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LETTER TO THE EDITOR

Microscopic model for microemulsions

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Abstract. We introduce a new microscopic model for microemulsions. The model applies to continuum fluids as well as to lattice systems. In a mean-field treatment we show that, below a critical temperature, a microemulsion is formed. Different geometrical structures of the microemulsion (lamellar, tubular and cubical) also appear. Explicit expressions for the surface tension at the three-phase coexistence are found for temperatures equal and close to zero. The surface tension is either zero or very low, depending on details of the model.

There has been an increasing interest in studying the properties of microemulsions and developing theories based on statistical mechanics to explain the special features of such systems. Basically such systems consist of two components—say oil and water—that do not mix at room temperature unless a third component, a surfactant, is added. The surfactant is a substance whose rod-like molecules have one end attractive to water and the other attractive to oil. Thus these molecules prefer to stay at the interface between oil and water, and as a result the surface tension is reduced. Due to this property the system sometimes prefers to have as many interfaces as possible, so that a microemulsion is formed. In this state of the system microscopic oil (or water) droplets surrounded by surfactant are dissolved in water (or oil), or thin lamellae (layers) of oil and water separated by surfactant are formed. Tube-like structures have also been observed [1]. The details of structure will depend upon the experimental situation which can be modified by introducing some additive [1, 2]. Experimentally the small surface tension of microemulsions is typically 10^{-2} – 10^{-4} times the surface tension of the pure oil–water interface [1, 2].

From the viewpoint of theory, microemulsions represent complex multicomponent systems where interactions with surfactant molecules depend on orientations. So far various models, both phenomenological [3] (a particularly elegant family of phenomenological models was introduced earlier by Talmon and Prager [3]) and with a basis in statistical mechanics [4–8], have been introduced for which explicit computations have been performed [3–8]. A common feature of such models is that they are designed to take into account the property that surfactant molecules are preferentially located between oil and water. Widom has introduced a simple Ising spin model for such a system. In the mean-field approximation the one-dimensional version (layered states) of his model corresponds to the ANNI model [9]. Schick and Wei-Heng Shih

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have introduced a spin-1 model [7] of a microemulsion. In both models the surface tension is found to be very low. More recently, a third interesting model was studied by Chen *et al* [8] (this work builds upon an earlier model introduced by Alexander [8]).

Here we introduce still another model, which we believe is in some ways closer to real systems. It contains only pair interactions that do not have an oscillating behaviour. The model is not restricted to lattice systems, but applies to continuum fluids as well. In this letter we describe the model and quote some results we have obtained. Details will be published in subsequent papers.

Basically the fluid consists of three species representing water, oil and surfactant whose interactions depend on orientation. The orientational dependence is a property shared, for instance, by polar fluids which have been extensively treated by statistical mechanical methods [10]. In ordered states, where the surfactant molecules will have preferred directions, numerical computation will be complicated due to the continuum of orientations. Thus we find it desirable to simplify the model such that in its simplest version the surfactant molecules have only two opposing orientations. Two opposing orientations in each of d directions are necessary to describe d -dimensional structures; thus, in the full d -dimensional version of the simplified model we assume $2d$ orientations of amphiphiles. To do computations on this model we use a trick originally used by Onsager, i.e. we regard various orientations of the amphiphile as different species of a mixture [11, 12]. Thus in its one-dimensional version the surfactant in our model reduces to two species by which we get a four-component mixture when the oil and water are included. In the d -dimensional version there are $2+2d$ species of particles. In the one-dimensional version the components are numbered from 1 to 4 in the following order; water (\circ), oil (\bullet), surfactant pointing to the right ($\circ\bullet$), and to the left ($\bullet\circ$). In the d -dimensional version particles pointing in $+x^i$ and $-x^i$ directions belong to the $(2i+1)$ th and to the $(2i+2)$ th components, respectively. In our convention either end of a surfactant molecule attracts a particle marked with the same colour. Because the two (or $2d$) 'special' components consist of the same particles in different orientations, the chemical potentials are identically the same and $\mu_i = \mu_3$ for $i \geq 3$.

The crucial properties of the interaction potentials in such a mixture are the following.

(i) Because of the different nature of the ends of the amphiphile, the interaction energy $u_{ij}(\mathbf{r}_j, \mathbf{r}_i)$ between an 'ordinary' ($i=1, 2$) and a surfactant ($j=3, 4$) particle at positions \mathbf{r}_i and \mathbf{r}_j , respectively, depends on $\text{sgn}(x_j^i - x_i^i)$, x_i^i and x_j^i being x^i coordinates of molecules. Similarly, in the d -dimensional version the interaction potential $u_{i,j}(\mathbf{r}_j - \mathbf{r}_i)$ depends on $\text{sgn}(x_j^k - x_i^k)$ if $i=1, 2$ and $j=1+2k, 2+2k$.

(ii) Since, in the absence of a surfactant, oil and water are not miscible, the attraction between like ordinary particles is much stronger than the interaction between different ones.

The simplest potentials exhibiting the above properties may be expressed in terms of symmetric [$b(\mathbf{r}) = b(-\mathbf{r})$] and antisymmetric [$c(\mathbf{r}) = -c(-\mathbf{r})$] functions in the following way. Among all particles there is a hard-core interaction. In the lattice case this is expressible as the exclusion of multiple occupancy of a cell. (In the simplest version of the continuum model it is a 'parallel hard-cube' core.) To the core terms one adds

$$u_{11}(\mathbf{r}) = u_{22}(\mathbf{r}) = -b(\mathbf{r}) \quad (1a)$$

$$u_{13}(\mathbf{r}) = u_{24}(\mathbf{r}) = -u_{14}(\mathbf{r}) = -u_{23}(\mathbf{r}) = -c(\mathbf{r}) \quad (1b)$$

$$u_{12}(\mathbf{r}) = u_{ij}(\mathbf{r}) = 0 \quad \text{if } i, j \geq 3. \quad (1c)$$

It may be noted that, assuming $u_{ij}(\mathbf{r}) = b(\mathbf{r})$ for all i , we would obtain a modified four-state Potts model with a 'screw' interaction (1b) added. In the d -dimensional version additional relations like (1b) with the $(1+2j)$ th and $(2+2j)$ th species replacing the third and fourth respectively, are assumed.

The model may be either on a lattice or in a continuum with respect to spatial positions. We develop both versions. In the lattice case the system is close packed such that each single cell is occupied by one particle. The nearest-neighbour interactions in the x^1 direction are $u_{ij} = -b$ for the pair (OO) and $u_{ij} = -c$ for the pair (O●). The rest of the interactions are determined by (1). In the x^j direction the interactions are the same for the $(1+2j)$ th and the $(2+2j)$ th types of particles replacing the third and fourth kinds, respectively. Both b and c are positive. There are two interaction parameters and three chemical potentials in the model. In the close-packed system the total number of particles is fixed and the two chemical potentials $\mu_i - \mu_3, i = 1, 2$, are left. We assume full symmetry between oil and water, i.e. $\mu_1 = \mu_2$ and obtain a three-dimensional phase diagram with independent parameters $\beta b, c/b, \mu/b$ where $\mu = \mu_1 - \mu_3$ and $\beta = (k_B T)^{-1}$. k_B and T being the Boltzmann constant and the temperature, respectively.

Within the Van der Waals (mean-field) theory the thermodynamic potential functional [13] generalised to a mixture is given by the expression

$$\Omega[\{\rho_i(\mathbf{r})\}] = F_h(\{\rho_i(\mathbf{r})\}) + \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' u_{ij}(\mathbf{r} - \mathbf{r}') \rho_i(\mathbf{r}) \rho_j(\mathbf{r}') - \mu_i \int d\mathbf{r} \rho_i(\mathbf{r}) \quad (2)$$

where the summation convention for repeated indices i, j is used. The $\rho_i(\mathbf{r})$ is the density of the i th component at position \mathbf{r} and F_h is the reference-system (hard-core) Helmholtz free energy. The Ω takes a minimum for the equilibrium density profile that will satisfy the expressions

$$\mu_i = \mu_i^h(\{\rho_i(\mathbf{r})\}) + \int d\mathbf{r}' u_{ij}(\mathbf{r} - \mathbf{r}') \rho_j(\mathbf{r}') \quad (3)$$

with μ_i^h the reference-system chemical potential of the i th component. The stability condition for the solutions of this equation will be

$$\int \int d\mathbf{r} d\mathbf{r}' \frac{\delta^2 \Omega}{\delta \rho_i(\mathbf{r}) \delta \rho_j(\mathbf{r}')} \delta \rho_i(\mathbf{r}) \delta \rho_j(\mathbf{r}') \geq 0. \quad (4)$$

Equality in (4) means that the system is at the point of being unstable, i.e. a phase transition will take place. The critical point will correspond to the highest temperature for which the equality in (4) occurs for the uniform phase ($\rho_i(\mathbf{r}) = \text{constant}$). Higher-order corrections to Ω must be positive at this point. Fourier transformed, condition (4) takes the form:

$$\sum_{\mathbf{k}} [\partial \mu_i^h / \partial \rho_j + \tilde{u}_{ij}(\mathbf{k})] c_i(\mathbf{k}) c_j^*(\mathbf{k}) \geq 0 \quad (5)$$

or equivalently

$$\det[\partial \mu_i^h / \partial \rho_j + \tilde{u}_{ij}(\mathbf{k})] \geq 0 \quad (6)$$

where $\tilde{u}_{ij}(\mathbf{k})$ and $c_i(\mathbf{k})$ are the Fourier transforms of $u_{ij}(\mathbf{r})$ and $\delta \rho_i(\mathbf{r})$, respectively. If the highest temperature with equality in (6) corresponds to $k \neq 0$, then an oscillating phase, which can represent a microemulsion, is formed for lower temperatures.

Let us consider the microemulsion model defined above. In its simplest four-component version $\rho(\mathbf{r}) = \rho(x)$, and (2) takes the form

$$\omega[\{\rho_i(x)\}] = f_h[\{\rho_i(x)\}] + \frac{1}{2} \int \int dx dx' \chi_{ij}(x-x') \rho_i(x) \rho_j(x') - \mu_i \int dx \rho_i(x) \quad (7)$$

where ω and f are potentials Ω and F per unit area, respectively, and $\chi_{ij}(x-x')$ are the interactions between layers at x and x' . To find the instability we should solve equation (6) with $\tilde{u}_{ij}(\mathbf{k})$ replaced by $\tilde{\chi}_{ij}(k)$.

For the actual calculations we assume the following forms for χ :

$$\chi_{11}(x) = -b \exp(-|x|\gamma_b) \quad (8a)$$

$$\chi_{13}(x) = -c \operatorname{sgn}(x) \exp(-|x|\gamma_c). \quad (8b)$$

Assuming $\gamma_b = \gamma_c = \gamma$, and fixing $\rho_1 = \rho_2, \rho_3 = \rho_4$ we find the critical temperature and the corresponding wavevector to be

$$k_B T_c = \begin{cases} \frac{2c}{\gamma} (\rho_1 \rho_3)^{1/2} \left[1 - \frac{b}{4c} \left(\frac{\rho_1}{\rho_3} \right)^{1/2} \right]^{-1} & \text{if } \rho_3/\rho_1 > (b/2c)^2 \\ \frac{2b}{\gamma} \rho_1 & \text{otherwise} \end{cases} \quad (9)$$

$$k_\gamma^2 = \left(\frac{k}{\gamma} \right)^2 = \begin{cases} 1 - (b/2c)(\rho_1/\rho_3)^{1/2} & \text{if } \rho_3/\rho_1 > (b/2c)^2 \\ 0 & \text{otherwise.} \end{cases} \quad (10)$$

The amplitudes (eigenvector) $c_i = c_i(k)$ for which the equality in (5) holds are

$$c_2 = -c_1 \quad c_4 = -c_3 = ik_\gamma (\rho_3/\rho_1)^{1/2} c_1. \quad (11)$$

The c_i represent the structure of the oscillating phase for small amplitudes of ordering. The structure will be a layered one in which oil and water alternate ($c_2 = -c_1$). Likewise the two orientations of the surfactant change, phase-shifted an angle $\pi/2$ compared to oil and water. In the d -dimensional version linear superpositions of one-dimensional fluctuations (10) and (11) in different directions will produce tube- and cube-like structures. In the lattice case the result is qualitatively the same [14].

The ground state of the model considered is determined by the values of the parameters b, c and μ . In the nearest-neighbour three-dimensional case the $T=0$ phase diagram is presented in figure 1, where the coordinates are $s = \mu + db, t = 2c - b$. An important feature of the model is that the phases of different geometrical types are present at $T=0$. For fixed interactions such that $2c > b$ there are phase transitions from pure oil and water to lamellar, from that to tubular, then to cubical and finally to pure surfactant phases with decreasing μ (increasing surfactant chemical potential). The uniform oil- and water-rich phases coexist with lamellar microemulsions only. Along the oil-microemulsion-water coexistence line lamellar phases of all possible lengths of water and oil segments separated by a single amphiphile are stable. As a result the surface tension between oil and water vanishes.

In the lattice case with second-neighbour interactions $u_{11}(2) = -b_1$ and $u_{13}(2) = -c_1$ included, and in the continuum version, the oil-water tension σ at the oil-microemulsion-water coexistence does not vanish under all conditions. In the lattice case ($d=1$)

$$\sigma = \begin{cases} b_1 - 2c_1 & \text{if } b_1 > 2c_1 \\ 0 & \text{if } b_1 < 2c_1. \end{cases} \quad (12)$$

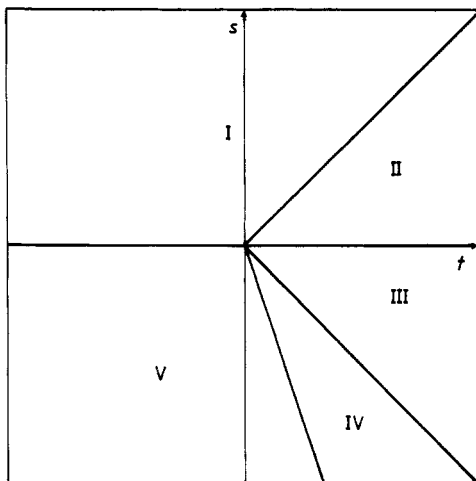


Figure 1. The $T = 0$ phase diagram of the 3D lattice model with nearest-neighbour interactions. Coordinates are $s = \mu + db$ and $t = 2c - b$. Regions I-V correspond to pure oil or water, lamellar (4), tubular (4, 4) cubical (4, 4, 4) and pure surfactant phases, respectively. Lamellar (4) phase has the oscillating structure $(\circ \circ \bullet \bullet \bullet \circ)$ in one direction and tubular (4, 4) and cubical (4, 4, 4) phases have similar oscillating structures in two and three directions, respectively.

In the continuum case (8) the σ is non-vanishing for $\gamma_b < \gamma_c$ [14]. The non-zero surface tension in both cases is due to the oil and water coexistence with specific finite-period microemulsions.

In the nearest-neighbour case the leading correction to the $T = 0$ oil-microemulsion-water coexistence line has been obtained within the mean-field theory, and for T close to zero the coexistence line in figure 1 is shifted to

$$s = t + \begin{cases} 2k_B T \exp(-db\beta) & \text{if } s > b \\ 2k_B T \exp\{-[s + (d - 1)b]\beta\} & \text{if } s < b. \end{cases} \quad (13)$$

Within the approximation, in which only the first-order correction to $T = 0$ density profiles is kept, the oscillating phases of periods $p \geq 6$ are stable at the oil-microemulsion-water coexistence line for $s < b$ and all the $p \geq 4$ phases are stable for $b < s < 4b$. Thus for $s \leq 4b$ the surface tension also vanishes to first order. For $s > 4b$, however, oil and water coexist with the period-4 microemulsion only and the asymptotic expression for the surface tension is

$$\sigma = k_B T \exp(-2db\beta) \quad T \rightarrow 0. \quad (14)$$

For the pure oil-water interface, $\sigma = b$ at $T = 0$. The critical temperature depends on surfactant concentration, and $k_B T_c \leq db$ where equality corresponds to $\rho_3 = 0, \rho_1 = \frac{1}{2}$ [14]. This would give the upper estimate $\sigma \leq db e^{-2}$ for all T of interest.

In the model that we have introduced, the potentials used appear to capture the key properties of the interactions between particles in the real systems. There are no assumptions such as oscillating potentials, three-body interactions (small in real systems), or infinite repulsion between oil and water, beyond the standard hard cores. As a result the model is reasonably simple, with only a few independent parameters. The model describes microemulsions of different geometrical structures and coexistence

between them. The surface tension is zero or very low. Non-symmetric states may also be considered. For $\rho_1 \gg \rho_2$ (or $\rho_2 \gg \rho_1$) cubical micelles are to be expected. The somewhat artificial shape of the micelle is the result of the discrete orientations of amphiphiles assumed in the model, along with the rectilinear geometry imposed by the hard cores. We note that there is no isotropic (disordered) phase at $T = 0$. In our model such a phase can only be expected for $T \neq 0$.

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