

A spin-1 lattice model of microemulsions at low temperatures

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Abstract. The phase diagram of a three-state microemulsion model at low temperatures is discussed. It is shown how, taking into account low-energy excitations, the ground-state phase diagram is modified and the degeneracy of a coexistence line bordering the region of lamellar phase is removed.

1. Introduction

Three-component mixtures of water, oil and amphiphiles exhibit very interesting behaviour as the temperature and concentration of the surfactant are varied. For a microscopic theory of these systems several Hamiltonians have been proposed [1–6]. In a first model, proposed by Widom [1, 2], formulated in terms of Ising variables, the three species of molecules occupy, with some constraints, the bonds of a lattice. More recently, a three-component lattice model has been proposed by Schick *et al* [3, 4] in order to illuminate some additional aspects of amphiphilic systems, among which are the microemulsion phase and the interfacial properties.

Previous studies [3, 4] based on a mean-field theory present an essential first step towards understanding the behaviour of the model. However, some features, such as the infinite degeneracy of the zero temperature state manifold occurring for some values of the amphiphile strength have not been covered by the mean-field approach.

In this paper we wish to show how one can account for fluctuations beyond the mean-field and to study rigorously, whenever it is possible, the phase diagram of the model. Namely, we use the standard low-temperature perturbation [7] in order to understand the influence of local excitations and to study the phase diagram.

The model considered is a simple three-component lattice system in dimension $d \geq 3$. To each site of a cubic lattice \mathbb{Z}^d is assigned a spin-1 variable s_i so that the values $s_i = 1, -1, 0$ correspond to the presence at site i of a molecule of water, oil, or amphiphile, respectively. The Hamiltonian is

$$\mathcal{H} = \sum_{(i,j)} J(s_i - s_j)^2 + \sum_i (Bs_i^2 - Hs_i) + \sum_{(i,j,k)} Ls_i(1 - s_j^2)s_k.$$

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The first term is the sum of pair interactions, assumed to be attractive between particles of the same kind ($J > 0$), and the second one contains the usual chemical potentials. With these two terms the Hamiltonian is a particular case of the Blume–Emery–Griffiths model [8], which describes a simple three-component mixture for the case of nearest neighbour interactions. Even though we assume that two particles of different kinds have the same pair interactions, the discussion for general pair interactions can be performed by following the same method which is used in the present work. The external field H is related to the chemical potential difference between oil and water and B is related to the chemical potential of the surfactant. The third sum extends over the sets (i, j, k) of three adjacent sites in a line and $L > 0$ is the strength of the amphiphilic interaction. This term distinguishes the molecule associated with spin 0 as an amphiphile and mimics its effect by favouring the configuration with 0 placed between + and –, all in a line.

2. Phase diagram with low-energy excitations

The *ground states* of the model are described as follows. If we assume that $L = 0$, the spins must be equal everywhere since $J > 0$. The system has three ground states, the (0), (+) and (–) states, where respectively s_i is equal to 0, +1 and –1 for all i . The energies per site in these states are

$$h^{(0)} = 0 \quad h^{(+)} = B - H \quad h^{(-)} = B + H$$

and the corresponding phase diagram is easily obtained.

The amphiphile interaction favours the configuration (+0–) on three aligned adjacent sites (i, j, k) . Such configurations appear in ground states if

$$L - 2J > 0$$

and, for this reason, we assume hereafter that this condition is satisfied. Then, at least for some values of B and H , it is clear that the system would favour having the L -bonds (or the sets of three adjacent sites) occupied as much as possible by such (+0–) configurations. This leads to a new family of ground states with a lamellar structure. To describe them more precisely we introduce some notation. We consider the planes $r(i) = \alpha_1 i_1 + \dots + \alpha_d i_d = z$, where all α 's are +1 or –1 and z is an integer. These planes will be called *diagonal planes*, they may have 2^{d-1} possible orientations. We consider the sequence of all diagonal planes of the lattice with a given fixed orientation. The configurations that assume a constant value in each plane of such a sequence will be called *layered* configurations. The *lamellar* ground states are the layered configurations obtained by putting all spins equal to 0 on every second plane of the sequence and alternatively equal to +1 and to –1 on the remaining planes. In other words, the sequence of spin values on the diagonal planes is the periodic sequence (0 + 0 – ...) of period four. This leads to $4 \times 2^{d-1} = 2^{d+1}$ equivalent (i.e. related by translations and rotations of the lattice) lamellar ground states. Their energy per site is

$$h^{(\text{lam})} = -\frac{d}{2}(L - 2J) + \frac{1}{2}B.$$

By comparing this expression with those corresponding to the other ground states we obtain the ground state phase diagram shown in figure 1.

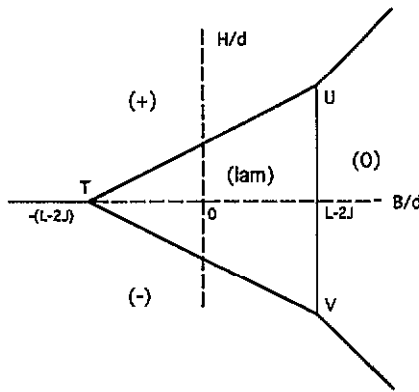


Figure 1. The ground state phase diagram.

The lamellar states are the unique ground states, for values of B and H in the triangular region

$$\frac{B}{d} < L - 2J \quad \frac{2H}{d} < L - 2J + \frac{B}{d} \quad -\frac{2H}{d} > L - 2J + \frac{B}{d}.$$

Outside this region we have the (+) state, if $H \geq 0$ and $H \geq B$; the (-) state, if $H \leq 0$ and $H \leq B$; and the (0) state, if $|H| \leq B$.

We next examine the coexistence lines of the phase diagram. On the separation line between the (0) and (lam) states, only these two states are ground states. The same situation occurs on the coexistence lines (0)/(+), (0)/(-) and (+)/(-). However, on the coexistence lines (+)/(lam) and (-)/(lam) infinitely many ground states occur. All of them have a layered structure and may be described by the sequence of spin values associated with the sequence of parallel diagonal planes. A particular role will be played by the periodic ground states associated with the periodic sequences $(0 + \dots + 0 - \dots -)$, in which $m \geq 1$ diagonal planes, where the spins are +, are separated from $n \geq 1$ diagonal planes, where the spins are -, by single planes, where the spins are 0. We use the notation (m, n) for these states of period $p = m + n + 2$. The periodic state (1,1) is the (lam) ground state considered above. The energy per site of these states is

$$h^{(m,n)} = h^{(+)} - \frac{2d}{p} (L - 2J) - \frac{2}{p} B + \frac{2(n+1)}{p} H.$$

This shows that all ground states with $(m, n = 1)$, and $(m = 1, n)$, are present, respectively, on the coexistence lines (+)/(lam) and (-)/(lam). All these states, for any m and n , are present at the triple point, where these two lines and the (+)/(-) coexistence line intersect.

Our aim is to show that the model considered, in the region $L - 2J > 0$, can be rigorously analysed at low temperatures. The phase diagram at low temperatures follows from a competition between energies of ground states taking into account additional contributions of entropies of low-energy excitations. These ideas are formalized in the Pirogov-Sinaï theory of low-temperature phase diagrams [7]. Here we will use an extension of this theory due to Bricmont and Slawny [9].

This extension concerns a mechanism of suppression of high-energy fluctuations. We first introduce some notions needed for the study of equilibrium states at low temperatures.

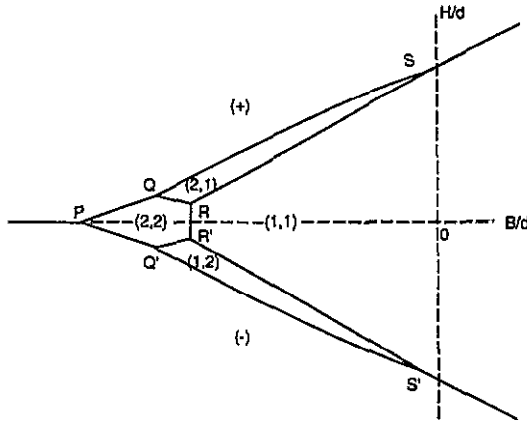


Figure 2. The sketch of the phase diagram with contributions of the lowest energy excitations taken into account.

of Λ). The activities $\varphi(Y)$ are small when the temperature is low. We use the convergent small activity expansion (in terms of the Ursell functions) to compute the free energy of the restricted ensemble. Since different ground states may have different excitations, and also different numbers of common excitations, the free energies of some of the associated restricted ensembles will be different.

Let us consider the case $E_0 = E = \max\{E_3, E_4\}$ in which all the excitations to be taken into account are of types X_1, \dots, X_4 described above. We use $f^{(m,n),E}$, or simply $f^{(m,n)}$, to denote the corresponding free energy per site when $G = (m, n)$ is one of the periodic ground states of the system. In this case, up to terms of order less than $\exp(-\beta E)$, the low-temperature expansion can be limited to the first term for each excitation considered, that is

$$f^{(m,n)} = h^{(m,n)} - \lim_{\Lambda \rightarrow \infty} (1/\beta|\Lambda|) \sum_Y \varphi(Y)$$

where $h^{(m,n)}$ is the ground state energy per site and the sum runs over the four types of excitations considered, contained in Λ and contributing to the restricted ensemble $\mathcal{E}(G, E)$ of the ground state $G = (m, n)$. Taking into account the geometric structure of these ground states, described above, we find

$$f^{(m,n)} = h^{(+)} - \frac{2d}{p} (L - 2J) - \frac{2}{p} B + \frac{2(n+1)}{p} H - \frac{2}{p} I(m \geq 2)\varphi_1 - \frac{2}{p} I(n \geq 2)\varphi_2 - \frac{1}{p} I(m = 1)\varphi_3 - \frac{1}{p} I(n = 1)\varphi_4.$$

In this formula, the first four terms correspond to the energy per site of the ground state, $\varphi_\ell = (1/\beta) \exp(-\beta E_\ell)$ for $\ell = 1, \dots, 4$, and I is the indicator of the condition shown in parentheses (it equals one if the condition is satisfied and is zero otherwise). On the other hand, for G equal to the (+) and (-) states, we have $f^{(+)} = h^{(+)}$ and $f^{(-)} = h^{(-)}$ (there are no excitations of these ground states of energies lower than E).

Having the free energies, we may draw the phase diagram for the restricted ensembles. We say that a point in the (B, H) -plane belongs to the G -state region whenever

$$t^{G,E}(B, H) = f^{G,E}(B, H) - \min_G f^{G,E}(B, H) = 0.$$

This phase diagram is schematically represented in figure 2.

The region $PQRR'Q'P$ around the point $B = -d(L - 2J)$, $H = 0$, is occupied by the restricted ensemble (2,2). For $H \geq 0$ this region is defined by the inequalities

$$H - \frac{1}{3}(dL - 2dJ + B) \leq \frac{1}{3}\varphi_2 + \frac{1}{3}\varphi_1$$

$$H + \frac{1}{3}(dL - 2dJ + B) \leq \frac{5}{3}\varphi_2 - \frac{1}{3}\varphi_1 - \varphi_4$$

$$dL - 2dJ + B \leq 2\varphi_2 + 2\varphi_1 - \frac{3}{2}\varphi_4.$$

The restricted ensemble (2,1) is present in the triangular region QRS , limited by the curve QR already described, and the two curves QS and RS , where

$$-2\varphi_1 + \frac{1}{4}\varphi_4 \leq H - \frac{1}{2}(dL - 2dJ + B) \leq \frac{2}{3}\varphi_1 + \frac{1}{3}\varphi_4.$$

Since the two bounds are inconsistent for low temperatures and $E_4 < E_1$, the region (2,1) ends at a point S , near to the point $B = 0$, $H = (d/2)(L - 2J)$. The curve SW , where

$$H - \frac{1}{2}(dL - 2dJ + B) = \frac{1}{2}\varphi_4$$

separates, together with the regions above, the (+) and (1,1) restricted ensembles. The lower part ($H < 0$) of the diagram follows by the symmetry with respect to the horizontal axis.

In the phase diagram of figure 2, the distance between the nearest curves is of order $\exp(-\beta E)$. If this order were considered to be negligible, we would only observe the region corresponding to the (2,2) restricted ensemble whose size is of order $\exp(-\beta E_2)$. At lower orders the phase diagram reduces to that for the ground states. On the other hand, the restricted ensembles (m, n) associated with the other periodic ground states belong to the coexistence curves PQS and $PQ'S'$ in figure 2. More precisely, all restricted ensembles with $m \geq 3$ and $n = 1$ coexist on the curve QS , for $m \geq 3$ and $n = 2$ they coexist on the curve PQ , and all states with $m \geq 3$ and $n \geq 3$ coexist at the point P .

3. Conclusions

The discussion presented above can be transformed into a rigorous statement about a full phase diagram (of the model with no restrictions on excitations) at low temperatures. Namely, one can show that there exists β_0 , such that for all temperatures $\beta > \beta_0$, there exists, in the plane (H, B) , an open region $\Omega(\beta)$ in the complement of the curves PQS and $PQ'S'$ of the phase diagram of the restricted ensembles (figure 2), whose distance from these curves is of order less than $\exp(-\beta E)$. In $\Omega(\beta)$ we have a complete phase diagram of the pure thermodynamic phases (extremal periodic Gibbs states of the system) which is a small deformation of the diagram of figure 2.

There are in $\Omega(\beta)$, six disjoint open regions, such that their closure jointly covers $\Omega(\beta)$, that correspond to the regions denoted (+), (-) and (m, n) with $m \leq 2$ and $n \leq 2$, in figure 2. In each of these regions there is a pure phase which is a small deformation of the associated ground state described above. The boundaries of these regions are smooth open arcs in which two distinct phases coexist. They meet, inside $\Omega(\beta)$, at two points (which correspond to the points R and R' of figure 2) in which three distinct pure phases coexist. These coexistence curves are deformations of the corresponding curves in figure 2 of order $\exp(-\beta E)$.

Moreover, the analysis developed in the present paper can be pursued by considering subsequent excitations of higher energies. This allows us to remove the degeneracy from the line PQS and obtain a rigorous full description of the phase diagram, in a corresponding region, of the system at low temperatures. This is in fact the main result of our work, which we are going to report only briefly in the following paragraphs (a more detailed discussion will be the subject of a separate publication).

First, we prove that, with appropriate definitions of the associated domains and boundaries, and for any E , all elementary excitations with energy less than E are removable. This allows us to consider restricted ensembles in which all these excitations are taken into account. We may then compute their free energy and, by using the function $t^{G,E}(B, H)$ as explained above, draw the corresponding phase diagram of the restricted ensembles. On the other hand, we prove that, for any given integer k , there is a value $E = E_k$ (which increases linearly with k), such that if all the elementary excitations with energy less than E_k are considered, then a phase diagram may be drawn that distinguishes all the regions belonging to the restricted ensembles associated with the ground states (m, n) for all m and n such that $\max\{m, n\} \leq k$. Then, as in the case of the lowest energy excitations that we have already discussed in some detail, these results lead to a rigorous statement on the equilibrium states of the system at low temperatures. Namely, one can show that there exists $\beta_0 = \beta_0(k)$ (where $\beta_0(k) \rightarrow \infty$ when $k \rightarrow \infty$) such that for all temperatures $\beta > \beta_0$, there exists in the plane (H, B) an open region $\Omega(\beta)$, in which we have a complete phase diagram of the pure thermodynamic phases, with separated regions for all pure phases (m, n) for which $\max\{m, n\} \leq k$. This phase diagram is a small deformation of the diagram of the associated restricted ensembles.

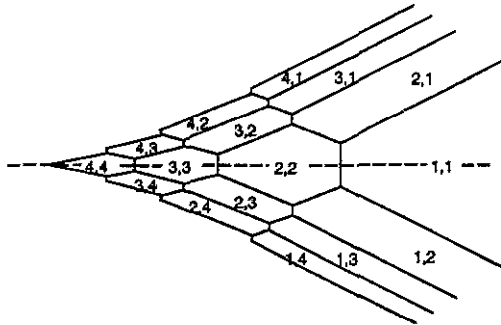


Figure 3. The sketch of a part of the phase diagram at low temperatures.

A sketch of the phase diagram is shown in figure 3. One finds that the phases are ordered according to increasing values of $(m+n)/p$ when B increases along lines parallel to the B axis while, going along lines parallel to the H axis, the values of $(m-n)/p$ increase when H increases. A first-order phase transition takes place when crossing the lines of coexistence which correspond to a discontinuity of one of the order parameters $\langle s_i^2 \rangle$ or $\langle s_i \rangle$. Notice that, as we mentioned above, when k becomes large, the inverse temperature β_0 , needed to ensure the existence of the state (m, n) as a separate phase, also becomes larger.

Some similarities between the behaviour of the model considered here and the behaviour of the axial next-nearest-neighbour Ising (ANNNI) model should be clear (see [10, 11]). However, the phase diagram that we were discussing above, is generated in the plane of

the surfactant, oil and water chemical potentials, with all interactions fixed. It yields a double infinite sequence of pure phases indexed by the values of m and n . We notice that a rigorous analysis of the model proposed by Widom [1,2] has been recently worked out by Dinaburg and Mazel [12] along lines similar to those developed in our work. They found, in the region that they were able to study, no ANNNI-like behaviour in that model, contrary to what was surmised in some earlier works (quoted in [12]). In this case, from infinitely many ground states, only a small number of pure phases persist at non-zero temperatures.

The surface tension behaves quite differently in systems with a finite and with an infinite number of ground states. In our case we find that the surface tension goes exponentially to zero as β tends to infinity. This is easy to understand: an interface between two phases does not cost any energy, but it costs the free energy of low-energy excitations. This is, actually, the basic mechanism that justifies the method used in this paper. Since the free energy of these excitations is exponentially small at low temperatures, the same is true for the surface tension.

Finally, the low surface tension between the oil-rich and water-rich phases, at a given temperature, also reflects the low free energy of the corresponding interface. In fact, since the excitations that distinguish between the ground states (m, n) and $(m - 1, n)$ have energy proportional to $k = \max\{m, n\}$, their free energy decays exponentially when k becomes large. Therefore, the surface tension between the phases (m, n) and $(m - 1, n)$ is exponentially small for large k .

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