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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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C. Buzano [a] , L. R. Evangelista [b] & A. Pelizzola [a]

[a] Dipartimento di Fisica and Istituto Nazionale di Fisica della Materia, Politecnico di Torino, Torino, Italia

[b] Departamento de Fisica, Universidade Estadual de Maringà, Maringà, Paranà, Brazil

Version of record first published: 24 Sep 2006.

To cite this article: C. Buzano , L. R. Evangelista & A. Pelizzola (1996): Structured Phases of a Three-Dimensional Vector Lattice Model for Oil-Water-Surfactant Mixtures, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 290:1, 41-48

To link to this article: http://dx.doi.org/10.1080/10587259608031890

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Mol. Cryst. Liq. Cryst., 1996, Vol. 290, pp. 41–48
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STRUCTURED PHASES OF A THREE-DIMENSIONAL VECTOR LATTICE MODEL FOR OIL-WATER-SURFACTANT MIXTURES

C. BUZANO[1], L.R. EVANGELISTA[2] and A. PELIZZOLA[1]
[1]Dipartimento di Fisica and Istituto Nazionale di Fisica della Materia, Politecnico di Torino, Torino, Italia
[2]Departamento de Fìsica, Universidade Estadual de Maringà, Maringà, Paranà, Brazil

Abstract A three-dimensional vector lattice model for a mixture of water, oil and amphiphile is considered on the simple cubic lattice. For a balanced system with equal water and oil concentrations the ground state exhibits, when the surfactant is strong, an ordered bicontinuous structure in addition to pure oil/water and pure surfactant states.
The model is transformed, integrating out exactly the surfactant orientational degrees of freedom, in an effective spin-1 model with two-, three-, five- and seven-body interactions with temperature dependent interaction strengths. This effective model is then investigated using the local mean-field approximation.
The phase diagram of the model is derived and discussed, with particular attention to the structured ordered phase. In the disordered phase a microemulsion region is also found.

Amphiphiles are molecules characterized by the presence of a polar or ionic head and a non-polar hydrocarbon tail. In a mixture with water and oil the heads of the amphiphile molecules tend to attract water, while their tails tend to attract oil, so that layers of amphiphiles will be found in between water and oil regions, drastically reducing the surface tension. For this reason amphihiles are often called also surfactants.

The surface activity of the amphihiles gives rise to very important consequences. At relatively low temperatures and high concentrations of amphiphiles structured phases are found, like the bicontinuous phase which will be discussed in the following. Such phases, often referred to also as modulated phases, have several different kind of topological arrangements, the common feature being that oil and water are always separated by sheets of amphiphile. At higher temperatures, where the mixture exhibits

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no long-range order, water and oil are still separated by fluctuating layers of amphiphile, and if their concentrations are nearly equal both components span the whole system, each one occupying a connected region in space, giving rise to a so-called microemulsion. From both the theoretical and the experimental point of view the microemulsion is identified by the presence of a maximum at non-zero wave number in the water-water structure function[1].

Among the various microscopic approaches proposed to study such systems from a theoretical point of view, a very important role is played by lattice models of three-component mixtures[2-4].

In the present paper we consider in some detail a model introduced by Ciach, Høye and Stell[4] for a mixture of water, oil and amphiphile, on a three-dimensional, simple cubic lattice. The model can be conveniently described as a spin-1 model with an additional vector degree of freedom per site. Let us first associate a spin-1 variable (z-component) $s(\mathbf{r}) = \pm 1,0$ to each site $\mathbf{r}$ of the lattice with the following meaning: $s(\mathbf{r}) = +1,0,-1$ represents a water, surfactant, oil molecule respectively. In addition, another variable $\mathbf{n}(\mathbf{r})$ is introduced to represent the surfactant orientational degree of freedom. This variable is a unit vector allowed to point toward any nearest neighbour site, and has therefore only six possible values. Furthermore, it becomes meaningless when $s(\mathbf{r}) \neq 0$. The amphiphile molecule has a hydrophilic head and a hydrophobic tail and $\mathbf{n}(\mathbf{r})$ can be thought of as the tail-to-head vector, and will be used to write the amphiphilic interaction term.

The model can be defined by specifying a Hamiltonian which is made up of several terms. First of all we have the water, oil and surfactant chemical potentials μ_w, μ_o and μ_s and the water-water, water-oil and oil-oil couplings, with energies denoted by $-\varepsilon_{ww}$, $-\varepsilon_{wo}$ and $-\varepsilon_{oo} = -\varepsilon_{ww}$, respectively. Then there is the amphiphilic coupling, with strength A, which, according to the hydrophilic character of the head of a surfactant molecule, favors configurations in which the variable $\mathbf{n}(\mathbf{r})$ points toward a water molecule. The model Hamiltonian can then be written in the form

$$\mathcal{H} = -\frac{J}{2}\sum_{\mathbf{r},\delta} s(\mathbf{r})s(\mathbf{r}+\delta) - \frac{K}{2}\sum_{\mathbf{r},\delta} s^2(\mathbf{r})s^2(\mathbf{r}+\delta) + \Delta\sum_{\mathbf{r}} s^2(\mathbf{r}) - H\sum_{\mathbf{r}} s(\mathbf{r})$$
$$-A\sum_{\mathbf{r},\delta}\left[1-s^2(\mathbf{r})\right]s(\mathbf{r}+\delta)\mathbf{n}(\mathbf{r})\cdot\delta\,, \tag{1}$$

where δ is a unit vector pointing towards nearest neighbours, $J=\frac{\varepsilon_{WW}-\varepsilon_{WO}}{2}$, $K=\frac{\varepsilon_{WW}+\varepsilon_{WO}}{2}$, $\Delta=\mu_S-\frac{\mu_W+\mu_O}{2}$ and $H=\frac{\mu_W-\mu_O}{2}$.

The Hamiltonian Equation (1) has a very interesting feature that allows it to be treated, al least in part, exactly. Since there is no direct amphiphile-amphiphile interaction one can integrate out exactly the orientational degrees of freedom $\mathbf{n}(\mathbf{r})$ and end up with an effective Hamiltonian $\mathcal{H}_{\text{eff}}$ involving only the spin variables, which can be defined by

$$\sum_{\{\mathbf{n}(\mathbf{r})\}}\exp(-\beta\mathcal{H}) = \exp(-\beta\mathcal{H}_{\text{eff}}), \tag{2}$$

where $\beta = 1/T$ and T, as customary, is the absolute temperature in units of the Boltzmann's constant. It is worth remarking here that this program has been carried out only in one and two dimensions[5,6]. In the present case the effective hamiltonian, apart from an unimportant additive constant, is given by

$$\mathcal{H}_{\text{eff}} = -\frac{J}{2}\sum_{\mathbf{r},\delta} s(\mathbf{r})s(\mathbf{r}+\delta) - \frac{K}{2}\sum_{\mathbf{r},\delta} s^2(\mathbf{r})s^2(\mathbf{r}+\delta) + \Delta\sum_{\mathbf{r}} s^2(\mathbf{r}) - H\sum_{\mathbf{r}} s(\mathbf{r})$$
$$-\sum_{\mathbf{r}}\left(1-s^2(\mathbf{r})\right)G_{\text{AMP}}(\mathbf{r}), \tag{3}$$

where

$$G_{\text{AMP}}(\mathbf{r}) = H_{001}\left(P_{001}+P_{010}+P_{100}\right)+H_{002}\left(P_{002}+P_{020}+P_{200}\right)+H_{011}\left(P_{011}+P_{101}+P_{110}\right)$$
$$+H_{012}\left(P_{012}+P_{120}+P_{201}+P_{210}+P_{102}+P_{021}\right)+H_{022}\left(P_{022}+P_{220}+P_{202}\right)$$
$$+H_{111}P_{111}+H_{112}\left(P_{112}+P_{121}+P_{211}\right)+H_{122}\left(P_{122}+P_{212}+P_{221}\right)+H_{222}P_{222}\,, \tag{4}$$

the H_{klm} are coefficients which depend only on βA (their explicit expressions are quite cumbersome and will be reported in a future publication), while setting $\mathbf{r}=(x,y,z)$ and $\Delta_x s = s(x+1,y,z)-s(x-1,y,z)$ (and similar definitions) one has

$$P_{klm} \equiv P_{klm}(\mathbf{r}) = \left(\Delta_x s\right)^{2k}\left(\Delta_y s\right)^{2l}\left(\Delta_z s\right)^{2m}. \tag{5}$$

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The effective hamiltonian we have obtained contains now multispin (up to 7 spins) interactions and, since we expect modulated phases, will be dealt with using a local mean-field approximation. Such an approximation can be stated as a variational principle, giving the free energy as a function of the local expectations $m(\mathbf{r})=\langle s(\mathbf{r})\rangle$ and $q(\mathbf{r})=\langle s^2(\mathbf{r})\rangle$. We have $F=\sum_{\mathbf{r}}(U(\mathbf{r})-TS(\mathbf{r}))$, where the local entropy is

$$S(\mathbf{r})=-\mathcal{L}\left(\frac{q(\mathbf{r})+m(\mathbf{r})}{2}\right)-\mathcal{L}(1-q(\mathbf{r}))-\mathcal{L}\left(\frac{q(\mathbf{r})-m(\mathbf{r})}{2}\right), \tag{6}$$

with $\mathcal{L}(x)=x\ln x$, and the local energy is

$$U(\mathbf{r})=-\frac{J}{2}\sum_{\mathbf{r},\delta}m(\mathbf{r})m(\mathbf{r}+\delta)-\frac{K}{2}\sum_{\mathbf{r},\delta}q(\mathbf{r})q(\mathbf{r}+\delta)+\Delta\sum_{\mathbf{r}}q(\mathbf{r})-H\sum_{\mathbf{r}}m(\mathbf{r})$$
$$-\sum_{\mathbf{r}}(1-q(\mathbf{r}))g_{\mathrm{AMP}}(\mathbf{r}), \tag{7}$$

where $g_{\mathrm{AMP}}(\mathbf{r})=\langle G_{\mathrm{AMP}}(\mathbf{r})\rangle$ can be written, according to Equation (4), as a linear combination of the functions $p_{klm}(\mathbf{r})=\langle P_{klm}(\mathbf{r})\rangle$, which in turn can be easily calculated, obtaining

$$p_{001}(x,y,z)=q(x,y,z+1)+q(x,y,z-1)-2m(x,y,z+1)m(x,y,z-1)$$
$$p_{002}(x,y,z)=q(x,y,z+1)+q(x,y,z-1)-8m(x,y,z+1)m(x,y,z-1)$$
$$+6q(x,y,z+1)q(x,y,z-1), \tag{8}$$

the corresponding equations for components x and y, and, assuming $p_{000}(x,y,z)=1$,

$$p_{klm}(x,y,z)=p_{k00}(x,y,z)p_{0l0}(x,y,z)p_{00m}(x,y,z). \tag{9}$$

Our free energy can be easily minimized with respect to $m(\mathbf{r})$ and $q(\mathbf{r})$ by standard numerical means, the only important issue being the choice of the $\mathbf{r}$ domain, which must be carefully determined depending on the phases expected. On the basis of the ground state analysis reported by Ciach[4] we expect uniform phases, like the disordered or the water/oil phases, for which $m(\mathbf{r})=m_0$ and $q(\mathbf{r})=q_0$ and a single-site domain is enough, and structured phases (at T = 0 only the bicontinuous phase is stable, while at finite temperatures lamellar phases might in principle appear), for the analysis of which one needs domains extending in one, two or three dimensions, with suitable boundary conditions.

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Before going on with the numerical investigation of the phase diagram it is however important to notice that some analytical progress can still be made in several directions (at least for $H = 0$, the case considered here), namely the determination of the critical temperature of the water/oil phase and the corresponding tricritical point, and also the determination of the Lifshitz line.

As far as the transition from the water/oil to the disordered phase is concerned, one can set $m(\mathbf{r}) = m_0$ and $q(\mathbf{r}) = q_0$ and study the free energy density of uniform phases. A standard (Landau-Ginzburg) expansion of the free energy around the disordered phase characterized by $m_0 = 0$ yields, after elimination of q_0, $F = F_0 + A_2 m_0^2 + A_4 m_0^4 + \cdots$, where A_2 and A_4 depend only on the temperature and the model parameters. The equations for the critical line and the tricritical point are then $A_2 = 0$ and $A_4 = 0$ respectively (once more the details are left for a future work).

The determination of the Lifshitz line is a bit more involved since it is based on the calculation of the low moment behaviour of the water-water structure function $S^{WW}(\mathbf{k})$. More precisely, the Lifshitz line is defined as the locus in the phase diagram at which the maximum of the water-water structure function moves away from $k = 0$, and this can be considered as a signal of the appearance of a microemulsion. We need now to expand the free energy in the fluctuations around the disordered phase; using

$$m(\mathbf{r}) = m_0 + \sum_{\mathbf{k}\neq 0} m_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

$$q(\mathbf{r}) = q_0 + \sum_{\mathbf{k}\neq 0} q_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \tag{10}$$

with $m_0 = 0$ and expanding the free energy up to second order in $m_{\mathbf{k}}$ and $q_{\mathbf{k}}$ we obtain

$$F = F_0 + \sum_{\mathbf{k}\neq 0} (\alpha_{\mathbf{k}} m_{\mathbf{k}} m_{-\mathbf{k}} + \beta_{\mathbf{k}} q_{\mathbf{k}} q_{-\mathbf{k}}) + \ldots, \tag{11}$$

where F_0 is the free energy of the uniform disordered phase, while $\alpha_{\mathbf{k}}$ and $\beta_{\mathbf{k}}$ are known functions of q_0, the temperature and the model parameters. It follows that

$$\langle m_{\mathbf{k}} m_{-\mathbf{k}} \rangle = \frac{T}{2\alpha_{\mathbf{k}}}$$

$$\langle q_{\mathbf{k}} q_{-\mathbf{k}} \rangle = \frac{T}{2\beta_{\mathbf{k}}}, \tag{12}$$

and the water-water structure function is therefore

$$S^{WW}(\mathbf{k}) = \left\langle \frac{q_{\mathbf{k}} + m_{\mathbf{k}}}{2} \cdot \frac{q_{-\mathbf{k}} + m_{-\mathbf{k}}}{2} \right\rangle = \frac{1}{4}\left(\langle q_{\mathbf{k}} q_{-\mathbf{k}} \rangle + \langle m_{\mathbf{k}} m_{-\mathbf{k}} \rangle\right) = \frac{T}{8}\left(\alpha_{\mathbf{k}}^{-1} + \beta_{\mathbf{k}}^{-1}\right), \qquad (13)$$

with an isotropic low moment behaviour: $S^{WW}(\mathbf{k}) = S_0^{WW} + S_2^{WW} k^2 + O(k^4)$, such that the Lifshitz line is given by the condition $S_2^{WW} = 0$.

We have analyzed the model in the case $K = J$ and $A = 2J$, that is for strong enough surfactant to obtain structured phases. An evaluation of the ground state shows that this threshold occurs at $A/(J+K) = 0.5$.

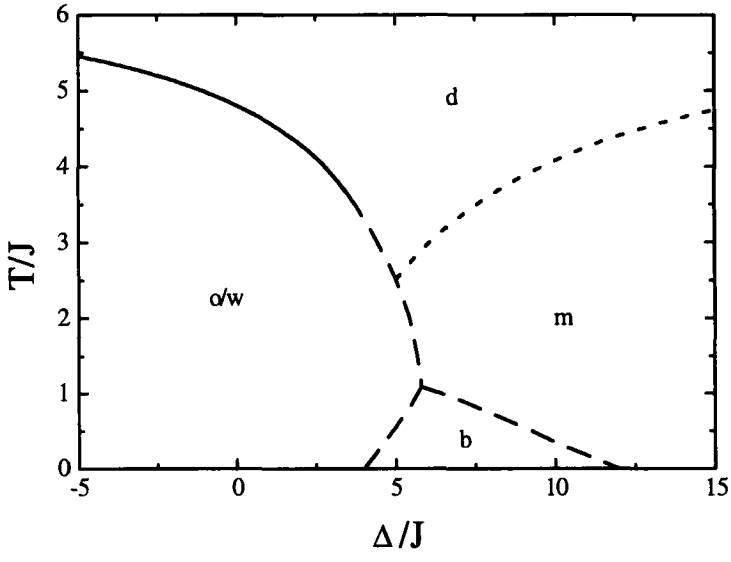

FIGURE 1 Phase diagram in the temperature vs. surfactant chemical potential plane. o/w denotes the oil-water rich phase, b the ordered bicontinuous phase, d the disordered phase and m the microemulsion region inside it.

In Figure 1 the phase diagram is plotted in the temperature vs. Δ (the surfactant chemical potential) plane.

The dashed lines represent first order transitions and the solid lines second order transitions. The dotted line represents the Lifshitz line, which in the disordered phase separated the disordered structured fluid (microemulsion) from the usual disordered

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one. It must be kept in mind that this is not a line of phase transitions. At lower temperatures we find an oil/water rich phase and a structured bicontinuous phase separated by a first order line. The oil/water and disordered phases are separated by a line of phase transitions which is partly second and partly first order, the Lifshitz line meeting the first order part. Thus we have the characteristic oil-water-microemulsion coexistence observed experimentally in many systems[7]. The bicontinuous ordered phase is separated by a first order transition from the microemulsion region and a four-phase (o/w/b/m) point exists at $\Delta/J = 5.82$, $T/J = 1.09$.

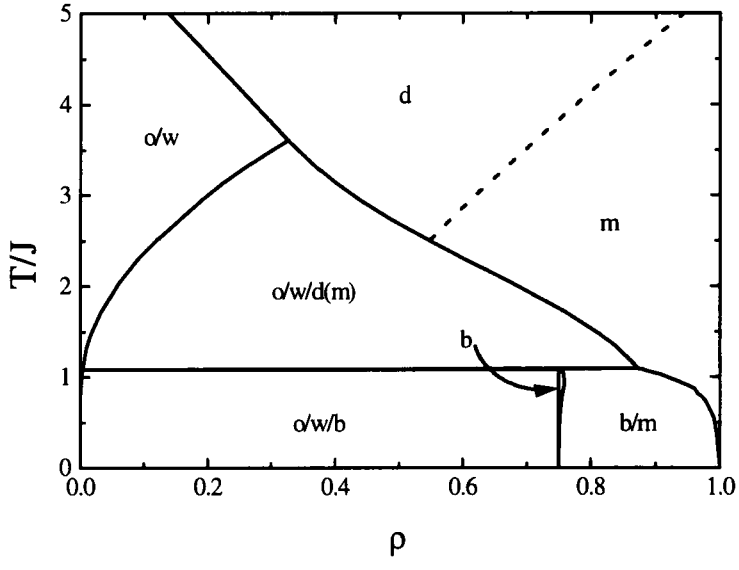

FIGURE 2 Phase diagram in the temperature vs. surfactant concentration plane. A/B, A/B/C ... denote coexistence of two or more phases A, B, ...

In the bicontinuous ordered phase oil and water molecules form two diamond lattices, shifted with respect to each other, and the surfactant particles form a net of oriented molecules placed in between the two diamond lattices. This phase of mutually intertwined oil and water-rich channels separated by a surfactant monolayer forming a surface of very large area is relevant for several physical properties like electrical conductivity and oil and water diffusivity.

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In Figure 2 the phase diagram is plotted in the T vs. $\rho = 1 - q$ (mean surfactant concentration) plane, with the first order line replaced by coexistence regions.

The present model has been previously analyzed by Ciach[4] in the case $K = J$ by means of an ordinary mean-field approach, and the case corrisponding to our Figures 1 and 2 was explicitly considered. Our improved treatment which integrates out exactly the surfactant orientational degrees of freedom gives some significant modifications in the location of the Lifshitz line and the tricritical point.

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REFERENCES

1. G. Gompper and M. Schick, in Phase Transitions and Critical Phenomena, vol. 16, ed. by C. Domb and J. L. Lebowitz (Academic, London, 1994).
2. M. W. Matsen and D. E. Sullivan, Phys. Rev. A, 41, 2021 (1990); J. Physique II, 2, 93 (1992); Phys. Rev. E, 51, 548 (1995).
3. M. Schick, Physica A, 172, 200 (1991); J. Lerczak, M. Schick and G. Gompper, Phys. Rev. A, 46, 985 (1992).
4. A. Ciach, J. S. Høye and G. Stell, J. Phys. A, 21, L777 (1988); J. Chem. Phys., 90, 1214 (1989); 95, 5300 (1991); A. Ciach and J. S. Høye, *ibid.* 90, 1222 (1989); A. Ciach, *ibid.* 96, 1399 (1992).
5. P. A. Slotte, Phys. Rev. A, 46, 6469 (1992).
6. M. S. Skaf and G. Stell, J. Chem. Phys., 97, 7699 (1992).
7. Physics of Amphiphilic Layers, ed. by J. Meunier, D. Langevin and N. Boccara, (Springer, Berlin, 1987).