Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Gautam I. Menon [a], Rahul Pandit [b] & Sriram Ramaswamy [b]

[a] Theoretical Physics Group, Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Mumbai, 400005, India

[b] Department of Physics, Indian Institute of Science, Bangalore, 560012, India

Version of record first published: 24 Sep 2006.

To cite this article: Gautam I. Menon , Rahul Pandit & Sriram Ramaswamy (1996): Sponge Phase Transitions from a Lattice Mode, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 288:1, 93-104

To link to this article: http://dx.doi.org/10.1080/10587259608034587

Mol. Cryst. Liq. Cryst., 1996, Vol. 288, pp. 93–104
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SPONGE PHASE TRANSITIONS FROM A LATTICE MODEL

GAUTAM I. MENON[(1)], RAHUL PANDIT[(2)*], SRIRAM RAMASWAMY[(2)*]
(1) Theoretical Physics Group, Tata Institute of Fundamental Research
Homi Bhabha Road, Colaba, Mumbai - 400005, INDIA.
(2) Department of Physics, Indian Institute of Science
Bangalore - 560012, INDIA.

Abstract We use Monte Carlo simulations to obtain thermodynamic functions and correlation functions in a lattice model we propose for sponge phases. We demonstrate that the surface-density correlation function dominates the scattering only along the symmetric-sponge (SS) to asymmetric-sponge (AS) phase boundary but not the boundary between the sponge-with-free-edges (SFE) and symmetric-sponge phases. At this second thermodynamic transition the scattering is dominated instead by an edge-density (or seam-density) correlation function. This prediction provides an unambiguous diagnostic for experiments in search of the SS-SFE transition.

A major challenge in the study of amphiphilic aggregates[1,2] is to understand the intriguing sponge or L_3 phases. These statistically isotropic assemblies of fluctuating, bilayer, fluid membranes, arise in water-surfactant solutions[3,4]. Three sponge phases have been proposed: the symmetric sponge (SS), the asymmetric sponge (AS), and the sponge with free edges (SFE)[3–8]. If curvature energies[9] are ignored[10], there are four parameters that govern the statistical mechanics of such phases: the energy costs μ per unit area of bilayer, E per unit length of perimeter or edge, S per unit length of seams (a T junction between bilayers), and X per unit length of bilayer crossings. The simplest model[4] sets $E = S = \infty$ and $X = 0$ (forbidding edges and seams) and the bilayer then divides space into two disjoint pieces, the inside **I** and the outside **O**. As μ increases, the system undergoes a continuous phase transition of three-dimensional Ising type, from the SS phase, with equal volumes of **I** and **O**, to the AS phase, where these volumes are unequal. An Ising order parameter

can clearly distinguish between equal and unequal volumes of **I** and **O**: it vanishes in the SS phase but not in the AS phase. This SS-AS transition has been seen in light-scattering experiments[4] whose results are consistent with a Ginzburg-Landau theory that couples the *observable* bilayer density to the *unobservable* Ising order parameter[5,11]. In experiments $E, S < \infty$ so edges and seams appear, the distinction between **I** and **O** cannot be made, and the (local) Ising order parameter is lost[12]. Yet the SS and AS phases persist and a new one, the SFE (which can be connected smoothly to the AS) appears, as shown[6,13] for $X = 0$ and $E = S$ by mapping the random bilayer problem onto a Z_2 gauge-Higgs model. The phase diagram of this model[14] is shown schematically in Fig. 1. There have been no predictions of scattering signatures at sponge phase transitions in models that allow for edges and seams. However, both SS-AS and candidates for SS-SFE transitions have been studied by scattering experiments[3–5,7,8]. We propose a model for random surfaces

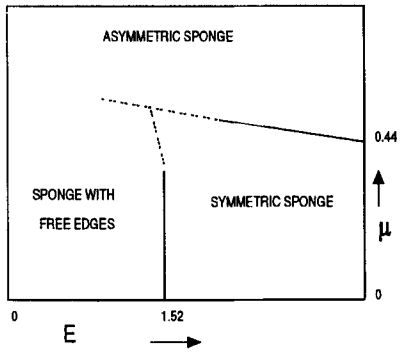

Figure 1: A schematic phase diagram (after Ref.[14]) for the $3-d$ Z_2 gauge-Higgs model as a function of the surface chemical potential μ and the cost for edges or seams E $(= S)$ showing the three phases symmetric sponge (SS), asymmetric sponge (AS), and sponge with free edges (SFE). Solid and dashed lines denote continuous and first-order boundaries, respectively. The first-order lines meet at a triple point; the continuous boundaries meet the first-order ones at tricritical points. Note that one can go from the AS to the SFE phase without crossing a phase boundary since the first-order boundary between them ends in a critical point.

which makes predictions for thermodynamic functions and concentration fluctuations near and at both SS-AS and SS-SFE transitions. Our model is appealing since it

assigns separate energy costs to edges, seams, and surface crossings. We study the simple case $E = S$ and $X = 0$, where our model is equivalent to that of Huse and Leibler[6], and more general cases ($E \neq S$ and $X \neq 0$) of physical interest. Our principal result is that *critical scattering from edges* dominates at the SS-SFE transition, both in the Z_2 gauge-Higgs case and in the limit ($E \neq S = X = \infty$) in which seams and crossing surfaces are forbidden. The scattering from the bilayer density field itself is all but featureless across the SS-SFE transition[15], but shows distinct signs of singular behaviour at the SS-AS transition. Our results have definite consequences for experiments: if molecules which adsorb preferentially at edges are introduced into the solution, then critical scattering from these molecules should provide an unambiguous diagnostic for the SS-SFE transition.

Our model is defined on a simple-cubic lattice with sites connected by links that can have two states: occupied or unoccupied. With each occupied link (oriented in the x, y or z directions) we associate a plaquette of surface by placing it at the centre of the link and normal to it. The set of plaquettes then forms a surface (of unrestricted topology), defined on a lattice dual to the lattice of sites. This link representation is the same as that of Menon and Pandit[16] for living polymers and proves convenient for our random-surface problem.

We assign positive energies μ to each occupied plaquette, E to each edge (an isolated plaquette has 4 edges, a closed surface none), S to each seam (3 plaquettes meeting at a T-junction), and X for surface crossings (4 plaquettes meeting at a common link). We study two sets of parameters: (a) $E = S$ and $X = 0$, i.e. the Z_2 gauge-Higgs model; and (b) $E \neq S = X = \infty$, the self-avoiding case. In both these cases, the model can be specified by E and μ in units of the temperature T.

We simulate our model by the Monte Carlo algorithm of Metropolis *et al.*[17] on lattices of (linear) size $L = 4 - 16$, i.e., our largest lattice can accomodate a maximum of 3×4096 plaquettes. We use periodic boundary conditions. Our basic Monte Carlo move consists of an attempt to update the state of a link (a plaquette in the surface representation). We also attempt multiple updates in which we simultaneously change the state of all links emanating from a single vertex. The links to be updated are chosen at random. Our simulations use four types of initial configurations: (1) an empty lattice (all link occupancies are zero); (2) a lamellar stacking of surfaces; (3) a disordered arrangement of surface formed by occupying links at random; and (4) equilibrated configurations generated (after a large number of runs) from any one of the previous three starting configurations. We equilibrate the system for 10^5 Monte Carlo steps per link (MCS). We then collect data for thermodynamic and structural quantities at intervals of 10 MCS. In our simulations

we monitor the number densities of edges N_e, surface crossings N_x, seams N_{se}, bends N_b, plaquettes N_p, as well as the total internal energy $\langle E \rangle$ and the specific heat C, normalized by the total number of links ($= 3 \times L^3$). We also measure the two-point (angle-averaged) correlation functions $g_s(r)$, $g_e(r)$, and $g_{se}(r)$ (proportional, respectively, to the conditional probabilities of finding an occupied plaquette, an edge, and a seam, at a radial distance r from one at $r = 0$). The data we collect are averaged over $6 - 10 \times 10^3$ independent measurements. We have checked our scheme by verifying that it yields the phase diagram for the Z_2 gauge-Higgs model[14], near the $E = \infty$ and $\mu = 0$ axes.

In the Z_2 gauge-Higgs model, if we set $E = S = \infty$ edges and seams are absent, only closed surfaces are generated (handles can be grown or removed by a sequence of our Monte Carlo moves). The model now becomes the three-dimensional $(3-d)$ Ising spin model, whose well-known transition turns out to be the SS-AS transition here[5]. In our simulations, the peak in C increases with L and its location shifts towards its $L \to \infty$ value ($\simeq 0.44$). The surface-density correlation function $g_s(r)$ shows distinct signs of becoming long-ranged at this transition; an analysis of correlation lengths will be presented elsewhere[18]. As we lower E, similar critical behaviour is obtained when we cross the continuous part of the SS-AS transition away from the pure spin axis (cf. Fig. 1). In particular, the divergence of C continues and $g_s(r)$ decays slowly at the transition and dominates the scattering since the edge-density correlation function $g_e(r)$ (not defined in the pure spin limit) decays more rapidly here[15,18].

The SS-SFE phase boundary can be obtained from plots of the energy density $\langle E \rangle$, edge density N_e, and the specific heat C versus edge cost E. We show this in the Z_2 gauge-Higgs limit in Figs. 2-4 (for $\mu = 0.2$). Sufficiently close to the pure-gauge axis (Fig. 1), this transition is continuous and finite-size effects are seen clearly in the height and location of the specific-heat peak. We have checked that the Ising specific heat exponent obtains in this limit and our best-fit values for the critical coupling are consistent with those of Jongeward *et al.*[14] Our central results (Figs. 5 and 6) show how $g_s(r)$ and $g_e(r)$ change as we scan across the SS-SFE transition ($\mu = 0.2$ and $1.45 < E < 1.55$ here). Note two striking features: (1) $g_s(r)$ is extremely short-ranged, extending over barely one or two inter-plaquette spacings and shows no detectable sign[15] of the SS-SFE transition (though it shows up clearly in C); and (2) $g_e(r)$ becomes extremely long ranged at the SS-SFE transition. Clearly one must probe edge-density correlations to see the SS-SFE transition in scattering experiments [15]. Not surprisingly, seam correlations also become long ranged across the SS-SFE transition in the $E = S$ case[18].

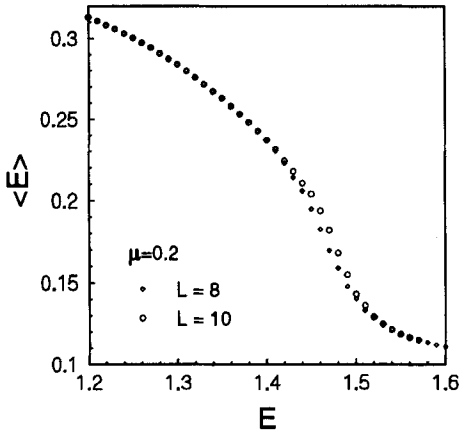

Figure 2: The energy density $\langle E \rangle$ versus edge cost E (= seam cost S) across the SS-SFE transition at chemical potential $\mu = 0.2$, with self-intersection cost $X = 0$. The weak nonanalytic behaviour at the transition becomes more apparent with increasing system size L.

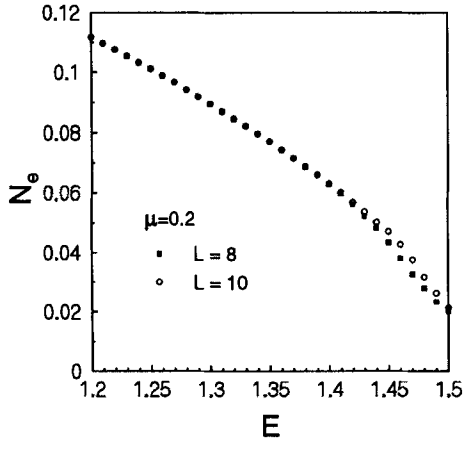

Figure 3: The edge density N_e versus edge cost E (= seam cost S) across the SS-SFE transition at chemical potential $\mu = 0.2$, with self-intersection cost $X = 0$. The weak nonanalytic behaviour at the transition is like that of the energy density in Fig. 2.

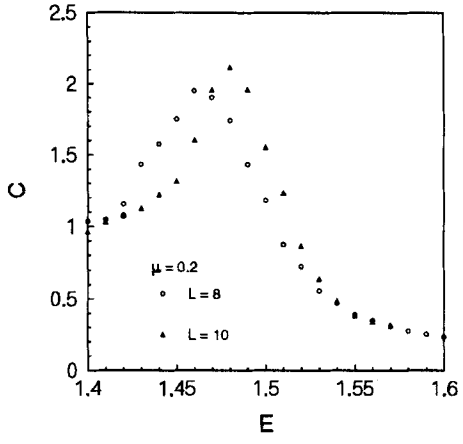

Figure 4: The specific heat C versus edge cost E (= seam cost S) across the SS-SFE transition at chemical potential $\mu = 0.2$, with self-intersection cost $X = 0$. The peak in C sharpens as the linear system size increases and moves towards its $L = \infty$ location ($E = E_c \simeq 1.52$); this signals the transition.

The Z_2 gauge-Higgs limit[6] is somewhat unphysical as a description of surfactant bilayers. First, it assigns identical costs to edge and seam, though they correspond to opposite signs of the monolayer curvature. Second, there is no cost for crossing surfaces ($X = 0$). Our model overcomes these deficiencies. It allows us, for example, to study the self-avoiding, no-seams limit $E \neq S = X = \infty$, where we find that the SS-SFE transition survives: Figs. 7-9 show the energy density $\langle E \rangle$, edge density N_e, and specific heat C versus edge cost E in this limit. Although these data are noisier than their Z_2 gauge-Higgs analogs (Fig. 2-4), it is obvious that the transition persists. The behaviour of $g_e(r)$ across the SS-SFE transition in this self-avoiding case is like its Z_2 gauge-Higgs counterpart (Fig. 6)[18].

Our work constitutes the first calculation of thermodynamic functions and scattering signatures at sponge phase transitions in a random-surface model with edges, seams, and surface crossings. It has been noted in the Z_2 gauge-Higgs literature[6,19] that Bloch walls (surfaces in our model) proliferate across the AS-SS transition, whereas vortices (edges and seams here) proliferate across the SS-SFE transition. We see this explicitly by monitoring densities such as N_e. However, it does not seem to have been appreciated so far that, as a result, $g_s(r)$ dominates the scattering across the former and $g_e(r)$ across the latter as we have shown *explicitly*, both in the

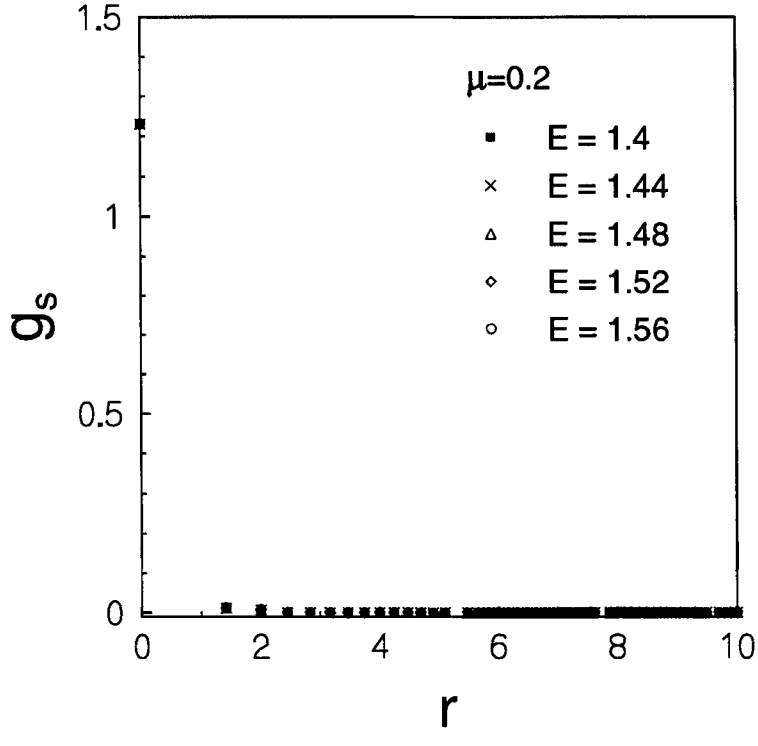

Figure 5: The plaquette correlation function $g_s(r)$ versus r in the surface model (see text), with $\mu = 0.2$, $S = E$ and $X = 0$ for different values of the edge cost E which straddle the SS-SFE transition. This correlation function shows no trace of becoming long ranged as the transition is approached.

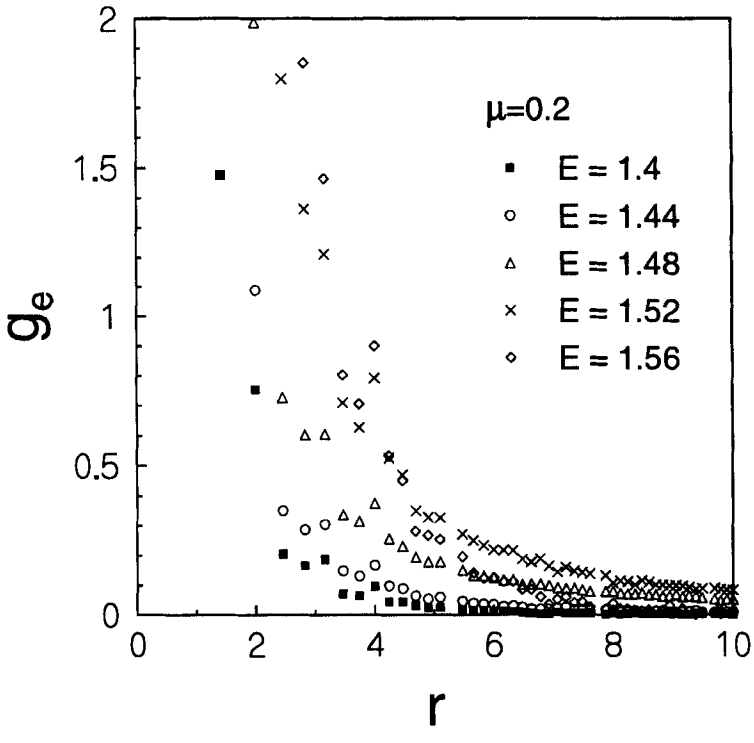

Figure 6: The edge correlation function $g_e(r)$ versus r in the surface model (see text), with chemical potential $\mu = 0.2$, and $X = 0$, for different values of the edge cost $E = S$ which straddle the SS-SFE transition. The considerable increase in edge correlations as the transition is approached is clearly evident.

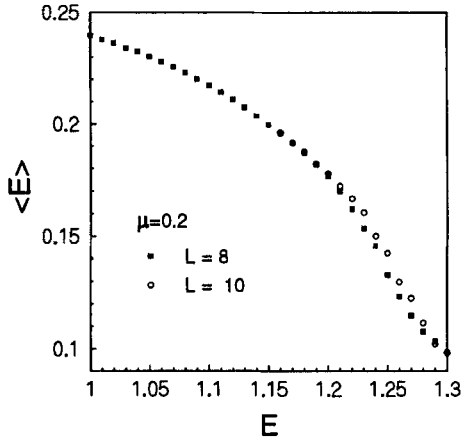

Figure 7: The energy density $\langle E \rangle$ versus edge cost E across the SS-SFE transition at chemical potential $\mu = 0.2$, for the self-avoiding case $S = X = \infty$. The weak non-analytic behaviour at the transition becomes more apparent with increasing system size L.

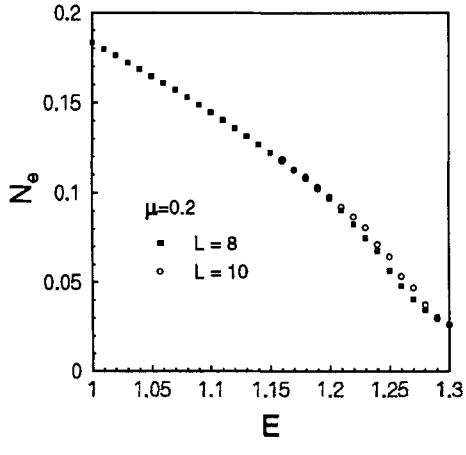

Figure 8: The edge density N_e versus edge cost E across the SS-SFE transition at chemical potential $\mu = 0.2$, for the self-avoiding case $S = X = \infty$. The weak nonanalytic behaviour at the transition is like that of the energy density in Fig. 7

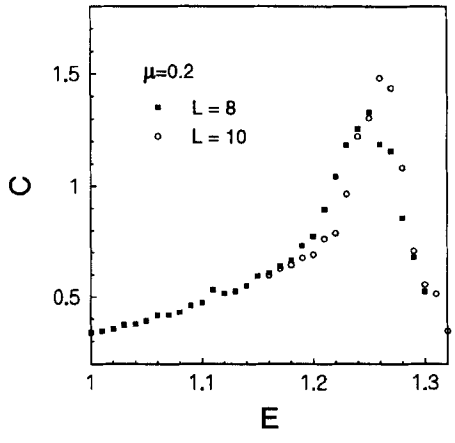

Figure 9: The specific heat C versus edge cost E across the SS-SFE transition at chemical potential $\mu = 0.2$ for the self-avoiding case $S = X = \infty$. The peak in C sharpens as the system size is increased consistent with a divergence as $L \to \infty$ at $E = E_c \simeq 1.28$.

Z_2 gauge-Higgs and self-avoiding cases. Thus we predict that the SS-SFE transition will show up clearly in scattering experiments if scattering from edges (or seams) is singled out. This should be experimentally testable. Indeed, in the light of our findings, it is not clear that recent experiments[7] are really seeing the SS-SFE transition. Further studies using our diagnostic are called for.

The generality of our model also allows us to envision phases (sponge-with-free-seams or SFS) in which there are seams but no edges ($S \neq E = \infty$); by changing S we should be able to induce an SS-SFS transition (only seams proliferate) at which the seam-density correlation function should dominate the scattering[20]. It would be interesting to search for an experimental system that shows an SS-SFS transition. An SFS would, moreover, be a fascinating, highly branched structure, possibly with nontrivial viscoelastic and transport properties.

We thank C. Coulon, D. Dhar, C. Jayaprakash, F. Nallet, and D. Roux for discussions and SERC (IISc, Bangalore) for computer resources. GIM and SR thank CSIR (India) and grant 607-1 of the Indo-French Centre for the Promotion of Advanced Research, respectively, for support.

* Also at : Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India.

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15. The bilayer density correlation function is, we believe, singular at the SS-SFE transition (except along the pure gauge axis of Fig. 1) but this singularity is masked in practical simulations (and experiments) by a very small amplitude. Thus the edge-density correlation function dominates the scattering at the SS-SFE transition. The converse applies across the SS-AS transition.

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20. We believe the SFE and SFS phases can be connected smoothly (like AS and SFE).