Are Sponge Phases of Membranes Experimental Gauge-Higgs Systems?

David A. Huse[(1)] and Stanislas Leibler[(2)]
[(1)]*AT&T Bell Laboratories, Murray Hill, New Jersey 07974*
[(2)]*Service de Physique Théorique de Saclay, F-91191 Gif-sur-Yvette, France*
(Received 13 August 1990)

A simple generalization of a continuum model of fluctuating membranes is considered in which one allows the existence of holes as structural defects. The proposed phase diagram of such systems includes, in particular, a variety of "sponge" phases now exhibiting edges in the form of closed loops or infinite lines. We show that the simplest theory describing the transitions between these phases is identical to the lattice gauge theory for a Z_2 Higgs system. We suggest, therefore, that sponge phases of amphiphilic films could form experimental models to check some of the nontrivial predictions of lattice gauge theories.

PACS numbers: 68.60.−p, 05.50.+q, 11.10.−z, 64.60.−i

Membranes built of bilayers of amphiphilic molecules can form a large variety of structures in aqueous solutions.[1] Some of them, such as lamellar or cubic phases of lyotropic liquid crystals,[2] are ordered, but many others present a random, disordered aspect. Among the most fascinating random structures are the so-called *sponge phases* in which the membranes divide the solvent into two interpenetrating continuous regions.[3-5] Such "bicontinuous" equilibrium structures have indeed been observed, and are now being intensively studied, e.g., in anomalous flow-birefringent isotropic (L_3) phases of some dilute surfactant solutions.[6] From the point of view of the theory of random surfaces the bicontinuous structures present the possibility of an unusual phase transition in which *the symmetry between the two sides of the surface is spontaneously broken.*[4] This "symmetric-sponge"–"asymmetric-sponge" transition, first postulated[7] and studied[5,8] theoretically, seems to be now observed experimentally in L_3 phases.[9]

The symmetry between the two sides of a bilayer membrane is the geometrical symmetry of the phenomenological random surface Hamiltonian, which for a noninterating membrane system can be written as[4]

$$\mathcal{H}_0=\int dS(r_0+\tfrac{1}{2}\kappa_0 H^2+\bar{\kappa}_0 K)\,, \qquad (1)$$

where the integral is over a self-avoiding surface of unconstrained topology and total area, H and K are the mean and the Gaussian curvature at a given point of the surface, r_0 is the chemical potential of membrane molecules, and κ_0 and $\bar{\kappa}_0$ are rigidity coefficients. The geometrical symmetry between the two sides of the membranes is expressed here through the absence of the so-called "spontaneous-curvature" term, linear in H. An important assumption underlying this Hamiltonian (1) is that the membrane has no edges. Indeed, if one allows, for instance, the presence of holes in the membranes, the very concept of the bicontinuous phase has to break down at some point. The possibility of the existence of holes and edges is not unrealistic,[10] since the line tension of an edge can be lowered by adding small amphiphilic impurities into the membrane or by changing the salinity of the aqueous solvent. In this Letter we present a theoretical study of the thermodynamical behavior of membrane systems with edges permitted. We argue, in particular, that allowing holes and edges strongly modifies the behavior of sponge phases.

The main conclusions of our study are summarized in a schematic phase diagram presented in Fig. 1, where $\beta=1/k_BT$. For the sake of simplicity we have supposed here that the Gaussian rigidity of the membranes, $\bar{\kappa}_0$, is zero[11] and have described the membranes at length

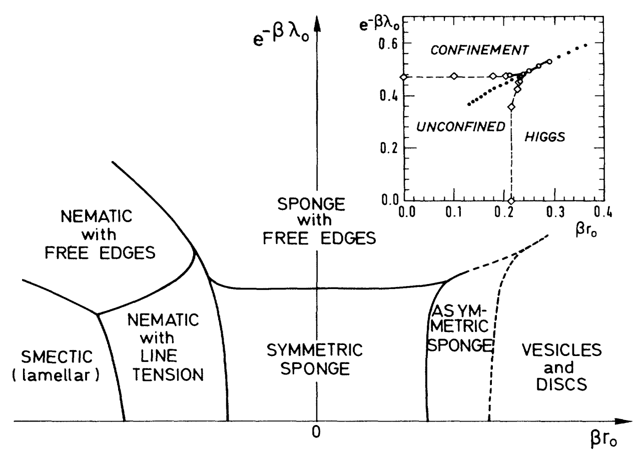

FIG. 1. Proposed schematic phase diagram for the membrane Hamiltonian $\mathcal{H}$ [Eqs. (1) and (2) with the Gaussian-curvature term neglected]. The dashed lines correspond to geometric (percolation) transitions, while the solid lines show the thermodynamic phase transitions. The order of each phase transition and even the very existence of some phases (such as the nematics) in general depends on details of the model. The properties of the various phases are described in the text. The $r_0>0$ part of the phase diagram with the sponge phases corresponds to the phase diagram of the Z_2 gauge-Higgs model shown in the inset (based on numerical simulations of Ref. 16). Notice that this diagram is self-dual. (In the inset the self-dual line is shown dotted, the continuous-phase-transition lines are dashed, and the first-order-transition lines are solid.) In particular, the Ising transition on the horizontal axis has its dual equivalent for the pure gauge model on the vertical axis.

scales larger than the persistence length $a \sim \xi_K$ (which means that we integrate the thermal fluctuations up to this scale so that the effective rigidity κ is of the order of $k_B T$).[4] In order to take into account the possibility of free edges we have added an extra term to the Hamiltonian, $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1$, with

$$\mathcal{H}_1 = \lambda_0 \int dl \,, \tag{2}$$

where the integral is over all edges and λ_0 is the chemical potential, per unit length, of the edges *"living" on the surfaces.* For infinite λ_0, edges are forbidden and one expects the structures described previously:[4,5] Under increasing r_0 lamellar smectic and nematic phases transform themselves into symmetric (tensionless or "relaxed"[4]) and asymmetric (tense[4]) sponges and finally become an ensemble of closed vesicles. It is quite possible that some of the intermediate nematic or sponge phases may not occur in many systems, instead being bypassed by first-order phase transitions. Here we will assume, as was done in Ref. 4, that all the transitions are continuous where possible and only weakly first order otherwise, so all possible regimes are present. Whether or not all the regimes shown in Fig. 1 can occur in one system is an interesting question. The nematic and smectic phases have long-range order in the orientation of the surfaces; the smectic phase also has quasi-long-range positional order.[4] Here we call a phase a "sponge" phase when it (i) does not have long-range orientational order and (ii) does have an infinite connected piece of surface present. For infinite λ_0 the distinction between the symmetric- and asymmetric-sponge phases is that in the latter the symmetry between the two sides of the surface is spontaneously broken, while it is preserved in the former. Also, the macroscopic (fully renormalized) surface tension r is positive in the asymmetric-sponge phase while it vanishes in the symmetric sponge.

When λ_0 is finite, edges are allowed and these two distinctions between the sponge phases become invalid. First, the bulk regions can no longer be unambiguously identified as being on one or the other side of the surface since the two sides are continuously connected around the edges. Second, a positive macroscopic surface tension can no longer be defined: If one tries to force such a surface across a macroscopic system to measure its tension, the system will lower its free energy by putting a macroscopic hole in the surface. However, a thermodynamic distinction between the symmetric- and asymmetric-sponge phases may now be made by examining the (fully renormalized) line tension λ of an edge.

One may (theoretically) measure λ by forcing in an edge as illustrated in Fig. 2(a). Points B and C are a distance l apart along the straight-line segment BC. An edge is constrained to lie on the curve $\tilde{BC}$ going indirectly from B to C which is of length L. The loop produced by BC and $\tilde{BC}$ lies in a plane on which it encloses area A. The excess free energy of this constrained system over

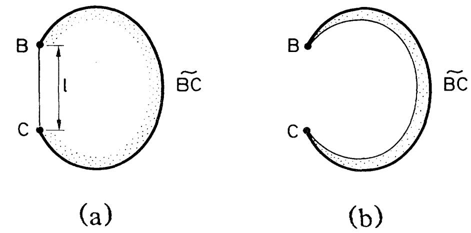

FIG. 2. A theoretical construction defining the macroscopic line tension of an edge, λ (see text). An edge is constrained to lie along the bold line, which we call $\tilde{BC}$. In the symmetric-sponge phase the edge will return from B to C very close to the straight line, as in (a). In the asymmetric-sponge and vesicles-and-discs regimes, on the other hand, the edge will be "slaved" by the surface and will follow closely the longer path $\tilde{BC}$ in order to minimize the area of the spanning surface, as in (b).

one without the constraint is $\Delta F \approx rA + \Lambda L + \lambda l$, for large l and A at least of order l^2. Λ is the free energy cost per unit length of imposing the constraint along $\tilde{BC}$. Let us consider how the edge returns—along a different path—from B to C. In *the asymmetric-sponge regime,* for large but finite λ_0 (as well as in the regime of "vesicles and discs," see below) it returns along a path very close to $\tilde{BC}$ in order to avoid making extra surface, as shown in Fig. 2(b). This happens even though the macroscopic surface tension r, as defined above, is *formally* equal to zero. It is, in some way that we have so far failed to make precise, a "reminiscence effect" of the fact that for infinite λ_0 the asymmetric sponge has $r > 0$. Thus, in this regime the edges are "slaved" to the surfaces and the line tension as defined above is also *formally* zero. In the symmetric-sponge phase, on the other hand, the edge may return along the shortest path, namely, BC, because creating the spanning surface of area A does not cost any free energy and is not avoided by the system. The line tension, defined above, is positive for some range of r_0 and λ_0. We will call the sponge phase with positive line tension *the symmetric sponge.*

There are three regimes in our phase diagram, namely, the *vesicles-and-discs, sponge-with-free-edges,* and asymmetric-sponge regimes; all are thermodynamically disordered, meaning they have no long-range order and surface and line tensions are, formally, zero. We may, however, make distinctions among these regimes based on the connectivity of the edge and surface configurations. Let us start at large r_0 and λ_0 where one finds only *finite* sheets of membrane in the form of closed (in general nonspherical) vesicles or (in general, nonflat and noncircular) "discs" with edges. As r_0 is then decreased at sufficiently large λ_0, an infinite piece of connected (percolating) surface appears, although the loops of edge remain finite; this is, in fact, the asymmetric-sponge regime. Again, because of the reminiscence effect the edges appear only in the form of finite loops (although the line tension λ is *formally* zero) in order to avoid forming an infinite spanning surface. However, at small enough λ_0 this effect is overcome by the entropy gain due to letting the edges proliferate. This results in the sponge-with-free-edges regime, which has infinite loops of edge present; since the surface must be attached to these edges, and infinite piece of surface must also be present. This regime can be entered directly from the vesicles-and-discs regime at large r_0, where the proliferation of edges forces the existence of an infinite, "seaweedlike" surface, or it may be entered directly from the asymmetric- or symmetric-sponge regimes, where an infinite connected piece of surface is already present. A plausible picture of the edge configurations in this sponge-with-free-edges regime is obtained by viewing the edges as a melt of ring polymers of arbitrary length. Then an individual edge performs a Gaussian random walk at long lengths and therefore has a nonzero probability of never closing on itself. Since an individual walk is not space filling, there must be an infinite number of infinitely long edges. However, two different such infinitely long edges will pass *near* each other infinitely many times, so the surface attached to one edge will almost certainly be connected with the surface attached to the other edge and we expect only one infinite piece of connected surface to be present.

The remaining three possible phases shown in Fig. 1 are the smectic (lamellar), the nematic with positive line tension, and the nematic with free edges (zero line tension). In contrast to sponge phases they are all orientationally ordered. Since the edges are dislocations of the smectic order, free edges necessarily destroy the smectic order, so only the nematic can exist when the line tension of an edge vanishes.

We show below that the part of the phase diagram in Fig. 1 involving the sponge phases is in fact equivalent to the phase diagram of the Z_2 gauge-Higgs system.[12] This simplest lattice-gauge-theory model, first introduced as a generalization of the Ising model,[13] was intensively studied in particle physics in order to understand the phenomenon of confinement.[12] In particular, the self-dual, three-dimensional version of this model was studied through mean-field methods,[12,14] perturbative techniques,[15] and numerical simulations.[16] The resulting phase diagram is shown in the inset of Fig. 1. It includes three distinct regions: (i) a region in which series expansion in the gauge coupling shows confinement (confinement region); (ii) a region where there is no confinement (unconfined region), separated from (i) for small Higgs couplings through a continuous Ising-like transition;[12] and (iii) a region where for continuous gauge groups the Higgs mechanism would take place (Higgs region). It was shown[17] that for this discrete Z_2 gauge group this region is in fact continuously connected to the confinement region by an analyticity domain with no thermodynamic singularities or phase transitions. These three regions correspond to the three sponge phases described above; namely, the symmetric-sponge phase corresponds to the unconfined phase, the sponge with free edges to the confinement region, whereas the asymmetric-sponge and vesicles-and-discs regimes correspond to the Higgs region. Of course, since the theory is self-dual, the Higgs and confinement regimes may be exchanged in this correspondence; e.g., in Ref. 8 the symmetric-to-asymmetric-sponge phase transition at infinite λ_0 is mapped onto a pure gauge theory.

The connection between random surfaces with edges and Z_2 Higgs lattice gauge theory is demonstrated by considering random surfaces on a lattice.[18] Thus, let us consider a random surface living on the plaquettes of a simple cubic lattice; the edges of the surface lie on the links of the lattice. Label the elementary cubes (bounded by six plaquettes) with indices i. Put Ising matter fields $\sigma_i = \pm 1$ in each elementary cube and Ising gauge fields $U_{ij} = \pm 1$ on each plaquette. The plaquette separating cubes i and j is denoted ij. Plaquette ij is occupied by the surface if $\sigma_i U_{ij} \sigma_j = -1$. The link shared by cubes i, j, k, and l has an edge on it if an odd number of the four adjacent plaquettes are occupied by the surface so that $U_{ij} U_{jk} U_{kl} U_{li} = -1$. The appropriate action in terms of these fields is then

$$\mathcal{S} = -\beta r_0 \sum_{\langle ij \rangle} \sigma_i U_{ij} \sigma_j - \beta \lambda_0 \sum_{\langle ijkl \rangle} U_{ij} U_{jk} U_{kl} U_{li} , \qquad (3)$$

where the sums run over all plaquettes and links, respectively. Because of the gauge invariance of (3), each distinct configuration of surface plaquettes and edges is represented by precisely 2^N gauge-equivalent configurations of the matter and gauge fields, where N is the number of cubes in the system. Thus the mapping from the lattice gauge theory to the surface-and-edge model is many to one, with a multiplicity independent of the configuration. For infinite λ_0 the gauge may be fixed so that all the gauge fields are equal to $+1$, resulting in the usual ferromagnetic Ising model for the matter fields. This, of course, has a critical point as r_0 is varied, which is the symmetric-to-asymmetric-sponge transition. The lattice theory is self-dual and this Ising-model line at infinite λ_0 is mapped onto the pure gauge line $r_0 = 0$ under duality. Thus the phase transition, as λ_0 is decreased at fixed $r_0 = 0$, from the symmetric-sponge phase to the sponge with free edges is also a critical transition in the Ising universality class. Monte Carlo simulations of the Z_2 Higgs system on the simple cubic lattice showed[16] that these Ising critical transitions become of first order when one is fairly near the triple point where the symmetric-sponge, asymmetric-sponge, and sponge-with-free-edges phases meet, as shown in the inset of Fig. 1. Similarly, a line of first-order phase transitions between the asymmetric sponge and the sponge with free edges extends out from the triple point along the self-dual line, terminating in a critical point beyond which there is no thermodynamic phase transition separating these two regimes. It is an interesting question whether these transitions are always of first order near the triple point. It may be that on another lattice or with other further-neighbor interactions the first-order transitions could be absent. Then the two Ising critical lines would meet at some sort of multicritical point, perhaps XY universality class. Note that the model, as introduced above on a simple cubic lattice, does permit "seam" defects (i.e., three occupied plaquettes that share one link) with the same local energy as simple edge defects. It also allows a limited set of other self-intersections (e.g., four occupied plaquettes sharing a link) at no energy cost. However, by adding additional local terms to the action (3) and/or using other lattices[8] one could easily generalize the model to allow these various defects to have independent energies. Of course, such terms will generally disrupt the precise self-duality of the above lattice model (3).

In dealing with complex fluids, such as amphiphilic films, one always must be cautious in applying the predictions of simple-minded theories to real experimental systems. Indeed, in the case of sponge phases, for example, two important experimental facts are neglected by our model. First, we have supposed that there is no direct molecular interaction between fluctuating membranes other than self-avoidance. This is, of course, not the case, especially for charged amphiphiles. Second, the sponge phases, as all other phases depicted in Fig. 1, are binary (or higher order) mixtures of amphiphiles and water. If one wants to study in detail the nature of phase transitions appearing in such systems, one cannot neglect a possible coupling between order parameters describing the fluctuating surfaces (or edge defects) and the binary mixture (density) order parameter.[19,20] Such couplings can modify, e.g., by "Fisher renormalization," the continuous transitions described above.

However, these and other additional features of real experimental systems can, in principle, be taken into account by extensions of our theory. One could then try to connect directly the results of experiments in sponge phases and some of the results presented here. Probably, the easiest way to introduce edge defects into the *pure* membrane systems is by changing the nature of the aqueous solvent (e.g., its salinity[10]), which in turn can modify the interactions of the amphiphiles and introduce a positive spontaneous curvature of each of the monolayers. This would result in lowering the free-energy cost of edges or holes. The holes could also be stabilized by introducing small amphiphilic impurities which can accumulate at the edges and lower their effective line tension. One can then study sponge phase transformations either through direct structural measurements (e.g., freeze-fracture microscopy,[21] light scattering, etc.) or through thermodynamic (e.g., specific-heat, susceptibility) experiments.

Although the detailed structure of the phase diagram shown in Fig. 1 (which itself is based only on numerical simulations[16] and simple approximation schemes[12]) could be modified through various additional effects mentioned above, we hope that the rather appealing connection between the thermodynamic behavior of sponge phases of membranes and gauge-Higgs theories, established in this Letter, will further stimulate both experimental and theoretical work on fluctuating membrane systems.

We thank F. David, J.-M. Drouffe, and D. Roux for useful discussions. S.L. would like to acknowledge the warm hospitality of B. Shraiman and AT&T Bell Laboratories.

[1]See, e.g., *Physics of Amphiphilic Layers,* edited by J. Meunier, D. Langevin, and N. Bocarra (Springer, Berlin, 1987).

[2]See, e.g., S. Leibler, in *Statistical Mechanics of Surfaces and Membranes,* edited by D. R. Nelson, T. Piran, and S. Weinberg (World Scientific, Singapore, 1989).

[3]L. E. Scriven, Nature (London) **263**, 123 (1976).

[4]D. A. Huse and S. Leibler, J. Phys. (Paris) **49**, 605 (1988).

[5]M. E. Cates *et al.*, Europhys. Lett. **5**, 733 (1988); **7**, 94(E) (1988).

[6]See, e.g., G. Porte *et al.*, J. Phys. (Paris) **49**, 511 (1988).

[7]See Ref. 4. Note that this paper considered balanced microemulsions rather than membrane-water systems. This article also used different names for the two bicontinuous phases: "random isotropic" which corresponds to symmetric sponge and "tense bicontinuous" which corresponds to asymmetric sponge. Here we use the more common names of Ref. 5. One should notice that the structure of real sponges is *not*, in general, that of the phases described in these random surface models. These phases and the transition between them were also considered by M. Karowski and H. J. Thun, Phys. Rev. Lett. **54**, 2556 (1985); M. Karowski, J. Phys. A **19**, 3375 (1986); and R. Shrader J. Stat. Phys. **40**, 533 (1985).

[8]F. David, Europhys. Lett. **9**, 575 (1989).

[9]D. Roux *et al.*, Europhys. Lett. **11**, 229 (1990).

[10]D. Roux (private communication).

[11]The presence of the Gaussian-curvature term can strongly modify the phase behavior of membrane phases. For instance, a negative value of κ_0 will favor ordered structures of bicontinuous phases (e.g., cubic crystals), as discussed in Ref. 4.

[12]For a review see, e.g., J.-M. Drouffe and J.-B. Zuber, Phys. Rep. **102**, 1 (1983).

[13]F. Wegner, J. Math. Phys. **12**, 2259 (1971).

[14]R. Balian, J.-M. Drouffe, and C. Itzykson, Phys. Rev. D **11**, 2098 (1975).

[15]See, e.g., E. Brézin and J.-M. Drouffe, Nucl. Phys. **B200**, 93 (1982).

[16]G. A. Jongeward, J. D. Stack, and C. Jayaprakash, Phys. Rev. D **21**, 3360 (1980).

[17]E. Fradkin and S. H. Shenker, Phys. Rev. D **19**, 3682 (1979).

[18]Related mappings between various random surface models and lattice gauge theories have been discussed by P. D. Gujrati, Phys. Rev. B **39**, 2494 (1989).

[19]M. E. Cates, J. Phys. (Paris), Colloq. **51**, C7-73 (1990), and references therein.

[20]In fact the amphiphilic films studied, for instance, in L_3 phases are often binary mixtures of surfactants. Therefore, one cannot neglect *a priori*, a possible coupling between the phenomena described here and composition fluctuations or phase separation of the amphiphiles within the membrane.

[21]R. Strey *et al.*, Langmuir (to be published).