted as morphological order parameters.6

Our model is specified in detail in Sec. II. Its ground states are discussed in Sec. III. In Sec. IV we proceed with a mean-field approximation to obtain the phase diagram which shows typical three-phase coexistence originating from a tricritical point, and an ordered bicontinuous phase resembling a “plumber’s nightmare”3 structure. The reliability of the mean-field approximation is tested by Monte Carlo simulations, presented in Sec. V. Furthermore, we calculated the liquid structure factors within an Ornstein–Zernike approach and also studied the behavior of the surface tension near the critical endpoints of the three-phase regime. The results are shown in Secs. VI and VII, respectively. In Sec. VIII we draw our conclusions. Since we employ some tools borrowed from integral geometry, which may not be so familiar, we collect these prerequisites in the Appendix.

II. MODEL HAMILTONIAN

Let us consider a three-dimensional Bravais lattice with periodic boundary conditions, having N sites and volume V, whose Wigner–Seitz (WS) cells contain either bulk water or oil. The amphiphiles are supposed to form an incompressible liquid monolayer adsorbed at the interface between oil and water. The monolayer is partitioned equally between oil and water. Thus, the covered interface represents a Gibbs dividing surface which may consist of several disjoint closed components. After choosing an orientation for the interface, a collection of water cells fixes uniquely an interfacial pattern, and vice versa. To specify configurations, we introduce occupation numbers \( t_i \), with \( t_i = 1 \) if the \( i \)th WS cell contains water, and \( t_i = 0 \) if it contains oil. We also denote water cells to be “occupied” and oil cells to be “empty.”

Geometrically, the collection of configurations represents a class \( \mathcal{S}_N \) of \( 2^N \) subsets of the three-dimensional ambient space. Each subset \( P(\mathcal{S}) \in \mathcal{S}_N \) is the union of occupied, closed and convex WS polyhedra, which may have common faces, edges or vertices. As pointed out in the Appendix, the geometrical and topological properties of these subsets may be characterized by the family of Minkowski functionals \( \{ W_\alpha(\mathcal{S}) \} \). Moreover, there is a theorem which asserts that any real-valued, additive, motion-invariant, and continuous functional on the class \( \mathcal{S}_N \) is a linear combination of the Minkowski functionals.7,8

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$\mathcal{H}(t,\{\epsilon_n\}) = \sum_{a=0}^{3} \epsilon_a W_a(t)$

$= \epsilon_0 \mathcal{H}(t) + \frac{1}{3} \epsilon_1 \mathcal{H}(t) + \frac{1}{3} \epsilon_2 \mathcal{H}(t) + \frac{4\pi}{3} \epsilon_3 X(t).$

Here $\mathcal{H}(t)$ denotes the total volume covered by the pattern $P(t)$, with the area $\mathcal{A}(t)$ and integral mean curvature $\mathcal{M}(t)$ of the interface $\partial P(t)$; finally, $X(t)$ denotes the combinatorial Euler characteristic of $P(t)$. We have $X=(\text{number of disconnected components})+(\text{number of tunnels})+(\text{number of cavities})$. For instance, $X=1$ for a cube, $X=0$ for a cube pierced by a tunnel (torus) and $X=2$ for a hollow cube. Multiply connected structures like those seen in freeze-fracture images of microemulsions yield $X<0$.

The Euler characteristic $X(P)$ is related with $X(\partial P)$ by $X(\partial P) = X(P)[1 - (1 - \dim P)]$. In the case of a smooth surface, $X(\partial P)$ is determined by the integral Gaussian curvature (see the Appendix) and is also related with the topological genus $g$ (number of handles) of $\partial P$ by $X(\partial P) = 2(1 - g)$. Although the local Gaussian curvature is singular at the vertices of a WS polyhedron, the Euler characteristic remains well defined and its double role both as an elastic energy term in the Hamiltonian and as a topological order parameter carries over to lattice patterns.

The criteria underlying the choice of the Hamiltonian (2.1) are natural; in particular, the requirement of additivity leads to extensive thermal averages $\langle W_a \rangle \propto V$ for our lattice model, and this secures a close linking of morphology with thermodynamics.

The bending energy of a membrane, arising from splay deformations and usually described by a mean curvature-squared term, is missing in the Hamiltonian (2.1), formally because this term is not additive; we postpone a discussion of this issue to the concluding Section. However, a short-ranged entropic repulsion between parts of the interface may be accommodated by taking a bcc lattice, whose geometry restricts the interface configurations automatically to self-avoiding ones.

We shall work with a grand ensemble of random interfaces. Consequently, the partition function is given by

$$\Xi_N(T,\mu,\{\epsilon_n\}) = \sum_t z(t) \exp[-\beta \mathcal{H}(t,\{\epsilon_n\})].$$

where $z(t) = \exp(\beta \mu \Sigma t_i)$ denotes the fugacity, and the sum runs over the $2^{N^3}$ configurations of occupied lattice cells.

The terms $\epsilon_a W_a(t)$ must have the dimension of energy; hence, the couplings $\epsilon_a$ vary with lattice distance $l$, say, according to $\epsilon_a \propto l^{\alpha-3}$. Later, when we examine the model phase diagram, we shall focus on parameters $\epsilon_1>0$, $\epsilon_2>0$. The area coefficient $\epsilon_0$ is taken to be positive to account for a short-range repulsion between the amphiphiles forming an incompressible film at the oil-water interface; furthermore, we are interested in phases with multiply connected microstructures, having $X(t)<0$, and these are favored by positive values of $\epsilon_1$. Consequently, the ratio $\epsilon_0/\epsilon_1^{1/2}$ provides the basic structural length scale of our model.

Of the four model parameters, $\epsilon_a$, three are experimentally controllable. The coefficients $\epsilon_0$ and $\epsilon_1$ can be adjusted by varying the chemical potentials of oil, water, and surfactants; the mean curvature coefficient $\epsilon_2$ is changed, for example, by varying the salinity of water in the case of ionic amphiphiles. Unfortunately, there appears to be no direct way to control the "topological potential" $\epsilon_3$.

We now transform the Hamiltonian (2.1) into a more explicit expression in terms of occupation numbers for a body-centered-cubic (bcc) lattice. The Wigner–Seitz (WS) cell is shown in Fig. 1. The edge length of the polyhedron $l=a\sqrt{2}/4$. The closed WS cell is the union of open $n$-dimensional lattice cells, $0\leq n<3$. There are five kinds of such $n$ cells: the set of interior points of the polyhedron ($n=3$), of the hexagonal $[n=2(h)]$ and square $[n=2(s)]$ faces, of the edges ($n=1$), and the set of vertices ($n=0$), the latter being open as well as closed. Thus, a pattern may also be considered as a collection of the open $n$ cells belonging to the occupied closed WS polyhedra (see the Appendix). The values $W_a(n)$ taken by the Minkowski functionals on an open $n$ cell are related with their values $W_a(n)$ on closed $n$ cells by Eq. (A20) with $d=3$ which yields

$$\tilde{W}_a(n) = (-1)^{n+a+1} W_a(n).$$

By using additivity and the fact that open $n$ cells on the lattice do not overlap, we find the values of the Minkowski functionals on the whole pattern $P=P(t)$ to be

$$W_a[P] = \sum_n \tilde{W}_a(n) N_a[P], \quad a=0, \ldots, 3,$$

where $N_a[P]$ denotes the number of $n$ cells present in $P(t)$. A face between two neighboring WS cells is present in a given configuration if at least one of the two WS cells is occupied. Likewise, an edge, where at most three WS cells can meet, is present if at least one of these cells is occupied; a vertex, where up to four WS cells can meet, is present if at least one of them is occupied. Therefore, we have

$$N_3(u) = \sum_i t_i = N - \sum_i u_i,$$

$$N_{2(h)}(u) = 4N - \sum_i' u_i u_j,$$

$$N_{2(s)}(u) = 3N - \sum_i'' u_i u_j,$$

$$N_1(u) = 12N - \sum_i''' u_i u_j u_k,$$

and

$$N_0(u) = 6N - \sum_i''''' u_i u_j u_k u_l.$$

Here we introduced the variables $u_i = 1 - t_i$ to obtain concise expressions for $N_a[P] = N_a(u)$, with $u = \{u_1, \ldots, u_N\}$. The primed and double primed sums are carried over all nearest-neighbor and all next-nearest-neighbor bonds, respectively.
The triple-primed sum runs over isosceles triangles, two of the vertices of these triangles being nearest neighbors, and the third a second neighbor to the previous two. Such are, e.g., the triangles $ABC$, $BCD$, $ABD$, and $ACD$ in Fig. 1. Finally, the four primed sum is carried over all tetrahedra of the bcc lattice whose faces are isosceles triangles as above; an example is the $ABCD$ tetrahedron shown in Fig. 1. The values of the Minkowski functionals $W_{\alpha}(n)$ are obtained by applying Steiner’s formula and are summarized in Table I. Combining these results, we find

$$W_0(u) = 8\sqrt{2}l^3 \sum_i (1 - u_i), \quad (2.10)$$

We note that in the case $h_2 = h_3 = 0$ the Hamiltonian (2.16) reduces to that of a conventional lattice-gas model with an additional next-nearest-neighbor coupling.

### Table I. The Minkowski functionals $W_\alpha(n)$, $\alpha = 0, 1, 2, 3$ for closed $n$ cells. The edge length of the WS polyhedron is denoted by $l$.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$W_0/l^3$</th>
<th>$W_1/l^2$</th>
<th>$W_2/l$</th>
<th>$W_3$</th>
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<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>$\sqrt{3}$</td>
<td>2/3</td>
<td>$4\sqrt{3}+2$</td>
</tr>
<tr>
<td>2 (h)</td>
<td>$\pi/3$</td>
<td>$\pi$</td>
<td>$2\pi/3$</td>
<td>$2\pi$</td>
</tr>
<tr>
<td>2 (s)</td>
<td>$4\pi/3$</td>
<td>$4\pi/3$</td>
<td>$4\pi/3$</td>
<td>$4\pi/3$</td>
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<tr>
<td>3</td>
<td>$4\pi/3$</td>
<td>$4\pi/3$</td>
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</tr>
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III. GROUND STATES

The ground states of the Hamiltonian (2.16) are found by a standard and straightforward procedure. The tetrahedron $ABCD$ shown in Fig. 1 is space filling upon successive reflections about its faces, and also contains each type of interaction entering the Hamiltonian. Therefore, it suffices to calculate the energies of the $2^4$ possible configurations of the four WS cells marked by the corners of a tetrahedron and to compare these in order to find the lowest ones in terms of the parameters $\{h_\alpha|\alpha=0,...,3\}$. As pointed out before, we are interested in parameters $h_3 > 0$, which encourages structures with negative Euler characteristic. In Fig. 2 we show the unit
cells of the five ground states I–V in this case. Solid and open dots represent WS cells filled with water and oil, respectively. The complete lattice configurations are generated by repeated reflections about planes parallel to the faces of a cube through the next-nearest-neighbor of the central site. The energies per site for the five phases read as

\[ E_1 = h_0, \quad E_2 = 0, \]
\[ E_4 = \frac{1}{2} (3h_0 + h_1 - h_2 + h_3), \]
\[ E_3 = \frac{1}{2} h_0 + \left( \frac{3}{2(3)^{1/2}+1} \right) h_1 - h_3, \]
\[ E_5 = \frac{1}{2} (h_0 + h_1 + h_2 + h_3). \]

The borderlines of stability in Fig. 2 are drawn for the special case \( h_0 = 0 \). The reflection symmetry of the stability regions about the horizontal axis arises from the antisymmetry of the mean curvature term in the Hamiltonian.

**IV. MEAN-FIELD APPROXIMATION**

In this section we examine the model phase diagram at finite temperatures \( T > 0 \) within a mean-field approximation (MFA) based on a single-site trial Hamiltonian

\[ \mathcal{H}_0 = \sum_i \lambda_i t_i, \]

with variational parameters \( \{ \lambda_i \} \). In this approach, where the lattice sites are occupied independently, the correlation functions, computed with the Boltzmann weight \( \exp(-\beta \mathcal{H}_0) \), factorize to

\[ \langle t_1 t_2 \ldots t_i \rangle_0 = \phi_1 \phi_2 \ldots \phi_i, \]

where \( \phi_i = \langle t_i \rangle_0 = 1 - \langle u_i \rangle_0 \). The variational procedure yields an approximate potential \( \tilde{\Omega} \) determined from

\[ \tilde{\Omega} = \min_{\Phi} \left( \mathcal{F}(\Phi) - \mu \sum_i \phi_i \right), \]

which provides an upper bound for the exact grand potential, \( \Omega \leq \tilde{\Omega} \). In Eq. (4.3) we have set \( \Phi = \{ \phi_1, \ldots, \phi_N \} \) and introduced the free energy functional

\[ \mathcal{F} = \mathcal{H}(\Phi) - TS_0(\Phi), \]

where \( \mathcal{H}(\Phi) = \langle \mathcal{H} \rangle_0 \) and \( S_0(\Phi) \) denotes the entropy of an ideal mixture.

We set \( h_3 = 1 \) so that energies are measured in units of \( h_3 \) and we absorb the parameter \( h_0 \) in the chemical potential in Eq. (2.2), i.e., we put \( h_0 = 0 \). With these simplifications we have \( \Omega = \Omega(T, \mu, h_1, h_2) \) with only the area and mean-couvature couplings \( h_1 \) and \( h_2 \) left as model parameters. Since we expect the phases appearing for \( T > 0 (k_B = 1) \) to inherit structural features from the ground states, we solve Eq. (4.3) with the ansatz

\[ \phi_i = \begin{cases} \phi_A & \text{if } i \in \Lambda_A, \\ \phi_B & \text{if } i \in \Lambda_B, \end{cases} \]

where \( \Lambda_A \) and \( \Lambda_B \) denote the two sc sublattices of the bcc lattice having \( N_A = N_B = N/2 \) lattice sites. It turns out to be more convenient to work with the total fraction of occupied sites \( \phi \), and the sublattice order parameter \( \psi \) given by

\[ \phi = \frac{1}{2} (\phi_A + \phi_B), \]

and

\[ \psi = \phi_A - \phi_B. \]

The computation of the mean-field values of the functionals \( \langle V_{\alpha} \rangle_0 \) entering in \( \mathcal{H}(\Phi) \) is a straightforward counting exercise. For \( v_{\alpha}(\phi, \psi) = \langle V_{\alpha} \rangle_0 / N \) we find

\[ v_0 = \phi, \]
\[ v_1 = \phi (1 - \phi) + \frac{x}{2} \psi^2, \]
\[ v_2 = \phi (1 - \phi) (1 - 2 \phi) + \frac{1}{2} \psi^2 - \frac{1}{2} \psi^2 \phi, \]
\[ v_3 = \phi (1 - \phi) (1 - 6 \phi + 6 \phi^2) - \psi^2 [3 \phi (1 - \phi) - \frac{1}{2}] - \frac{1}{2} \psi^4. \]

The mixing entropy per site, \( s(\phi, \psi) = S_0(\phi, \psi) / N \) reads as

\[ s(\phi, \psi) = - \frac{1}{2} \left[ \phi + \psi \right] \ln \left( \phi + \psi \right) + \left( 1 - \phi - \frac{1}{2} \right) \]
\[ \times \left[ \ln \left( 1 - \phi - \frac{1}{2} \right) + \left( \phi - \frac{1}{2} \right) \ln \left( \phi - \frac{1}{2} \right) \right] + \left( 1 - \phi + \frac{1}{2} \right) \ln \left( 1 - \phi + \frac{1}{2} \right). \]

In the preceding sections we focused attention on the ensemble of oil-water interfaces and their degrees of freedom; the surfactants dropped out of sight. However, now they will be returned. As mentioned at the beginning, we
assume an interface to be saturated with amphiphiles, the latter forming an incompressible liquid film with thickness \( \delta \). In a given configuration of occupied cells, having area \( \mathcal{A} \), the total volume occupied by the film is approximated to first order in \( \delta \) by the expression

\[ \mathcal{F}_f = \mathcal{A} \delta. \]  

(4.13)

Thus, we obtain the mean volume fraction of surfactants to be

\[ \phi_f = \frac{\langle \mathcal{F}_f \rangle}{V} = \frac{\delta \langle \mathcal{A} \rangle}{V} = \frac{3[4(3)^{1/2}+2]}{8(2)^{1/2} l^2} \]  

(4.14)

with \( l = l_0 \delta \) and \( V = 8\sqrt{2}Nl^3 \), \( l_0 \) being the edge length of the bcc WS cell. The definitions of the Gibbs dividing surface (see Sec. II) and of \( \phi_s \) imply that \( \phi_w = \phi - \phi_s/2 \) and \( \phi_s = 1 - \phi - \phi_f/2 \) for the volume fractions of bulk water and oil. The inequalities \( \phi_s \leq 2\phi \), \( \phi_s \leq 2(1 - \phi) \), \( 0 \leq \phi_s \leq 1 \), and \( 0 \leq \phi_f \leq 1 \), yield a triangle of allowed values in the \( (\phi_f, \phi_s) \) plane.

The volume fraction \( \phi_f \) enters in the mean-field Hamiltonian \( \mathcal{H}(\Phi) = \mathcal{H}(\phi_1, \phi_2) \) only implicitly via the dependence of \( h_1 \) and \( h_2 \) on the cell size \( l \), see Eq. (2.14). To make this scale dependence of the Hamiltonian explicit, we write

\[ h_1 = [4(3)^{1/2}+2] c_1 \delta^2 \hat{l}^2 = \gamma \hat{l}^2 \]  

(4.15)

and

\[ h_2 = 2 \pi \epsilon_2 \delta \hat{l} = \xi \hat{l}. \]  

(4.16)

Then the free energy functional \( \mathcal{F}/N = f \) reads as

\[ f = \gamma \hat{l}^2 v_1 + \xi \hat{l} v_2 + v_3 - T S_0, \]  

(4.17)

with \( v_a = v_a(\phi, \psi) \) and \( S_0 = s_0(\phi, \psi) \) given by Eqs. (4.9)–(4.11) and (4.12) \((h_0=0, h_1=1 = k_B)\). According to Eq. (4.4), the task is now to evaluate

\[ \frac{\Omega}{N} = \min_{\phi, \psi} \left\{ f(\phi, \psi) - \mu \phi \right\}. \]  

(4.18)

We first consider an oil-water balanced mixture with vanishing spontaneous curvature, \( \epsilon_2 = 0 \). The coefficient \( \epsilon_1 \delta^3 \) in \( h_1 \) of Eq. (4.15) will be considered to be a fixed molecular surface energy. We search for the global minima of \( f(\phi, \psi) - \mu \phi \) on the \( (\phi, \psi) \) plane, in terms of \( T \), \( \mu \), and \( \hat{l} \). For each triple of these parameters, the numerical minimization yields a family of pairs \( (\phi^{(a)}, \psi^{(a)}) \), \( a = 1, \ldots, n \), if there are \( n \) coexisting stable phases. The corresponding values \( \phi^{(a)} \) are then obtained from Eq. (4.14). Accordingly, the cell size relates the surfactant volume fraction \( \phi_f \) with \( (\phi, \psi) \) and is not treated as an independent variational parameter.

To narrow down the choices of \( T \), \( \mu \), and \( h_1 \), we started by looking for disordered phases with \( \phi = 0 \). This case can be examined analytically and we found a tricritical point \( T_{\phi=0} = 9/2, \mu_{\phi=0} = 0 \ (\phi^{(a)} = 1/2), h_{1,\phi=0} = 11 \). In the numerical minimization for \( \phi \neq 0 \), we focus on temperatures below the tricritical point and on low values for the volume fraction of surfactants such that the nearest-neighbor distance exceeds the thickness of the film (i.e., \( \hat{l} \approx 0.6 \)). To ensure the latter obvious requirement, we choose \( \epsilon_1 \delta^3 = 3 \times 10^{-3} \).

In Fig. 3 we report phase diagrams for temperatures \( T = 1.5, 1.0, \) and \( 0.8 \). The prominent feature at \( T = 1.5 \) [Fig. 3(a)] is the coexistence of three disordered phases (\( \phi = 0 \)). The middle phase \( (m) \) has negative Euler characteristic \( (\chi) \), and vanishing mean curvature \( (M) \), indicating a bicontinuous structure; the oil-rich \( (w/o) \) phase (on the left) and the water-rich \( (o/w) \) phase both have \( \chi > 0 \), but \( M(w/o) > 0 \) whereas \( M(o/w) < 0 \), implying a micellar structure of the minority phase in both cases. The Euler characteristic is indeed negative for the range \( 0.22 < \phi < 0.78 \), as can be inferred from Eq. (4.11) with \( \phi = 0 \). The two-phase regions of \( (m) \) \( (w/o) \) and \( (m) \ (o/w) \) terminate at critical points, indicated by dots. By increasing the temperature, the three-phase triangle shrinks and the values of the Euler characteristic of the \( (w/o) \) and \( (o/w) \) phases become negative. This purely morphological transition may be viewed as a percolation of globules containing the minority phase and appears to have no thermodynamic significance.

At \( T = 1.0 \) [Fig. 3(b)] the three-phase coexistence persists. However, an additional ordered phase occurs, occupying a narrow strip around \( \phi = \frac{1}{2} \). This phase \( (pn) \) originates from the “antiferromagnetic” ground state (see Fig. 2) and has a sublattice order parameter \( \psi(pn) \neq 0 \). Furthermore, its Euler characteristic is negative and the total mean curvature per site of the interface between the two sublattices remains small throughout its domain of stability. Thus, the interface resembles features of a periodic minimal surface and the whole structure of interwoven coherent oil and water tubes looks like a “plumber’s nightmare”.

Upon lowering the temperature down to \( T = 0.8 \) [Fig. 3(c)] two more three-phase coexistence regions appear and the random isotropic middle phase becomes enclosed in the narrow white triangle near the center of the diagram. In view of its morphological signatures, the middle phase looks like a bicontinuous microemulsion and may be viewed as a molten plumber’s nightmare phase. This interpretation is further supported by the form of its structure factor discussed in Sec. VI.

Let us finally take into account a spontaneous mean curvature. The effect of \( \epsilon_2 > 0 \) on the three-phase triangle is illustrated in Fig. 3(d). When the coupling \( \epsilon_2 \) increases further, the tielines \( (ab) \) and \( (ac) \) approach each other until the phases \( (b) \) and \( (c) \) merge with the squeezed-in critical phase to form a critical endpoint.

Experimentally, the spontaneous curvature in oil-brine mixtures with ionic surfactants can be changed at fixed temperature (as done here) by salting the brine. The variation with the salinity of the three-phase triangle is sometimes described by taking cuts along \( \phi = \frac{1}{2} \) on the \( (\phi, \psi) \) diagram \( \chi \) and plotting the \( \phi_3 \) values for the points \( F, G, \) and \( H \) shown in Fig. 3(d). Our example of the ensuing “fish” is displayed in Fig. 4.

V. MONTE CARLO SIMULATIONS

In this section we present results obtained from Monte Carlo simulations made, in particular, to check the mean-field prediction of a three-phase coexistence. A simulation
yields a histogram of the frequency distribution \( \mathcal{H}(Q; T, \{h_n\}) \) of the coverage \( Q = \sum_i i \). From \( -\ln \mathcal{H} \) we obtain the canonical free energy and thus the \((\phi, T)\) phase diagram of the model.

In order to accurately sample the statistics for the whole range of values for \( Q, (0 \leq Q \leq N) \), we adopt a method of sampling known as “window sampling.”\(^{14,15}\) The whole range of the coverage \( Q \) is divided into \( M \) “windows” of width \( w \) each, i.e., \( N = Mw \). We perform \( M \) independent simulations, one for every window. Any attempted move is automatically rejected if it takes the number of occupied sites of the configuration outside the given window. Otherwise, attempted moves are accepted or rejected according to the usual Boltzmann criterion.

We consider a system in a 10×10×10 box (1000 WS cells) which is a parallelepiped having the shape of the primitive unit cell of the bcc lattice. We use periodic boundary conditions in all directions. The range of coverage \( 0 \leq Q \leq 1000 \) is divided into 100 windows, each covering 10 successive values of \( Q \). We choose to “flip” the \( \ell_i \)’s sequentially rather than randomly, and define a “Monte Carlo pass” as the number of Monte Carlo moves needed so that an attempt has been made to flip every particle in the system once, i.e., one thousand attempted Monte Carlo moves in our...
We initially perform 20 000 passes per window for equilibration and, subsequently, an additional 400 000 passes per window during which measurements are being taken. We make a measurement every 20 passes, for a total of 20 000 per window, or two million for the whole range of coverage. We also keep track of the values of the functionals $V_a$ for every configuration. This allows us to calculate the averages of these functionals as functions of coverage and temperature, and compare those with the MFA averages; the latter are independent of temperature and of the values of the energy parameters in the Hamiltonian.

The simulations were performed for the choice of energy parameters $h_1=0$, $h_2=2.8$, $h_3=0$, and $h_3=1$. This choice was made to suppress the ordered plumber’s nightmare phase. The $(\phi,T)$ phase diagram is depicted in Fig. 5. The critical temperature is overestimated by MFA, as expected. However, the simulations confirm the existence of a triple point, where the MFA differs mostly from the simulations for $\phi<0.2$ and $\phi>0.8$, and that the MFA understimates the connectivity of the pattern, since the region of negative values of the Euler characteristic is wider in the simulation result.

VI. STRUCTURE FACTORS

While the $(\rho n)$ phase arising in our model is well characterized by its periodic long-range order, the interpretation of the distinct features exhibited by the disordered phases has been based only on their global morphology. More detailed information on the nature of the middle phase, in particular, is provided by correlation functions such as $\Gamma_{ij}$. The computation of the direct correlation function is straightforward (although a bit tedious) and so we present only the final result:

$$\phi(1-\phi)K(q) = \beta \left[ (3)^{1/2} h_1 \right] u_1(\phi) + h_2 v_2(\phi)$$

$$+ 2 h_3 v_3(\phi) \left[ \frac{2 h_1}{3 [2 (3)^{1/2} + 1]} \right] S_1(q) + \left[ \frac{2 h_1}{3 [2 (3)^{1/2} + 1]} \right] S_2(q).$$

where $K(q) = \sum_k K_{ik} e^{i q \cdot R_k}$, $\Gamma(q) = \sum_j \Gamma_{kj} e^{i q \cdot R_j}$.

Fig. 6. The Euler characteristic per site vs coverage, with the same model parameters as in Fig. 5. Upper curve, MFA result; lower curve, simulation result for $T=0.82$. The arrows mark the temperature-independent MF values of the zeros.

FIG. 5. The $(\phi,T)$ phase diagram of the model with parameters $h_0=0$, $h_1=2.8$, $h_2=0$, and $h_3=1$. Solid lines, MFA result; (+), simulation results. The diamonds mark the zeros of the temperature-dependent Euler characteristic from simulations. The arrows mark the temperature-independent MF values of the zeros.
The $v_s$'s are obtained from Eqs. (4.9)–(4.11) for $\psi=0$. The expressions $S_1(\mathbf{q})$ and $S_2(\mathbf{q})$ are given by

$$S_1(\mathbf{q}) = \cos \left( \frac{1}{2} \left( q_x + q_y + q_z \right) \right) + \cos \left( \frac{1}{2} \left( q_x - q_y + q_z \right) \right) + \cos \left( \frac{1}{2} \left( -q_x + q_y + q_z \right) \right),$$

$$S_2(\mathbf{q}) = \cos (aq_x) + \cos (aq_y) + \cos (aq_z),$$

with $\mathbf{q} = (q_x, q_y, q_z)$.

To reduce the effects arising from the lattice anisotropy we proceed with the rotationally averaged structured factor

$$\bar{\Gamma}(q) = \frac{1}{4\pi} \int d\mathbf{n} \bar{\Gamma}(q\mathbf{n}).$$

Figure 7(a) shows the points $C, D, E,$ and $F$ in the $(\phi, \psi)$ plane (corresponding to the values $l=8, 6, 5,$ and 3) where we have evaluated structure factors, again taking $\epsilon_1 \delta^2 = 3 \times 10^{-3}$ and $\xi = 0$ (no spontaneous internal curvature). In Fig. 7(b) we show the structure factors for these points.

The general features of these graphs are like those obtained earlier from a lattice model based on the bending energy.\textsuperscript{4,16} We also regard the peaks near $qa=7$ to be a lattice artefact. Both the position $q_{\text{max}}$ of the first peak and the value $\bar{\Gamma}(q_{\text{max}})\bar{\Gamma}(0)$ increase with the surfactant volume fraction $\phi_s$. The change in $q_{\text{max}}$ is seen more clearly if we recall that the lattice constant $a$ depends on $\phi_s$. If we take the half wavelength $\lambda/2 = \pi q_{\text{max}}$ as a measure for the typical size of spatial domains causing a peak in the structure factor, we find that $\lambda/2 \approx a(\phi_s) = 2\sqrt{2l(\phi_s)} \delta$, yielding $\lambda/2 \approx 23\delta$ at point $C$ [see Fig. 7(a)] and $\lambda/2 \approx 9\delta$ at point $F$.

The peaks at nonzero $q$ values below $qa=\pi$ only appear in the $(\phi, \psi)$ region enclosed by the dotted line in Fig. 7(a). Consequently, such a peak is absent for the middle phase on the three-phase triangle. The form of this “Lifshitz line” is found by expanding $K(\mathbf{q}) = K_0 + K_1 q^2 + K_2(n)q^4 + \cdots$ and setting $K_1(\phi_s, \psi_s) = 0$, the coefficient $K_1$ being a scalar because of cubic symmetry. The explicit expression is given in Eq. (7.2) where $a^2 \beta m = K_1$. The inset in Fig. 7(b) shows the structure factors obtained by using the aforementioned low-$q$ expansion up to $O(q^4)$ in $\bar{\Gamma}(q)$ before taking the rotational average. This procedure removes spurious lattice effects but also shifts the peak position to smaller $q$ values.

**VII. SURFACE TENSIONS**

A prominent feature of the middle phase on the three-phase triangle is its very low surface tension with each of the two coexisting phases.\textsuperscript{17,18} In order to see whether this spectacular reduction (which persists to temperatures well below the tricritical point) is reflected in our model, we examine the surface tensions between the phases $(ac)$ and $(cb)$ [see Fig. 3(d)] as functions of the curvature coupling $\epsilon_c$.

We assume that the coverage $\Phi$ varies slowly on the lattice scale as the interface between two of the three coexisting phases (at fixed, common values of $T, \mu, \hat{I}$) is crossed. Hence, the field $\Phi$ can be interpolated by a smooth field $\phi(\mathbf{r})$ such that $\phi_s = \phi(\mathbf{r} = \mathbf{R}_s)$. By invoking a van der Waals type approximation,\textsuperscript{19} we calculate the local coverage $\phi(\mathbf{r})$ from the variational equation (4.3) combined with a gradient expansion of the MF Hamiltonian $\bar{\mathcal{H}}(\Phi)$. In this procedure the term $\bar{\mathcal{H}}(\Phi) - \mu \Sigma \phi_i$ in Eq. (4.3) is replaced by the functional

$$\tilde{\mathcal{H}}[\phi] = \frac{1}{v_c} \int d^3r \left[ g(\phi(\mathbf{r})) + \frac{a^2}{2} m(\phi(\mathbf{r})) (\nabla \phi)^2 \right],$$

where $g(\phi) = f(\phi) - \mu \phi - \tilde{\mathcal{H}}/N$; the MF potential $\tilde{\mathcal{H}}/N$ of the coexisting phases has been subtracted for convenience. The function $f(\phi)$ can be read off from Eq. (4.17) after setting $\psi=0$; $v_c = a^3/2$ denotes the WS cell volume. Finally,

$$m(\phi) = \frac{9(3)^{1/2} + 2}{3[(43)^{1/2} + 2]} h_1 + \frac{11}{6} h_2 (1 - 2\phi) + 2h_3 (2 - 11\phi + 11\phi^2).$$
The equilibrium profile $\tilde{\phi}(r)$ is found by minimizing $\tilde{\Omega}[\phi]$ while the cell size $\tilde{t}$ is kept fixed.

For a planar interface perpendicular to the $z$ direction we must solve

$$\frac{1}{2} m(\phi) \frac{d \phi}{dz}^2 = g(\phi)$$

(7.3)

for $\tilde{\phi}(z)$ with the bulk phase values for $\tilde{\phi}(\pm \infty)$. The surface tension $\sigma$ is defined by

$$\sigma = \frac{1}{F} \tilde{\Omega}[\tilde{\phi}],$$

(7.4)

where $F$ is the area of the planar interface. In the case of the $(ac)$ interface, for instance, we find

$$\sigma_{ac} \delta^2 = \frac{(2)^{1/2}}{4l^2} \int_{\phi_0}^{\phi_1} d\phi \sqrt{m(\phi)g(\phi)},$$

(7.5)

where $\phi_{a,c}$ denote the corresponding bulk values. The dependence of $\sigma_{ac}$ on the curvature coupling $\varepsilon_2$ is implicit in $m$, $g$, $\phi_a$, $\phi_c$, and $\hat{l}$. We calculate the surface tensions at temperature $T=3.5$.

When we have three coexisting phases the calculation of the surface tensions $\sigma_{ac}$ and $\sigma_{ab}$ by means of Eq. (7.5) is unambiguous. Beyond the critical endpoint (CEP) where the three-phase triangle has collapsed into a tieline we select a pair of coexisting phases by fixing $\hat{l}$ to the value it has at the CEP. In this way we arrive at the curves depicted in Fig. 8. At the left CEP the surface tension $\sigma_{ac}$ vanishes, and the same is true for $\sigma_{ab}$ at the right CEP. Within the three-phase region between the CEP's the potential $g(\phi)$ has three degenerate minima and therefore we find that $\sigma_{ab} = \sigma_{ac} + \sigma_{cb}$, indicating complete wetting of the oil-rich and the water-rich phases by the middle phase.

In Fig. 9 we show the calculated profile $\tilde{\phi}(z)$ of the interface between the water-rich phase and the oil-water balanced middle phase. $\varepsilon_2 = 0$, calculated analytically by fitting the quantity $\sqrt{g(\phi)/m(\phi)}$ with a cubic polynomial. The profile is asymmetric, extending deeper into the middle phase, and has a width of about 30 lattice constants. The surface tension grows and the thickness decreases upon lowering the temperature.

VIII. SUMMARY AND CONCLUDING REMARKS

Our random surface model defined by the Hamiltonian (2.1), reproduces quite a few salient features observed in mixtures of oil, water, and surfactants, namely (i) a coexistence regime of oil-rich and water-rich phases with an isotropic bicontinuous middle phase, originating from a tricritical point; (ii) an ordered phase, known as "plumber's nightmare;" (iii) a peak in the liquid structure factor at a nonzero wave vector, and (iv) a drastic reduction of surface tensions in the three-phase coexistence regime, caused by incipient critical endpoints.

To arrive at these results, we have chosen the model parameters $\{h_{ij}\}$ in Eq. (2.16) such that the phases are stabilized by the balance between a positive surface tension $h_1 - k_BT$ of the incompressible surfactant film and a positive topological potential $h_3 \sim k_BT$, which prefers a large interface area to accommodate many handles (i.e., multiply connected oil and water domains) and thereby assists the entropic tendency to disperse the amphiphilic molecules. Our insistence on $h_3 > 0$ puts low statistical weights on configurations of surfactant aggregates having excessive surface area combined with small values of the Euler characteristic and thus destabilizes lamellar phases, for example.

The currently popular statistical models for an ensemble of surfactants films ("membrane models") employ the Helfrich Hamiltonian which is of the form of Eq. (2.1) but contains an additional bending energy contribution

$$\mathcal{H}_{bend} = \frac{k_0}{2} \int_S df(c_1^2 + c_2^2),$$

(8.1)

where $c_{1,2}$ are the principal curvatures of the surface film $S$ and $k_0$ is a (bare) bending rigidity. Here we shall add a few remarks to justify the omission of $\mathcal{H}_{bend}$ in the present ap-
proach with attention focused on model couplings which are complementary to the usually considered regime of parameters and where \( \mathcal{H}_{\text{bend}} \) describes the relevant energetics.

The theorem of Hadwiger\(^1\) guarantees that our Hamiltonian includes all additive geometric invariants, whose thermal averages are extensive. However, the thermodynamic requirement of extensive internal energy does not imply that the Hamiltonian must be manifestly additive. In the studies of microemulsion phases employing the Helfrich Hamiltonian\(^2,22\) the Euler characteristic is ignored\(^23\) and attention is focused on a scale \( \xi \) -dependent bending energy \( \mathcal{H}_{\text{bend}}(\xi) \) obtained by replacing \( k_B T \) with a renormalized rigidity \( k(\xi) \) to account for the reduction of the bare rigidity \( k_0 \) caused by short-wavelength thermal film undulations. The scale dependence of \( \mathcal{H}(\xi) \) is known explicitly only to leading order in \( k_B T/k_0 \ll 1 \), and reads\(^24,23\) as

\[
\mathcal{H}(\xi) = \kappa_1(\xi) = \kappa_0 - \frac{3}{4} k_B T \ln \left( \frac{\xi}{\delta} \right),
\]

where we used the film thickness to provide a microscopic cutoff. The length \( \xi_\delta \) at which \( \kappa(\xi) \) has dropped to values of the order \( k_0 T \) is estimated from \( k_1(\xi_\delta) = 0 \). The persistence length\(^26\) \( \xi_p \) defines the basic length scale in this approach. In the rigidity dominated regime, \( \xi < \xi_p \), an isolated film is likely to be locally flat: for \( \xi > \xi_p \), where \( \kappa(\xi) \) is negligible compared with \( k_B T \), thermal fluctuations dominate over the rigidity and the film is crumpled. Our morphological model incorporates the energetics of an ensemble of randomly folded, multiply connected, and self-avoiding films, and thus deals with lengths beyond \( \xi_p \), where \( \mathcal{H}_{\text{bend}}(\xi) \) may indeed be omitted.

In our calculations we had to assume that the scale dependence of the parameters \( \epsilon_n \), viewed as renormalized effective couplings, can be approximated by their “naive” scaling behavior, \( \epsilon_n(\xi) \sim \xi^{-n} \), since a nonperturbative renormalization theory as required for length scales exceeding the persistence length is still lacking.

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**APPENDIX**

Here we gather some useful concepts from integral geometry, to introduce the Minkowski functionals and describe their properties.\(^6,7,8,27\) To begin with, let us consider a closed, bounded, and convex subset (closed body) \( K \) in three-dimensional Euclidean space \( \mathbb{E}^3 \), with a regular boundary \( \partial K \). The set of all such bodies is denoted by \( \mathcal{K} \). If the principal radii of curvature of \( K \) are \( R_1 \) and \( R_2 \), then the surface area \( \mathcal{A} \) of the body is given by

\[
\mathcal{A} = \int_{\partial K} ds = \int_{S^2} R_1 R_2 \, d\Omega,
\]

where \( df \) is the area element on \( \partial K \) and \( d\sigma \) is the area element of the spherical image of \( K \) under the Gaussian map. A parallel body \( K_\rho \) consists of all points within a distance \( \rho \) from \( K \). Hence, the area \( \mathcal{A}_\rho \) of \( K_\rho \) is given by

\[
\mathcal{A}_\rho = \int_{S^2} (R_1 + \rho) (R_2 + \rho) \, d\Omega = \mathcal{A} + 2 \rho \mathcal{A} + \frac{\mathcal{A}}{2} \rho^2.
\]

The quantities \( \mathcal{A} \) and \( \mathcal{V} \) in Eq. (A2) denote the integral mean curvature of \( \partial K \),

\[
\mathcal{M} = \frac{1}{2} \int_{\partial K} \left( \frac{1}{R_1} + \frac{1}{R_2} - \frac{1}{R_3} \right) \, ds,
\]

and the integral Gaussian curvature of \( \partial K \),

\[
\mathcal{V} = \int_{\partial K} \frac{1}{R_1 R_2 R_3} \, ds.
\]

If \( \mathcal{V} \) denotes the volume of \( K \), and \( \mathcal{V}_\rho \) that of \( K_\rho \), then

\[
\mathcal{V}_\rho = \mathcal{V} + \int_0^\rho \mathcal{A}_\sigma \, d\rho = \mathcal{V} + \mathcal{A} + \mathcal{A} \rho + \mathcal{A} \rho^2 + \frac{4}{3} \rho^3,
\]

since \( \mathcal{V} = 4\pi R^3 \) for any convex body. Equation (A5) is a special case of Steiner’s formula, which states that the parallel volume of any convex body \( K \), embedded in \( \mathbb{E}^d \), can be expressed as

\[
\mathcal{V}_\rho(K) = \sum_{a=0}^d \left( \frac{d}{a} \right) \mathcal{W}_a(K) \rho^a,
\]

which defines the Minkowski functionals \( \mathcal{W}_a(K) \), \( a = 0, \ldots, d \) of \( K \subset \mathbb{E}^d \). A comparison between Eqs. (A5) and (A6) for \( d = 3 \) immediately yields

\[
\mathcal{W}^3_0(K) = \mathcal{V}(K), \quad 3 \mathcal{W}^3_1(K) = \mathcal{A}(K), \quad 3 \mathcal{W}^3_3(K) = \mathcal{V}(K) = 4 \pi X(K),
\]

where \( X(K) = 1 \) is the Euler characteristic of a convex body. With the help of Eq. (A6), the definition of the Minkowski functionals can be extended to include polyhedral bodies (whose boundary is not regular), and to “improper” bodies embedded in \( \mathbb{E}^d \) whose dimensionality \( n \) is less than \( d \). For instance, consider first a closed cube \( Q \) of edge length \( a \). The parallel volume \( \mathcal{V}_\rho(Q) \) is given by

\[
\mathcal{V}_\rho(Q) = a^3 + 6a^2 \rho + 12a \frac{\pi}{4} \rho^2 + 8 \frac{4\pi}{24} \rho^3,
\]

which implies

\[
\mathcal{W}^3_0(Q) = a^3, \quad \mathcal{W}^3_1(Q) = 2a^2, \quad \mathcal{W}^3_2(Q) = \frac{4 \pi}{3}.
\]

Next, we consider a closed square \( T \) of edge length \( a \), embedded in three-dimensional space. The parallel volume \( \mathcal{V}_\rho(T) \) is obtained as

\[
\mathcal{V}_\rho(T) = 2a^2 \rho^4 + 4 \frac{\pi a}{2} \rho^3 + 4 \frac{4\pi}{3} \rho^3.
\]
and, therefore,
\[
W_0^{(3)}(T) = 0, \quad W_1^{(3)}(T) = \frac{2\pi}{3} a^2,
\]
\[
W_2^{(3)}(T) = \frac{2\pi}{3} a, \quad W_3^{(3)}(T) = \frac{4\pi}{3}.
\]

The volume of the \( n \)-dimensional unit ball is \( \omega_n = \frac{\pi^{n/2}}{\Gamma(1+n/2)} \). The “Steiner measures” or “intrinsic volumes” defined by
\[
\mu_n = \frac{1}{\omega_n} W_{d-n}, \quad \alpha = 0, \ldots, d,
\]
turn out to be independent of the ambient space, i.e., if \( K \subset \mathbb{R}^d \subset \mathbb{R}^d' \), then the value of \( \mu_n(K) \) is the same whether computed in \( \mathbb{R}^d \) or in \( \mathbb{R}^d' \).

The Minkowski functionals have some important properties, namely the following.

Additivity: If \( K \in \mathcal{K} \) is bisected by a planar cut into two parts \( K_1, K_2 \in \mathcal{K} \), so that \( K = K_1 \cup K_2 \), then
\[
W_0(K) = W_0(K_1) + W_0(K_2) - W_0(K_1 \cap K_2), \quad \alpha = 0, \ldots, d,
\]
where we omit the superscript \( d \) from now on.

Motion invariance: Let \( G \) be the set of all motions (translations and rotations) in \( \mathbb{R}^d \). Let \( g \in G \), and denote by \( gK \in \mathcal{K} \) the result of the action of \( g \) on \( K \), then
\[
W_0(gK) = W_0(K), \quad \alpha = 0, \ldots, d.
\]

Continuity: If \( K_n \) approximates \( K \) for \( n \to \infty \), then
\[
W_0(K_n) \to W_0(K), \quad \alpha = 0, \ldots, d.
\]

Up to this point, the discussion has been limited to convex bodies. To extend the scope in order to deal with more general shapes, we consider the class \( \mathcal{P} \) of subsets of \( \mathbb{R}^d \) which are constructed from finite unions and intersections of convex bodies, and which includes the empty set \( \emptyset \). The Euler characteristic is defined by
\[
X(A) = \begin{cases} 1, & \text{for convex } A \in \mathcal{K}, A \neq \emptyset, \\ 0, & \text{for } A = \emptyset \end{cases}
\]
and extended to \( \mathcal{P} \) via additivity:
\[
X(A \cup B) = X(A) + X(B) - X(A \cap B)
\]
for any \( A, B \in \mathcal{P} \). The motion invariance of \( X \) is obvious; furthermore, \( X \) agrees with the Euler characteristic introduced in algebraic topology, when the latter is restricted on \( \mathcal{K} \). The remaining Minkowski functionals are now defined for \( A \in \mathcal{P} \) through
\[
W_0(A) = \int X(A \cap E_\alpha) dE_\alpha, \quad \alpha = 0, \ldots, d - 1,
\]
where \( E_\alpha \) is an \( \alpha \)-dimensional plane in \( \mathbb{R}^d \), and the integral runs over all positions of \( E_\alpha \) weighted with the kinematical density \( dE_\alpha \). The latter is normalized so that \( W_0(B_{r-1}) = \omega_d \) for a \( d \)-dimensional unit ball \( B_{r-1} \). For a convex body \( A \), Eq. (A18) reproduces the functionals obtained from Steiner’s formula (A6). Their extension to \( \mathcal{P} \) via Eq. (A18) inherits from \( X \) the properties of motion invariance and additivity. Hence, we find by induction:
\[
W_0(A \cup \bigcup_{i=0}^{N-1} K_i) = \sum_i W_0(K_i) - \sum_{i<j} W_0(K_i \cap K_j) + \cdots + (-1)^N W_0(K_1 \cap K_2 \cap \ldots \cap K_N)
\]
to hold for \( \alpha = 0, \ldots, d \), where we set \( W_d = \omega_d X \).

In Sec. II we have to evaluate expressions such as Eq. (A19) where the bodies \( K_i \) are polyhedral lattice cells. Any closed polyhedron \( C \) may be figured as a union of the disjoint collection of its vertices, its open edges, faces and interior \( \bar{C} = C \setminus \partial C \). The values of the Minkowski functionals on the open interior of a \( n \)-dimensional body \( A \in \mathcal{P} \), \( n \leq d \), are determined according to
\[
W_0(A) = (-1)^d + n + a W_0(A).
\]
The relation (A20) is deduced from Eqs. (A17) and (A18) and the definition
\[
X(A) = (-1)^n, \quad n = \dim A
\]
for the Euler characteristic of the interior \( A \) of a convex body \( A \neq \emptyset \). To illustrate the consistency of Eq. (A21) with Eq. (A16) consider a closed line segment \( S \) (dim \( S = 1 \)), which is the union \( S = \bar{S} \cup P \cup Q \) of the open interval \( \bar{S} \) and the two endpoints \( P, Q \). Since points are open as well as closed convex bodies, and the sets \( \bar{S}, P, Q \) are disjoint we find
\[
X(S) = X(\bar{S}) + X(P) + X(Q) = -1 + 1 + 1 = 1
\]
In dealing with a lattice model, it is convenient to work with disjoint open sets in order to reduce the number of terms in expressions such as Eq. (A19).
However, the importance of the renormalized Gaussian curvature energy of membrane models has been stressed recently by L. Golubović, Phys. Rev. E 50, R2419 (1994) and D. Morse, ibid. 50, R2423 (1994).

