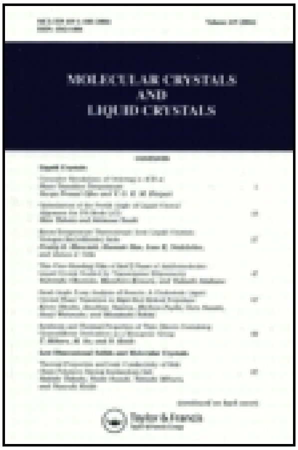

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Micellar Solutions and Microemulsions on a Lattice

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An alternative approach to micellar solutions and microemulsions, based on the Ising and Baxter decorated models, is proposed.

Keywords: micellars, microemulsions, lattice, phase transitions

The most successful microscopic approach to the surfactant-liquids problem may be thought to be lattice theories. Wheeler and Widom[1] were the first to consider such a theory, based on Ising spin-½ model. Now most of the papers deal with Ising spin-I model,[2–5] two different interpretations being used, namely, surfactant or liquids atoms are identified as lattice bonds or sites. The alternative theory, using decorated lattice model, is presented in this work.

For the beginning we consider the following expression for Hamiltonian

$$\hat{H} = -\frac{J + J_1}{2}\sum_{i,j}\sigma_i\sigma_j - \frac{J - J_1}{2}\sum_{i,j}\sigma_i S_{ij}\sigma_j - H\sum_i \sigma_i - \mathcal{H}\sum_{i,j} S_{ij} - \mathcal{F}\sum_{i,j} S_{ij}\sigma_i \qquad (1)$$

decorated Ising-model Hamiltonian[6,7] on a square lattice. Let the two values of the Ising spin $\sigma_i = \pm I$ describe two different kinds of liquid molecules A or B, and the decoration spin $S_{ij} = \pm I$, disposed on the bonds, describe the absence or presence of the impurity molecule. It is natural to define the impurity as a surfactant molecule if it's energy is minimal when bonds are occupied by liquid molecules of different kind, i.e., $J_1 < 0$.

Thermodynamical potential Ω of the system with the Hamiltonian (I) may be written in the following form[6]

$$\Omega = -\frac{T}{N}\ln Sp\left\{\exp\left(-\frac{\hat{H}}{T}\right)\right\} = \Omega_{is}(J', H') - TL \qquad (2)$$

where Ω_{is} is the Ising thermodynamical potential with $J' = J_1 + J/2 + TL_2$, $H' = H + 4TL_1$, and N-number of the bonds.

$$L = \frac{I}{2} \ln 2Ch\left(\frac{J - J_1}{2T} - \frac{\mathcal{H}}{T}\right)$$

$$+ \frac{I}{4} \ln 4Ch\left(\frac{J - J_1}{2T} + \frac{\mathcal{H}}{T} + \frac{2\mathcal{F}}{T}\right) Ch\left(\frac{J - J_1}{2T} + \frac{\mathcal{H}}{T} - \frac{2\mathcal{F}}{T}\right)$$

$$L = \frac{I}{4} \ln 2Ch\left(\frac{J - J_1}{2T} + \frac{\mathcal{H}}{T} + \frac{2\mathcal{F}}{T}\right) - \frac{I}{4} \ln 2Ch\left(\frac{J - J_1}{2T} + \frac{\mathcal{H}}{T} - \frac{2\mathcal{F}}{T}\right)$$

$$L = -\frac{I}{2} \ln 2Ch\left(\frac{J - J_1}{2T} - \frac{\mathcal{H}}{T}\right)$$

$$+ \frac{I}{4} \ln 4Ch\left(\frac{J - J_1}{2T} + \frac{\mathcal{H}}{T} + \frac{2\mathcal{F}}{T}\right) Ch\left(\frac{J - J_1}{2T} + \frac{\mathcal{H}}{T} - \frac{2\mathcal{F}}{T}\right) \quad (3)$$

The average value of spin $\langle S_{ij}\rangle$, the S-lattice magnetization in a system considered is connected with the impurity concentration c:

$$\mathcal{M} = -\frac{\partial\Omega}{\partial\mathcal{H}} = \left\langle S_{ij}\right\rangle = (I - 2c)$$

For free energy $F_c = \Omega - \mathcal{H}\ \partial\Omega/\partial\mathcal{H}$ in the case of $\mathcal{F} = 0$, $H = 0$ we obtain the results first presented by Lushnikov[7]

$$F_c = -TF((I - \xi)y^2 + \xi v^2) + Tc \ln \xi$$

$$+ T(I - c) \ln (I - \xi) - cJ_1 - (I - c)J \quad (4)$$

where ξ should be determined from

$$-\frac{c}{\xi(v^2 - y^2)} + \frac{I - c}{(I - \xi)(v^2 - y^2)} + F'((I - \xi)y^2 + \xi v^2) = 0 \quad (5)$$

and

$$F(\eta) = \frac{I}{4}\ln\eta(I-\eta^2) + \frac{I}{8_\pi}\int_0^{2\pi}\ln(A-\cos\varphi+\sqrt{(A-\cos\varphi)^2-I})d\varphi$$

$$A = \frac{(I+\eta^2)^2}{2\eta(I-\eta^2)}, \qquad \Omega_{is} = -TF - J$$

$$y = \exp\left(-\frac{J}{T}\right), v = \exp\left(-\frac{J_1}{T}\right), \eta = \exp\left(-\frac{2J'}{T}\right) = (I-\xi^2)y^2 + \xi v^2 \qquad (6)$$

Phase diagram is presented on Figure 1 in the case of $J > 0, J_1 < 0$. Singularities of the $F(\eta)$ function at $\eta_c = \sqrt{2} \pm I$ result in phase transition lines, starting at the point $c = 0$, $T_c = 2J/\ln(\sqrt{2}+I)$ (Ising ferromagnetic phase transition) or $c = I$, $T_c = -2J_1/\ln(\sqrt{2}+I)$ (antiferromagnetic case).

Let us show that in a ferromagnetic order region (or in the region of two liquids coexistence) there exist different phases. For this purpose we solve equation (5) using the low-temperature expansion of $F(\eta) = I/2\ \eta^4 \cdot c$ being nonzero, and T being negligibly small, the second term in (5) vanishes and the result is $c = 2\eta^4$ or $\xi = \eta v^{-2} = c/2^{1/4}\ v^{-2}$, hence, for the free energy we obtain:

$$F = \frac{I}{2}\left(T\frac{c}{2}\ln\frac{c}{2e} + 4J_1\frac{c}{2} + 4J\frac{c}{2}\right) - J \qquad (7)$$

The expression in brackets represents the free energy (per site) of a gas of the particles with intrinsic energy $4(J_1 + J)$ and concentration $c/2$. Such a particle is constructed of the inverted $\sigma-$ spin surrounded by four impurities, and naturally may be interpreted as a micelle in our model.

In the case $3J + J_1 > O$ expression (7) is valid at low temperature, until $c \sim \exp(8J_1/3T)$ (region I Figure 1). If $c \gtrsim \exp(8J_1/3T)$ the solution of (5) is $\xi = c$ (third term in (5) is small) and

$$F_c = -J + c(J - J_1) + Tc\ln c + T(I-c)\ln(I-c) \qquad (8)$$

is the free energy of impurity gas without inverted σ-spins, i.e. $c = \exp(8J_1/3T)$ is the critical micelle concentration (CMC). Physical reason of micellar destruction is the increasing of the entropy in the impurity gas phase.

If $3J + J_1 < 0$ another physical mechanism is working. Entropy rise is due to redistribution of the impurities on expanded surface caused by thermal σ-fluctuations. The solution of (5) takes the form $\xi = 2cv^{-2}y^{-6}$ which gives:

$$F_c = -J - \frac{T}{2}\exp\left(-8\frac{J}{T}\right) + c(7J + J_1) + Tc\ln\left(\frac{c}{2e}\right) \qquad (9)$$

This expression shows that the impurity correlates with inverted σ-spin, and this

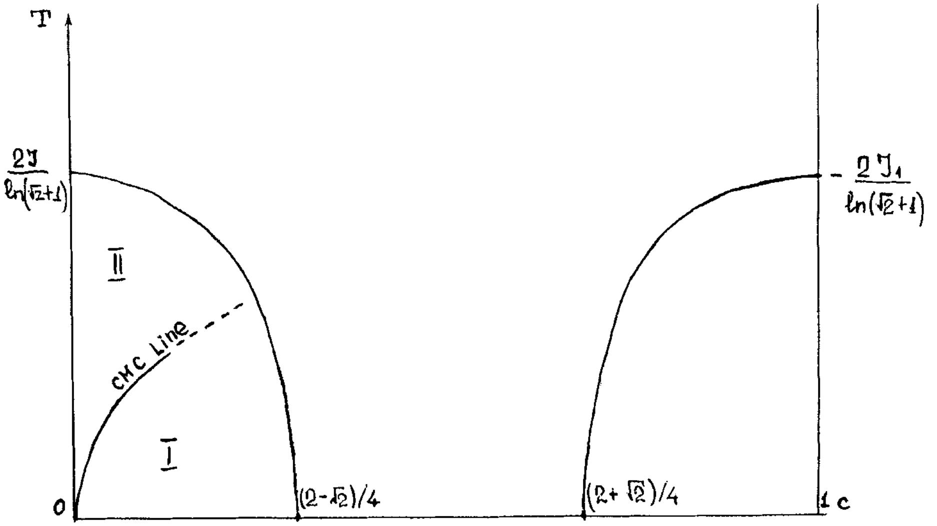

FIGURE 1 Phase diagram of decorated Ising model.

phase may be called the "strongly polarized gas" or the "incomplete micelle phase". It exists in the region II (Figure 1), but the boundary is now given by the line $c \approx \exp(-8J/T)$. It should be noted that in both cases of the micellar destruction crossover behaviour takes place.

Isomorphism of the decorated Ising model and Ising model makes it possible to connect σ-operators mean values in these models

$$\left\langle \sigma_i \right\rangle = M(J, J_1, H, \mathcal{H}) = M_0(J', H')$$
$$\left\langle \sigma_i \sigma_j \right\rangle = P(J, J_1, H, \mathcal{H}) = P_0(J', H') \qquad (10)$$

where subscript zero applies to Ising model.

More complicated expressions appear for mean values containing S_{ij}, but the simplest ones, such as $\mathcal{M} = \langle S_{ij} \rangle$, $\mathcal{P} = \langle \sigma_i S_{ij} \sigma_j \rangle$, $Q = \langle S_{ij} \sigma_i \rangle$ also may be expressed through M_0, P_0, for example ($\mathcal{F} = 0$)

$$\mathcal{P} = \frac{I - P_0(J', H')}{2} \operatorname{th}\left(\frac{J - J_1}{2T} - \frac{\mathcal{H}}{T}\right) + \frac{I + P_0(J', H')}{2} \operatorname{th}\left(\frac{J - J_1}{2T} + \frac{\mathcal{H}}{T}\right) \qquad (11)$$

In the case $H = \mathcal{F} = 0$ σ-operators mean values depend on $\eta = \exp(-2J'/T)$

only. The η = const isomorphism line, or, in other words, constant value σ-correlators line runs from T-axis point $T = -2J/\ln\eta$ to c-axis point $c = \eta F'(\eta)$, as it is shown in Figure 2. Small η and T give rise to the appearance of micelles, i.e. single σ-spin inversion. While the value of η is increased the more complicated σ-configurations appear. But at low temperatures $\mathscr{P} = I$, i.e. all the impurities stick to a surface. If the surface is sufficiently expanded such a phase may be interpreted as microemulsion. The crossover behaviour on η = const line transforms microemulsion to the Ising model critical fluctuations in a way, that a narrow T critical fluctuations region corresponds to a wide c microemulsion region. It should be noted that if the isomorphic variables $\mathscr{H}$, T are used, microemulsion still may be interpret as the critical fluctuations for low J', and the critical T region is narrow, in accordance with isomorphism (see $\mathscr{H}$ = const line on Figure 2). Isomorphism also permits us to define microemulsions cluster size. The constant value $\langle\sigma_i\sigma_j\rangle$ on η = const line, induces the correlations radius r_c defined by $\langle\sigma_i\sigma_j\rangle \sim \exp(-|i - j|/r_c)$ to be constant too. In Ising model r_c is the size of the σ-inverted clusters. On the η = const line all σ-configurations contribute equally and therefore r_c may be also interpreted as the microemulsion clusters size.

Ising model surface tension satisfies $\sigma/T = r_c$ relation, hence, the condition r_c = const on isomorphism line reduces significally microemulsion surface tension.

Crossover behaviour, for instance of $\mathscr{P}$, leads one to consider the possibility of the other phase transitions, besides the Ising one. The vanishing of the corresponding generating terms in Hamiltonian gives the trivial results, as a consequence of the high Hamiltonian symmetry. This symmetry may be broken spontaneously, when higher order terms are being introduced. Physically this means more complex

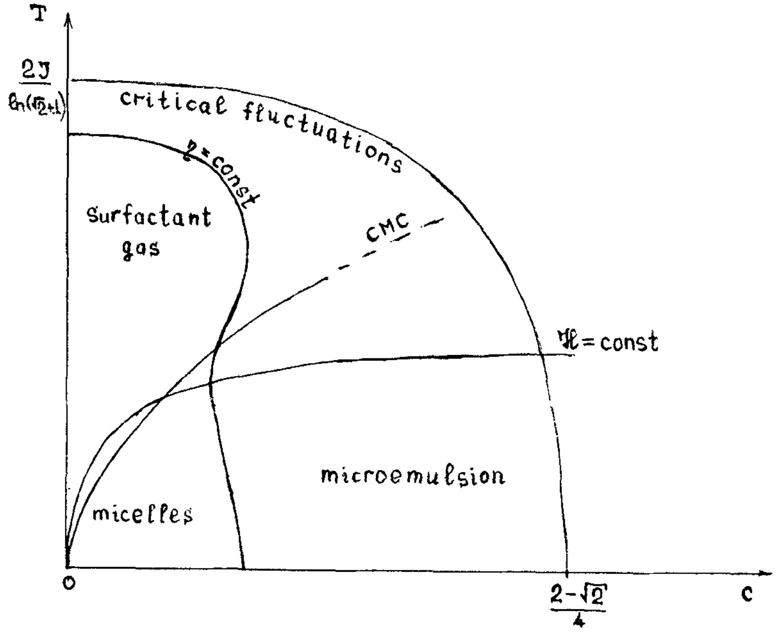

FIGURE 2 Low-temperature phases.

interaction in the system. It is natural to do it basing on the eight-vertex Baxter model[8] decorating it in the Ising model manner (I).

$$\hat{H}_{D8} = -\frac{J+J_1}{2}\sum_{i,j}\sigma_i\sigma_j - \frac{J-J_1}{2}\sum_{i,j}\sigma_i\sigma_j S_{ij} - \mathcal{H}\sum_{i,j} S_{ij}$$

$$- H\sum_{i} {}_{i} - J_{2}\sum_{i,k} {}_{i}\,{}_{k} - J_{4}\sum_{i,j,k,l} {}_{i}\,{}_{j}\,{}_{k}\,{}_{l} \qquad (12)$$

Here i,j,k,l denote the sites of the quadratic cell. As before the relations (2),(3) remain valid, $\Omega_{is}(J', H')$ being substituted by $\Omega_8(J', H', J, J)$. Low-temperature analysis shows that in the case of strong surface activity (J_2, J_4 are small) there exist both micellar and microemulsion phases, but the CMC line now is defined from the following condition $3J + J_1 = -4J_2 - 4J_4 - H$. If H (chemical potential of liquid molecules A or B) acting on σ-particles is zero and J' – the effective $\sigma - \sigma$ interaction or the external field in a Baxter model also vanishes, the system has a low-temperature phase transition at $T \sim J_2, J_4$ leading to three phase coexistence.[8] Two of them are Ising-like ferromagnetic states with micellar and microemulsion structure, and the third is Ising antiferromagnetic-like state, which is surfactant rich. This phase we interpret as the middle-phase.

The low-temperature phase diagram is presented on Figure 3. The three phase

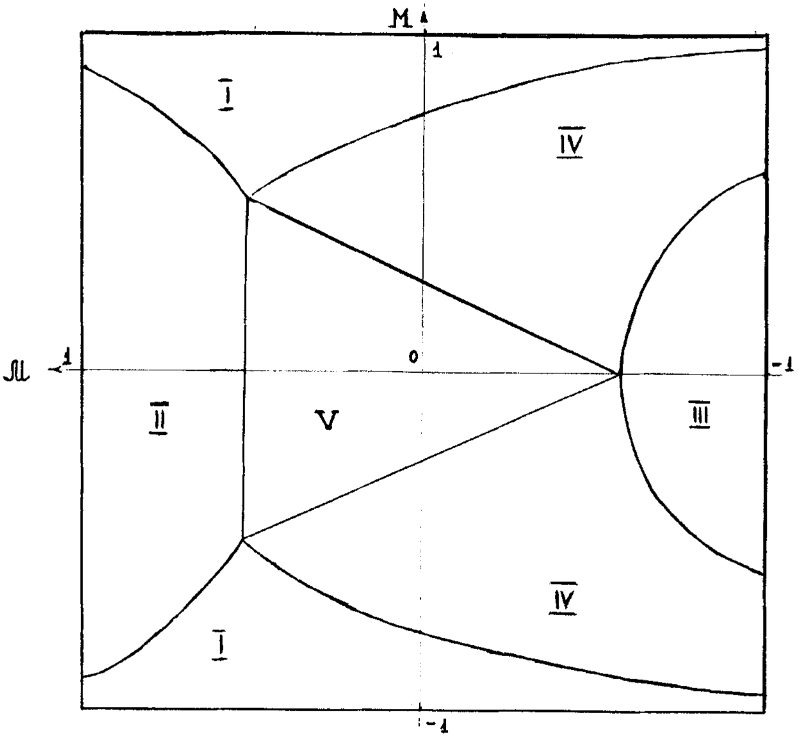

FIGURE 3 Low-temperature phase diagram of decorated Baxter model.

coexistence takes place in region V. II, IV-two phase coexistence regions, I and III-ferromagnetic and antiferromagnetic phase regions.

In conclusion, let us summarize the results of this work:

1. Ising and Baxter decorated models are proposed for liquids-surfactant system's description.
2. It's shown, that low-temperature phases contain the micellar and monomer surfactant solutions.
3. The correspondence between the critical fluctuation and microemulsion is demonstrated, the microemulsion cluster size is equal to correlation radius.
4. Antiferromagnetic phase, coexisting with ferromagnetic one because of spontaneously broken symmetry, arising from vanishing of effective interaction ($J' = 0$), is supposed to be a middle-phase.

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