A Lattice-Gas Hamiltonian
for Micellar Binary Solutions

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An explicit Ising-spin lattice Hamiltonian is proposed as a model for studying the phase diagrams of micellar binary solutions on the micellar length scale. Incorporating many essential features, it can be used to check the validity of a previously suggested scenario for nonuniversality at the consolute point.

Multicomponent systems incorporating surfactants (amphiphilic molecules) in solution with water and/or oil exhibit very interesting behavior as temperature T and surfactant concentration c_s are varied. Experimental studies show that the amphiphiles self-associate into micelles, bilayers, and vesicles of various shapes and sizes.[2] In micellar binary solutions (MBS), e.g., surfactants and water only, the aggregates typically have one "narrow" dimension limited by the length of two amphiphiles. As one varies T and c_s, the system displays a variety of distributions of aggregates: a monodisperse distribution of spherical micelles (zero-dimensional aggregates), a polydisperse distribution of rodlike micelles (one-dimensional aggregates), or bilayers (two-dimensional aggregates).[3] The aggregates may form either an isotropic liquid phase or a variety of condensed lyotropic mesophases.[4]

Typical T–c_s phase diagram for nonionic MBS of polyoxyethylene glycole monoethers, $CH_3(CH_2)_{n-1}O(CH_2CH_2O)_m H$ (commonly abre-

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viated as $C_n E_m$), in water, can be found in Ref. 4. The lyotropic meso-phases appear at low-T and high-c_s regions. At higher T and above the critical micelled concentration (CMC), these MBS exhibit a phase separation curve with a lower consolute point, from a single isotropic liquid phase into two similar phases, one micelle-rich and the other micelle-poor, all three phases containing either a monodisperse distribution of spherical micelles or a polydisperse distribution of rodlike ones. Sur-prisingly, the critical behavior in different $C_n E_m$/water systems appears to be nonuniversal,[4-6] with critical indices depending on (n, m) and the solvent being H_2O or D_2O.

Naively, systems near the consolute point can be thought of as binary fluid mixtures, so that one expects them to belong to the Ising universality class. To understand qualitatively such nonuniversal behavior, Shnidman[7-9] recently proposed a lattice-gas model. It is based on constructing a coarse-grained representation of MBS with different types of aggregates in terms of Ising spins $S_{i,j,k} = \pm 1$ on a cubic lattice (subscripts label sites) with $+1$ spins corresponding to micellar sections, and -1 spins to regions of comparable size predominantly occupied by solvent. A single $+1$ spin completely surrounded by -1 spins is identified with a spherical micelle, a linear chain of $+1$ spins surrounded by -1 spins corresponds to a rodlike micelle, and a plane of $+1$ spins surrounded by -1 spins represents a bilayer. The short-range intermicellar attraction giving rise to phase separation was modeled in Ref. 7 by the ordinary ferromagnetic Ising interaction. As usual, a homogeneous magnetic field H plays the role of the chemical potential for micelles. A key ingredient, which distinguishes this model from Ising's, is the representation of some of the shorter ranged *intra*micellar interactions responsible for aggregation. Since, in the model, an entire micelle section is mapped into a single spin, only energy differen-ces between spherical and rodlike micelles can be considered. Indeed, existing thermodynamic theories of micellar structure[2],5 show that the internal (free) energy associated with a spherical micelle and a spherical end-cap section of comparable size in a rodlike micelle is higher than the intramicellar energy of a cylindrical section of the same size. In the Ising-spin language, such excess energies can be modeled by assigning *additional values* H_0 and $H_0/2$ to the configurations with isolated $+1$ spins (spherical micelles) and end spins of $+1$ spin chains (end caps), respectively.

To analyze the critical behavior of such a model, a standard renor-malization group approach was employed.[7-9] Arguments were presented for H_0 remaining invariant under renormalization of interactions and

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length scales on the intermicellar level. *Assuming* the marginality of H_0, a simple Migdal–Kadanoff scheme demonstrates that H_0 enters into the recursions for T and H, resulting in an H_0-dependent fixed point. Further, critical indices v and γ were found to decrease monotonically with increasing H_0, in a manner reminiscent of experimental results in $C_n E_m$/water MBS.

A major deficiency of this scenario for nonuniversality is the absence of an explicit Ising-spin Hamiltonian incorporating the intramicellar interactions responsible for aggregation. Several authors[11-14] critized this scenario and proposed explicit Hamiltonians which are supposed to represent the parameter H_0. They found that H_0 is in fact not marginal, but irrelevant, so that the critical behavior always belongs to the Ising universality class. Unfortunately, these Hamiltonians do not reproduce the correct energetics associated with configurations that represent spherical and rodlike micelles. In this paper we present an explicit Ising-spin Hamiltonian for MBS, incorporating the features listed above.

For simplicity, and following earlier practice,[7-9,11-14] we first construct a two-dimensional version on a square lattice. The Hamiltonian $\mathcal{H}$ is a sum of three terms, each standing for a physically different contribution: (a) $\mathcal{H}_K$, effective at the intramicellar length scale, representing many-body interactions responsible for self-association, and controlling the size and shape distribution of aggregates; (b) $\mathcal{H}_J$, describing effective short-range attraction between the aggregates at the larger intermicellar length scale; and (c) $\mathcal{H}_H$, controlling the concentration of aggregates.
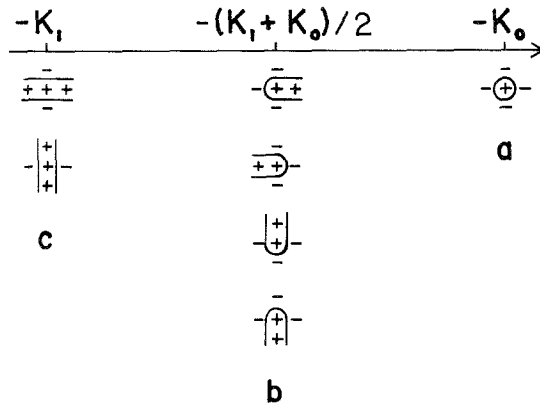

Fig. 1. Local configurations and intramicellar energies associated with a $+1$ spin representing different types of micellar sections in the construction of Eq. (3). (a) A spherical micelle. (b) End-cap sections in rodlike micelles. (c) Cylindrical sections in rodlike micelles. The case $K_1 > K_0 > 0$ is shown. Lines represent the micellar interface between amphiphiles ($+$) and water ($-$). For all other configurations, $\mathcal{H}_K$ is zero.

The first term, which incorporates the excess energy H_0, must distinguish $+1$ spins that represent spherical micelles from those representing micelle sections in rodlike micelles. We assign negative energies $-K_0$ and $-K_1$, respectively, for formation of these aggregates. For an end cap, the average $-(K_0 + K_1)/2$ is chosen. Thus, $H_0 = K_1 - K_0$. To keep $\mathscr{H}_K$ as simple as possible, we specify, around a $+1$ spin, the configurations of only the nearest neighbor (NN) spins. Refering to Fig. 1, these three configurations are, respectively, a $+1$ spin with all four of its NN sites occupied by -1 spins, a $+1$ spin with *three* of the four NN sites coccupied by -1 spins, and a $+1$ spin with precisely two NN $+1$ spins forming a straight line of three.

To take into account these configurations and construct $\mathscr{H}_K$ explicitly, it is convenient to use lattice-gas variables (spin projection operators):

$$t_{i,j} = (1 + S_{i,j})/2, \qquad \tilde{t}_{i,j} = (1 - S_{i,j})/2 \tag{1}$$

projecting onto $S = +1$ and -1, respectively. For further convenience, define the bilinear products:

$$u_{ij} \equiv t_{i-1,j} t_{i+1,j} \tag{2a}$$

$$\tilde{u}_{ij} \equiv \tilde{t}_{i-1,j} \tilde{t}_{i+1,j} \tag{2b}$$

$$w_{ij} \equiv t_{i-1,j} \tilde{t}_{i+1,j} + \tilde{t}_{i-1,j} t_{i+1,j} \tag{2c}$$

and similiar ones with $i \leftrightarrow j$. In terms of these operators, $\mathscr{H}_K$ is

$$\mathscr{H}_K = -K_0 \sum t \tilde{u}_i \tilde{u}_j - \tfrac{1}{2}(K_0 + K_1) \sum t(w_i \tilde{u}_j + \tilde{u}_i w_j)$$
$$- K_1 \sum t(u_i \tilde{u}_j + \tilde{u}_i u_j) \tag{3}$$

where we have suppressed all but the underlined indices. Here and hereafter, summations are over all site indices. Note that the couplings involve up to five spins. For closer resemblance to real systems, $\mathscr{H}_K$ may be "finite-tuned" without introducing additional coupling constants, by specifying the configurations of spins in a larger neighborhood. For example, we can multiply (3) by $\prod_{p,q = \pm 1} \tilde{t}_{i+p, j+q}$, so that the next nearest neighbor of a $+1$ spin is water.

Next, in constructing the intermicellar interaction $\mathscr{H}_J$, we take into account three important points. First, to overcome the problem of polydispersity of rodlike micelles, it should be a sum of interactions between micellar sections rather than directly between micelles as a whole. Second, the range of the intermicellar interaction should be greater than one lattice spacing, since a single lattice spacing is already needed for

defining the narrow dimension of a micelle. For simplicity, we choose this range to be *two* lattice spacings. Third, to distinguish *inter-* from *intra-* micellar interactions, $\mathcal{H}_J$ should not contribute to the latter. A Hamiltonian satisfying all these conditions is

$$\mathcal{H}_J = -J \sum \tilde{\imath}(u_i + u_j) \tag{4}$$

with $J > 0$ for intermicellar attraction. Note that a two-spin ferromagnetic coupling of the form $-JS_{1,j}(S_{1+2,j} + S_{1,j+2})$ satisfies the first two conditions, but not the third.

Finally,

$$\mathcal{H}_H = -H \sum S$$

represents the usual chemical potential for controlling the concentration of amphiphiles (micelles) in the grand canonical formulation.

Summarizing, the explicit, total Hamiltonian we propose is

$$\mathcal{H} = \mathcal{H}_K + \mathcal{H}_J + \mathcal{H}_H \tag{6}$$

This Hamiltonian is defined at the coarsed-grained length scale given by the "narrow" micellar dimension. Unlike the Hamiltonian introduced in Ref. 9, it does not reflect properties of MBS associated with the finer length scale of monomers, such as the phenomenon of CMC. However, it has the advantage of being more amenable to computer simulations.

The phase diagram associated with this model is displayed in a four-dimensional parameter space spanned by K_0, K_1, J, and H. For $K_1 \ll K_0$, $J \ll k_B T$, and $H < 0$, the system is expected to be an isotropic monodisperse distribution of "spherical micelles." In the opposite limit, $K_1 \gg K_0$, we expect a polydisperse distribution of "rodlike micelles." At large enough J, the system should sepatate into two isotropic phases: one micelle-poor and the other micelle-rich. Note that $\mathcal{H}$ contains odd-spin interactions, so that the critical point is unlikely to be at $H = 0$. We expect an upper consolute point if J is assumed to be independent of T. To obtain a coexistence curve with a lower consolute point such as in $C_n E_m$/water MBS, we may either introduce additional degrees of freedom[15] or assume a specific function $J(T)$. In deed, there is some experimental evidence[16] on the T dependence of the effective attraction between amphiphile-coated mica surface in water. Finally, for $K_0 \ll K_1$ and large $H > 0$, a square lattice analog of the hexagonal lyotroic phase may occur; i.e., a periodic stacking of linear "rods" of indefinite length.

Generalizing this model to a three-dimensional one on the cubic lattice is straightforward. Of course, sites are labeled by (i, j, k), so that the com-

pact notation in (3) should be used with care. For example, u_k means $u_{i,j,k} \equiv t_{i,j,k-1} t_{i,j,k+1}$. For $\mathscr{H}_K$, we need a new coupling, K_2, to represent the formation of two-dimensional aggregates (planes of $+1$ spins surrounded by -1 spins), which are lattice analogs of coarse-grained micellar bilayers (Fig. 1c). Note that couplings in $\mathscr{H}_K$ will involve up to seven spins, since a site now has six NN sites. Explicitly, $\mathscr{H}_K$ is

$$
\begin{aligned}
\mathscr{H}_K = & -K_0 \sum t\tilde{u}_i \tilde{u}_j \tilde{u}_k - \tfrac{1}{2}(K_0 + K_1) \sum t(w_i \tilde{u}_j \tilde{u}_k + \tilde{u}_i w_j \tilde{u}_k + \tilde{u}_i \tilde{u}_j w_k) \\
& -K_1 \sum t(u_i \tilde{u}_j \tilde{u}_k + \tilde{u}_i u_j \tilde{u}_k + \tilde{u}_i \tilde{u}_j u_k) \\
& -\tfrac{1}{2}(K_1 + K_2) \sum t(w_i u_j \tilde{u}_k + u_i w_j \tilde{u}_k + u_i w_j \tilde{u}_k + u_i \tilde{u}_j w_k \\
& \quad + w_i \tilde{u}_j u_k + \tilde{u}_i w_j u_k + \tilde{u}_i u_j w_k) \\
& -K_2 \sum t(u_i u_j \tilde{u}_k + u_i \tilde{u}_j u_k + \tilde{u}_i u_j u_k)
\end{aligned}
\tag{7}
$$

For $\mathscr{H}_J$, we must add a third term, $\tilde{t}u_k$, to (4). Finally, the form of $\mathscr{H}_H$ is still (5) and the total $\mathscr{H}$ is just the sum of the three.

Qualitative remarks regarding the expected phase diagram, similar to those for the two-dimensional model, apply here. Of course, the "hexagonal" phase would appear as parallel "rods" arranged in a square array when $K_1 \gg K_0$, K_2 and H is large. The analog of the lamellar phase should occur when $K_2 \gg K_0, K_1$, i.e., periodic stacking of "bilayers" represented by planes of $+1$ spins.

One motivation for constructing an explicit $\mathscr{H}$ is to provide a concrete model for Monte Carlo studies. It would be interesting to check if the conjectured phase diagram is correct. Further, we believe that this $\mathscr{H}$ properly represents the description given in Ref. 7, arguing for the existence of a marginal interaction as the origin of nonuniversality at the consolute point. If simulations find a coexistence of two isotropic phases at low concentrations ($m \approx -1$), then more sophisticated renormalization group techniques can be brought in to confirm or reject the mechanism for nonuniversality proposed. At present, the criticisms[11-14] of this mechanism do not help to clarify the situation, since they are based on inappropriate models or crude renormalization group schemes. For the remainder of this paper, we point out some essential differences between our Hamiltonian and others in the literature.

Caflisch et al.[11] claimed that the Hamiltonian implied in Ref. 7 is equivalent to the ordinary Ising model with NN ferromagnetic two-spin couplings. Our Hamiltonian reflects a system with two essential length scales associated with inter- and intramicellar interactions, the latter coupling a spin and all its nearest neighbors, so as to reflect different energies associated with micelle sections in different local geometries.

Reatto has proposed[12,13] an intramicellar interaction in this spirit. However, his energetics is quite distinct from ours, as a comparison between Figs. 1 and 2 shows. Indeed, the spin configurations repesenting spherical micelles and end-cap sections of rodlike micelles [cases (a) and (b) in both figures] are the same. However, the number of configurations he assigns the intramicellar energy associated with a cylindrical section of rodlike micelles is much greater than in our model (Fig. 2c versus Fig. 1c). We believe that these additional local configurations misrepresent a coarse-grained MBS in two important ways. First, an essential characteristic of aggregates is their having at least one "narrow" dimension (which is essentially the combined length of two surfactant tails). In our coarse-grained
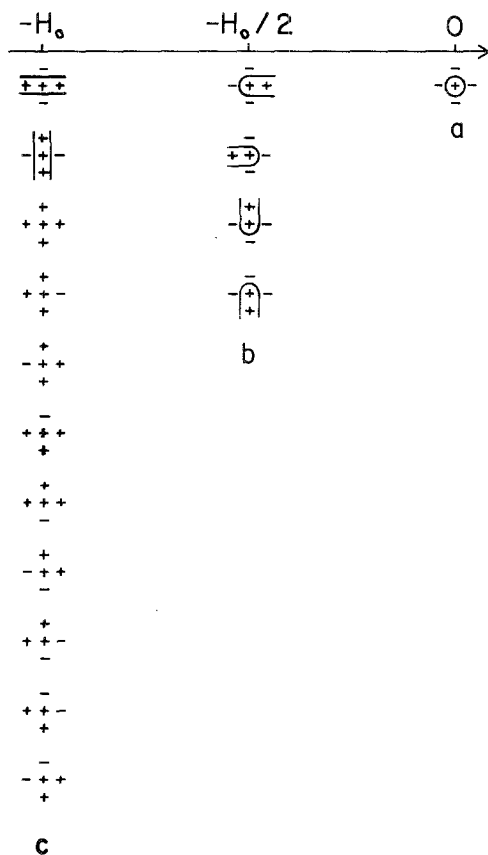

Fig. 2. Local configurations and intramicellar energies in Reatto's model. (a) A spherical micelle. (b) End-cap secions in rodlike micelles. (c) Cylindrical sections in rodlike micelles. Only configurations identical to those of Fig. 1 have the micellar interface outlined.

picture, a single $+1$ spin represents a micellar section, so that the lattice spacing *is* this "narrow" dimension. Therefore, both NN sites along at least one of the axes should be occupied by -1 spins. Second, since intramicellar energies are strongly dependent on the local geometry of surfactant packing, right-angle bending of rodlike miscelles on the length scale of the "narrow" dimension should be very unfavorable. Reatto assigns the same energy to such "bent" configurations as to unbent ones. Assigning the same energy to these extra configurations destroys local anisotropy, an essential feature of MBS with rodlike micelles. Moreover, Reatto's model does not make the distinction between length scales associated with inter- and intramicellar interactions, since his intermicellar interaction has the range of only *one* lattice spacing. For these reasons, we do not believe that Reatto's Hamiltonian is a viable model for MBS.

Crisanti and Peliti[14] pointed out correctly that recursion relations dependent on H_0 can be reproduced by starting with the ordinary Ising model and manipulating the bonds to be moved in the Migdal–Kadanoff scheme. This is a criticism of the inadequacy and uncertainty in using this scheme, showing the necessity of performing a more dependable renormalization group analysis on a more realistic Hamiltonian. We believe that the ones we proposed should be adequate for this study.

Finally, we briefly compare our model with Widom's,[17,18] also couched in the language of Ising spins and lattice gas. The latter is designed for microemulsions, which, unlike our binary mixtures, consist of three components (e.g., water, surfactant, oil). The micelles in microemulsions are swollen with the third component, and there is no natural length scale for coarse-grained representation of micellar sections such as the "narrow" micellar dimension in MBS. Since amphiphiles belonging to a single micelle may be further apart than ones in neighboring micelles, it is difficult to make the distinction between inter- and intra*micellar* interactions. Further, packing constraints on surfactants are more relaxed in microemulsions than in MBS. Consequently, micelles in microemulsions cannot be represented by just a few fixed shapes on a single coarse-grained level. Preferred local geometries in microemulsions are best described in terms of spontaneous local curvature[18,19] of the micellar interface. Thus, lattice-gas models for microemulsions[17,18] assign $+/-$ spins to water/oil regions, allowing all the amphiphiles to reside on the interface between them. Hamiltonians represent lattice analogs of spontaneous local curvature of this interface. In the limit of vanishing concentration of one of the nonsurfacant components, these models would have neither interfaces nor surfactants, instead of a viable model for MBS. Hence our model is quite distinct from lattice-gas models for microemulsions, and is useful in very different physical situations.

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NOTE ADDED IN PROOF

Fisher proposed, in *Phys. Rev. Lett.* **57**:1911 (1986), an alternative scenario where the true critical behaviour belongs to the Ising universality class and the observed nonuniversality arises from the details of crossover. He pointed out the importance of further neighbor interactions if a lattice model were to reproduce such behavior. We propose an *explicit* Hamiltonian with (effectively) *competing* interactions. The phase diagram is expected to be richer and critical behavior more difficult to predict. We hope that simulations will point a clearer direction for further analysis.

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