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A LATTICE GAS MODEL FOR MICROEMULSIONS

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Résumé. — On étudie les propriétés d'un réseau de spins de type similaire à celui d'Ising. Il présente une transition d'une phase homogène à une phase séparée en fonction de la concentration de surfactant similaire au comportement observé lors de l'apparition de microémulsions. Lorsqu'on néglige les interactions directes entre les molécules de surfactant, le modèle est identique à un modèle d'Ising avec des interactions effectives fonctions de la concentration de surfactant. On prévoit un diagramme de phase de type liquide binaire avec des indices d'Ising renormalisés près du point critique à température constante. On suggère que les microémulsions doivent être traitées comme des systèmes avec des paramètres d'ordre couplés : le scalaire de type liquide binaire est couplé au surfactant de caractère vectoriel qui interagit avec les gradients de densité. Le rôle des interactions entre molécules de surfactant ainsi que l'effet des interactions à longue distance sont brièvement discutés selon cette approche.

Abstract. — A decorated lattice gas model is described which exhibits a transition from the phase-separated to the homogeneous state as the concentration of a surfactant is changed, in agreement with observed microemulsion behaviour. The model also has ordered mesophase regions for suitable concentrations. When direct surfactant interactions are neglected the model can be mapped onto an Ising model with effective interactions depending on the surfactant concentration. A binary liquid type of phase diagram with renormalized Ising indices near the critical point in the constant-temperature plane is predicted. It is suggested that microemulsions should be treated as systems with coupled ordered parameters, the underlying binary liquid scalar being coupled to a vector-like surfactant interacting with the density gradients. The role of surfactant-surfactant interactions and long range interactions are discussed briefly from this point of view.

The purpose of this note is to present a simple model for the microemulsion transition [1, 2] based on phenomenological considerations. Our underlying assumption in constructing the model is that these systems should be regarded as binary liquid mixtures modified by a vector-like surfactant which interacts with the concentration gradients. We construct a simple lattice gas model with these properties. The model predicts a microemulsion type of transition with a line of critical points and renormalized Ising indices.

In relating these predictions to physical systems one has to check whether qualitatively important simplifications have been incorporated into the model. We discuss this briefly. A different attempt to relate microemulsions to a more general classification of phase transitions was made recently by Skoulios [3].

Consider a lattice fully covered with two types of atoms, say A and B. For simplicity we only consider

n.n. interactions in the initial discussion. This restriction will be removed, in part, later. We describe the surfactant as a property of the (n.n.) bonds. The bond can be in three states. It can be empty-with no surfactant. If there is a surfactant on the bond we allow two orientations to describe the fact that a surfactant has a preferred orientation at an interface but not otherwise.

Describing the lattice states by an Ising spin ($\sigma = \pm 1$) and the bond states by a 3-state decorating spin ($\tau = 0, \pm 1$) we can write the energy per bond as

$$E_{ij} = \frac{1}{8}(1 - \tau_{ij}^2) [(1 + \sigma_i)(1 + \sigma_j)e_1 + (1 - \sigma_i)(1 - \sigma_j)f_1 + 2(1 - \sigma_i\sigma_j)g_1] + \frac{1}{4}\tau_{ij}^2 [(1 + \sigma_i)(1 + \sigma_j)e_2 + (1 - \sigma_i)(1 - \sigma_j)f_2] + \frac{1}{8}(\tau_{ij}^2 - \tau_{ij}) [(1 + \sigma_i)(1 - \sigma_j)g_2^+ + (1 - \sigma_i)(1 + \sigma_j)g_2^-] + \frac{1}{8}(\tau_{ij}^2 + \tau_{ij}) [(1 - \sigma_i)(1 + \sigma_j)g_2^+ + (1 + \sigma_i)(1 - \sigma_j)g_2^-] \quad (1)$$

The first term on the r.h.s. of equation (1) describes the interactions when there is no surfactant on the bond ($\tau_{ij} = 0$). In the brackets e_1 is the AA interaction energy, f_1 the BB interaction energy and g_1 the AB

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interaction. The second term describes the, in general modified, AA and BB interactions when there is a surfactant on the bond. Finally the last two terms describe the AB interaction for the two orientations ($\tau = \pm 1$) on the bond. All energies (e_i, f_i, g_i) are in units of $k_B T$. The partition function is

$$Z = \sum_{\tau_{ij}, \sigma_i} \exp - \left[\sum_{\text{bonds}} (E_{ij} + \mu_s \tau_{ij}^2) + \sum_i h_L \sigma_i \right] \quad (2)$$

where the chemical potential μ_s determines the concentration of surfactant and h_L the relative concentration of A and B on the lattice. Note that we have neglected any explicit interactions between surfactant molecules (i.e. decorating spins). The importance of this approximation will be discussed below. The summation over τ_{ij} is trivial. The result can be written in Ising form

$$Z = \sum_i \exp - \sum_b F_{ij} - \sum_i h_L \sigma_i \quad (3)$$

where

$$F_{ij} = -J \sigma_i \sigma_j - H(\sigma_i + \sigma_j) - G \quad (4)$$

and

$$J = \frac{1}{4} \ln \left[\frac{(e^{-e_1} + 2e^{-(e_2+\mu_s)})(e^{-f_1} + 2e^{-(f_2+\mu_s)})}{[e^{-g_1} + (e^{-g_2^+} + e^{-g_2^-})e^{-\mu_s}]^2} \right] \quad (5a)$$

$$H = \frac{1}{4} \ln \left(\frac{e^{-e_1} + 2e^{-(e_2+\mu_s)}}{e^{-f_1} + 2e^{-(f_2+\mu_s)}} \right) \quad (5b)$$

$$G = \frac{1}{4} \left[\ln(e^{-e_1} + 2e^{-(e_2+\mu_s)}) + \ln(e^{-f_1} + 2e^{-(f_2+\mu_s)}) + 2 \ln(e^{-g_1} + (e^{-g_2^+} + e^{-g_2^-})e^{-\mu_s}) \right] \quad (5c)$$

The decorated lattice gas thus maps exactly onto an Ising model with the effective interactions of eq. (4). The phase diagram, the correlation functions, and the free energy can be read off from those of the Ising model with the appropriate constraints.

As a function of μ_s the effective interaction J changes continuously from

$$J_1 = \frac{1}{4}(2g_1 - e_1 - f_1) \quad (6a)$$

for $\mu_s = +\infty$ (no surfactant) to

$$J_2 = -\frac{1}{4} \{ (e_2 + f_2) + 2 \ln [(e^{-g_2^+} + e^{-g_2^-})/2] \} \quad (6b)$$

for $\mu_s = -\infty$.

The physically interesting case is when J_1 is positive and large

$$J_1 > J_c \quad (7)$$

where J_c is the value of J at the Ising model Curie point. We also want the surfactant to favour AB pairs so that we assume

$$J_1 > J_2. \quad (8)$$

It is convenient to consider the phase diagram on the $\mu_s - C_A$ plane (at constant temperature). We assume that the parameters are such that J is a monotonic function of μ_s (4). The diagram is then similar to that of the magnetic system on the M-T plane. The only real difference is that J can change sign. If J_2 is sufficiently negative

$$J_2 < -J_c \quad (9)$$

this leads to an ordered (antiferromagnetic) region for a range of concentrations and sufficiently negative μ_s . We are mainly interested in the transition from the (ferromagnetic) two-phase regime to the homogeneous phase. As for a binary mixture this is usually first order and has a critical point at

$$C_A = C_c (= \frac{1}{2}); \quad \mu_s = \mu_c(T) \quad (10)$$

where μ_s is defined by

$$J(\mu_c, T) = J_c. \quad (11)$$

In the vicinity of the critical point one predicts Ising indices for the critical behaviour. The indices are however renormalized by the constraint on the density of surfactant [5-7]. Quite generally one has

$$C_s \sim \frac{\partial F(\mu_s, C_A)}{\partial \mu_s} \propto \frac{\partial F}{\partial J}(J, C_A) + \text{Regular terms} \quad (12)$$

so that near μ_c

$$C_s - C_s^c \sim (\mu_c - \mu_s)^{1-\alpha}; \quad C_A = C_c, \quad \mu_s < \mu_c \quad (13)$$

where α is the specific heat index. We shall not discuss the somewhat more complex behaviour for $C_A \neq C_c$ here. For $\alpha > 0$ equation (13) implies a renormalization of the indices when C_s rather than μ_s is the independent variable [5-7].

In discussing microemulsions one is mainly interested in the correlation function of the concentration. Near the critical point the fluctuations should be large and dominated by a coherence length

$$\xi(C_s) \sim (C_s - C_s^c)^{-\frac{\nu}{1-\alpha}}. \quad (14)$$

One predicts fairly long wave fluctuations (i.e. large regions which are predominately of one liquid) in the isotropic phase near the critical point. The surfactant will be concentrated at the A-B boundaries when $g_2(J_2)$ is large and negative.

Intuitively it seems difficult to associate microemulsions with the fluctuations in a binary mixture. One tends to think of such fluctuations as smooth and continuous while the interfaces between the two liquids in microemulsions are presumably sharper and the A and B regions are expected to be relatively pure and compact on a microscopic scale [2]. We believe

that the model can be made more realistic in this sense by two generalizations :

a) Quite generally the coherence length ξ only determines the long distance behaviour of the correlation function. The microscopic short distance behaviour is determined by the physical range of the interactions and by the lattice spacing (or hard core radius). In the n.n. model we have considered the only microscopic distance is the lattice distance so that no large correlated regions are predicted far from the transition. One can however add relatively long range attractive interactions (of range ξ_0) to the energy given by equation (1) while retaining the decoration only on the nn bonds. Such a model can also be mapped onto an Ising model. The main features of our argument (e.g., equations (13) and (14)) remain valid [8]. The short range correlation functions are however modified. Configurations with more compact A and B regions over the range of the interaction should be favoured. The structure of the ordered state is also modified.

b) A much more serious modification is the introduction of surfactant repulsions. These are certainly important physically. Their effect on the short range correlation functions will favour compact spherical regions. When they are included the mapping onto the Ising model no longer holds. The effect of the constraints on the critical behaviour might become much more complex [7, 9, 10] and the critical point may disappear.

The neglect of these interactions is probably the most serious defect of the simple lattice gas model. It is also curious that the vector character of the surfactant plays no real role when interactions are not included.

c) It should also be noted that the model is symmetrical between the two curvatures of the interface

expect through the constraints on the concentrations. This may be unrealistic. It is believed [11] that the preference for a definite curvature (convex towards A or B) plays an important role in determining the lyotropic mesophase structures. Microemulsions are also asymmetrical in this sense. This is presumably related to b).

d) Long range interactions may also be important in the ordered phases.

We believe that the limitations cited under # b and c constitute serious shortcomings. We have not succeeded in devising any simple surfactant interactions which could be incorporated in the lattice gas model without losing its usefulness. It is however fairly easy to do this in a phenomenological Landau type theory [12]. The inclusion of these terms seems to be essential in obtaining a realistic description of the ordered mesophases. They do not seem to play any important role near the microemulsion transition considered here. We therefore believe that the discussion of microemulsions in terms of the present model is meaningful.

Finally we would like to suggest that lyotropic mesophases (e.g. soap-water systems) should probably also be described using similar concepts. It is well known that the lipid regions in such systems are, to a good approximation, liquids. Surface effects, resulting from the fact that the polar head and the lipid chain belong to the same molecule, are relatively unimportant [3], at least energetically. The constraints on the densities are however much more stringent so that the transition region considered here is not physically accessible.

A detailed discussion using a Landau type free energy will be presented separately.

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