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Simple microscopic model of a ternary amphiphilic system—phase
diagram and mesoscopic correlations

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Проста мікроскопічна модель для опису мезоскопічних кореляцій в тернарній амфіфільній системі

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Анотація. Розглянуто просту мікроскопічну континуальну (негратакову) модель тернарної амфіфільної системи. Використовуючи певну модифікацію методу колективних змінних виведено ефективний гамільтоніан Ландау–Ґінсбурґа–Вільсона, що має форму вперше запропоновану Тйобнером та Стрейєм. Обчислено фазову діаграму в наближенні середнього поля та обговорено структурні властивості однорідної фази.

Simple microscopic model of a ternary amphiphilic system—phase diagram and mesoscopic correlations

M. Holovko, S. Kondrat

Abstract. We consider a simple microscopic, continuous (off-lattice) model of a ternary amphiphilic system. An effective Landau–Ginsburg–Wilson hamiltonian of the Teubner–Strey form is derived using a version of the collective variables method. Mean-field phase diagram is calculated and structural properties of the homogeneous phase are discussed.

1. Introduction

The physics of amphiphilic systems is important in many areas, including industrial and domestic applications like washing, cleaning, emulsification et al. Amphiphilic molecules (surfactants) consists of two different parts: a hydrophobic (oil-like) tail and hydrophilic (water-like) head. Due to such a chemical structure they self-assemble into surfaces in a water and/or oil solution so that the tails are separated from the water and the heads are separated from the oil. Depending on thermodynamical conditions (i.e., temperature, surfactant concentration, etc) these surfaces arrange themselves into a large variety of structures such as micelles, vesicles, lamellas and complex bicontinuous phases. In the bicontinuous phase (or microemulsion) the system is homogeneous and disordered on macroscopic length scales but it is highly inhomogeneous on mesoscopic scales.

Most theoretical approaches to amphiphilic systems employ lattice models (see, e.g., Refs. [1–8]). In the lattice models, the surfactants and other "molecules" are placed on the lattice sites, with certain constraints, and with different strengths for the relevant intermolecular (attractive) forces. Such lattice models are sometimes called "semi-microscopic" (or "quasi-microscopic") models because the lattice site usually corresponds to a cluster of molecules rather then to a single molecule [8]. Although they exhibit rich phase behaviour and share many important properties of realistic systems, they cannot be applied accurately to problems at the molecular level.

Another approach is a Landau-like theory in which one or more order parameters are introduced and a Landau–Ginsburg–Wilson (LGW) free energy functional (also called an effective LGW hamiltonian) is constructed on the basis of symmetry considerations (see, e.g., Refs. [1, 9–12]); it often appears as a more correct description of amphiphilic systems. It is worthwhile to mention here the functional due to Teubner and Strey [9], which leads naturally to two correlation lengths characterizing microemulsions, and which has been very successful in interpretation of small angle neutron scattering experiments. However, the parameters which appears in such a functional are only indirectly related to intermolecular interactions and are usually left in a purely phenomenological sense.

There have also been introduced so-called "charge frustrated" models, both microscopic lattice [4–7] and field-theoretical [13–15], which are based on the electrostatic analogy of amphiphilic systems. The main idea is that due to the intra-molecular structure of surfactant molecules there should be Coulombic terms in a free-energy functional or (lattice) microscopic hamiltonian. Recently, we have derived the charge-frustrated free-energy functional from a simple microscopic continuous model by using the collective variable technique [16]. In this paper we make an attempt to derive a LGW functional of the Teubner–Strey form from a similar microscopic model. To accomplish this task we employ again the collective variables method, though slightly modified on account of the local incompressibility condition which is used in the present derivation of the Teubner–Strey functional. This local incompressibility is plausible in the long-wavelength limit, and its use is also partially motivated by the fact that it often appears naturally in lattice models; the effect of its relaxation will be studied in future works.

The remainder of the paper is arranged as follows. In section 2.1 we present the details of the model. The method of collective variables is recalled and discussed in sections 2.2 and 2.3, while some technical details are left to appendix A. In section 3 we derive the Teubner–Strey functional and calculate the mean-field phase diagram. Structural properties of a homogeneous phase (microemulsion) are studied in section 4. Finally, our results are summarized and discussed in section 5.

2. Model and method

2.1. Model

We consider a ternary mixture consisting of molecules A and B, representing a polar water-like and non-polar oil-like solvent, respectively, and molecules S representing surfactants. The latter molecules are modelled by two types of particles, viz., by particles S_A (A-like) and S_B (B-like) whose centers are located at a fixed distance ℓ. For simplicity we assume that particles A, B, S_A and S_B are spherical hard-cores with the same radius d. The interparticle interaction potential is divided into a short-range repulsive part $\xi_{ab}(r)$ and an isotropic long-range part $v_{ab}(r)$, where a, b denotes the sort of particles (A, B, S_A and S_B). Thus, the potential function of the model can be presented as a sum $U = U_1 + U_R$, where

$$U_1 = \frac{1}{2} \sum_{a,b} \sum_{i,j}^{N_a, N_b} v_{ab}(r_{ij}), \qquad (2.1a)$$

$$U_R = \frac{1}{2} \sum_{a,b} \sum_{i,j}^{N_a, N_b} \xi_{ab}(r_{ij}) + \sum_{i,j}^{N_S} \xi_S(r_{ij}). \qquad (2.1b)$$

Here N_a is a number of particles of a-th sort, with $N_S = N_{S_A} = N_{S_B}$, and $\xi_S(r)$ symbolizes "sticky site" interaction of the surfactant components. Note that the part of U_R (for $a, b \in \mathcal{S} := \{S_A, S_B\}$) corresponds to the well-known reference interaction site model (RISM) [17, 18].

In order to make calculations more transparent we restrict our considerations to the following simple case. We assume that particles of both sorts A and S_A interact via the same potential $v_A(r)$, and, similarly, particles of both sorts B and S_B interact via the same $v_B(r)$. Finally, the interaction between the particles of either sort A or S_A and the particles of either sort B or S_B is described by $v_{AB}(r)$. In other words, sorts A and S_A are identical, as well as sorts B and S_B are identical, differing only in that the particles S_A and S_B form a dimer imitating the surfactant molecule.

It will prove useful to introduce

$$\epsilon_a = -\left(4\pi d^3/3\right)^{-1} \int_V \mathrm{d}\mathbf{r}\, v_a(r), \quad a = A, B; \qquad (2.2a)$$

$$\epsilon_{AB} = \left(2\pi d^3/3\right)^{-1} \int_V \mathrm{d}\mathbf{r}\, v_{AB}(r), \qquad (2.2b)$$

and

$$\Lambda = 1 + \epsilon_B/\epsilon_A + \epsilon_{AB}/\epsilon_A, \qquad (2.2c)$$

where V is the volume. Here positive ϵ_A and ϵ_B describes attraction, whereas $\epsilon_{AB} > 0$ corresponds to repulsion. The parameter Λ describes mutual solvability of particles A and B, in the case that the surfactant molecules are not present; it corresponds roughly to the surface tension between the components A and B. Note that there are only two independent energy parameters, inasmuch as ϵ_A is taken as an energy unit, and that there is no parameter which can be related to the amphiphilicity of the surfactant molecule. Furthermore, the second parameter, $\varepsilon = 1 - \epsilon_B/\epsilon_A$, will not appear in the following because of the local incompressibility condition; this will become apparent later.

2.2. Grand partition function

In order to study thermodynamical and structural properties of the model one needs to calculate the grand partition function. In the following we need to calculate the partition function with local density constraints, specifically, with the local incompressibility condition. To do this we use the following method. We first introduce field variables which satisfy

$\langle \varphi_a(\mathbf{r}) \rangle = \langle \hat{n}_{N_a}(\mathbf{r}) \rangle$, where $\hat{n}_{N_a}(\mathbf{r}) = \sum_i^{N_a} \delta(\mathbf{r} - \mathbf{r}_i^a)$ is the local density operator and $\langle \ldots \rangle$ means an equilibrium ensemble average. Next, the partition function is expressed as a functional integral over these fields. The local density constraints are then taken into account in a rather natural way by inserting the corresponding delta functions into the functional integral. The details of the approach are discussed in appendix A. Here we only note that short-range and long-range interactions are treated in a different manner. Basically, the idea is as follows [19]. Long-range potentials $v_{ab}(r)$ are assumed smooth enough (belonging to L_2 class of functions) and they appear explicitly in the partition function. A system with only short-range interactions (U_R), referred to as a reference system, is usually assumed isotropic and, although it does not have such nice properties, it is quite well studied and its thermodynamical and structural properties are assumed to be known. It is also assumed that the reference system does *not* undergo phase transitions in the range of the model parameters under consideration. The contribution from the underlying reference system is taken into account in the Jacobian of the transition to the field variables. Following this approach one finds for the grand partition function (see appendix A, eq. (A.8))

$$\Xi \propto \int \prod_a \mathcal{D}\varphi_{a,\mathbf{k}}\, \mathcal{M}[\{\varphi_{a,\mathbf{k}}\}]\, \mathcal{J}[\{\varphi_{a,\mathbf{k}}\}] \qquad (2.3)$$

$$\times \exp\left\{ \sum_a \mu_a^{(1)} \varphi_{a,\mathbf{0}} - \frac{\beta}{2(2\pi)^3} \sum_{a,b} \int \mathrm{d}\mathbf{k}\, \varphi_{a,\mathbf{k}}\, v_{ab}(k) \varphi_{b,\mathbf{k}}^* \right\},$$

where $\mu_a^{(1)}$ is the chemical potential of the a-th sort of particles (see eq. (A.9b)), β is inverse of the temperature multiplied by the Boltsmann constant, and $\varphi_{a,\mathbf{k}}$ and $v_{ab}(k)$ is the (three dimensional) Fourier transform of $\varphi_a(\mathbf{r})$ and $v_{ab}(r)$, respectively ($k = |\mathbf{k}|$). $\mathcal{M}[\{\varphi_{a,\mathbf{k}}\}]$ is the functional delta function which reflects the local incompressibility condition; we return to this later. The Jacobian $\mathcal{J}[\{\varphi_{a,\mathbf{k}}\}]$ is given by (see appendix A, eqs. (A.16) and (A.18))

$$\mathcal{J}[\{\varphi_{a,\mathbf{k}}\}] = \int \prod_a \frac{\mathcal{D}\nu_{a,\mathbf{k}}}{2\pi} \exp\left\{ \frac{iV}{2(2\pi)^3} \int \mathrm{d}\mathbf{k} \sum_a \nu_{a,\mathbf{k}}^*\, \varphi_{a,\mathbf{k}} \right. \qquad (2.4)$$

$$\left. + \sum_{n>0} \frac{(-iV)^n}{(2\pi)^{3n} n!} \sum_{\{a_i\}} \int \mathrm{d}\mathbf{k}_1 \cdots \mathrm{d}\mathbf{k}_n\, u_{a_1 \cdots a_n}(\{\mathbf{k}_i\})\, \nu_{a_1,\mathbf{k}_1}^* \cdots \nu_{a_n,\mathbf{k}_n}^* \right\},$$

where $u_{a_1 \cdots a_n}(\{\mathbf{k}_i\})$ (for $i = 1, \cdots, n$) is the n-particle structure factor of the reference system times an average number of particles of a-th

sort $\bar{N}_a$. Evaluation of $\mathcal{J}$ is a rather difficult mathematical problem and hereafter we restrict our considerations to the harmonic (Gaussian) approximation, leaving only the terms up to the quadratic order in $\nu_{a,\mathbf{k}}$. In this approximation one can readily calculate $\mathcal{J}$ analytically to obtain

$$
\mathcal{J}_G\left[\{\varphi_{a,\mathbf{k}}\}\right] \quad \propto \quad \exp\left\{\sum_{a,b} u_{ab}^{-1}(0)\bar{N}_b\,\varphi_{a,\mathbf{0}}\right. \tag{2.5}
$$

$$
\left. -\frac{V}{2(2\pi)^3}\sum_{a,b}\int \mathrm{d}\mathbf{k}\,\varphi_{a,\mathbf{k}}u_{ab}^{-1}(k)\varphi_{a,\mathbf{k}}^{*}\right\},
$$

where $u_{ab}^{-1}(k)$ is the ab-th element of matrix inverse of the matrix $\hat{u}(k)$ made out of components $u_{ab}(k)$, and we have used the fact that $u_a(\mathbf{k}) = \bar{N}_a\,\delta_{\mathbf{k},\mathbf{0}}$ and $u_{ab}(\mathbf{k},\mathbf{k}') = u_{ab}(k)\,\delta_{\mathbf{k},-\mathbf{k}'}$ for an isotropic reference system.

We note that within this approximation an expression in the exponent in eq. (2.3) remains quadratic in $\varphi_{a,\mathbf{k}}$; it suffices for our present purposes. An inclusion of the higher order terms in $\nu_{a,\mathbf{k}}$ in eq. (2.4) gives rise to higher order terms in $\varphi_{a,\mathbf{k}}$ in eq. (2.5), and modifies its quadratic part too. Numerically, however, the quadratic term is not altered too much [20]. One therefore expects that the Gaussian approximation should yield *qualitatively* correct results, at least in some range of the model parameters. It should be noted, however, that under certain circumstances the higher order terms in $\varphi_{a,\mathbf{k}}$ would manifest themselves even if only the quadratic term is of interest.

2.3. Structure factors of the reference system

To complete this section we recall the form of structure factors of the RISM model and calculate $\hat{u}^{-1}(k)$; it is needed to compute the Jacobian (2.5).

One has for an isotropic system:

$$
u_{ab}(r) = \bar{N}_a\left[\delta(r)\,\delta_{ab} + \varrho_b\,h_{ab}(r)\right]; \qquad h_{ab}(r) = g_{ab}(r) - 1\,, \tag{2.6}
$$

where $h_{ab}(r)$ is a pair correlation function, $g_{ab}(r)$ is a distribution function and $\varrho_a = \bar{N}_a/V$. Following the work by Cummings and Stell [18] we write for the distribution function of the surfactant components:

$$
g_{ab}(r) = \frac{(1-\delta_{ab})\,\delta(r-\ell)}{4\pi\varrho_a\ell^2} + g_{ab}^{(0)}(r)\,, \quad a,b \in \mathcal{S}\,, \tag{2.7}
$$

where the first term on the right-hand side of eq. (2.7) is the intramolecular structure factor of the surfactant molecules and $g_{ab}^{(0)}(r)$ is the

distribution function of the system with the short-range repulsive interactions (the first term of U_R, see eq. (2.1)). We recall that $\varrho_{S_A} = \varrho_{S_B} = \varrho_S$. Combining eqs. (2.7) and (2.6) and taking Fourier transform one finds for the symmetrized $u_{ab}(k)$:

$$
\begin{aligned}
u_{ab}(k) &= \left(\bar{N}_a\bar{N}_b\right)^{1/2}\left[\Delta_{ab}(k) + (\varrho_a\varrho_b)^{1/2}\,h_{ab}^{(0)}(k)\right]; \\
\Delta_{ab}(k) &= \delta_{ab} + (1-\delta_{ab})\,\delta_{a,\mathcal{S}}\delta_{b,\mathcal{S}}\,\frac{\sin(k\ell)}{k\ell}\,.
\end{aligned} \tag{2.8}
$$

Finally, using the site-site Ornstein–Zernike equation [18, 19] we obtain for the elements of matrix inverse of $\hat{u}(k)$:

$$
u_{ab}^{-1}(k) = \left(\bar{N}_a\bar{N}_b\right)^{-1/2}\left[\Delta_{ab}^{-1}(k) - (\varrho_a\varrho_b)^{1/2}\,c_{ab}^{(0)}(k)\right], \tag{2.9}
$$

where $c_{ab}^{(0)}(k)$ is the Fourier transformed direct correlation function of the system with the short-range repulsive interactions. In the assumption that sizes of all particles are equal, and for a hard-core potential $\xi_{ab}(r) = \xi_{hs}(r)$, one has $c_{ab}^{(0)}(k) = c_{hs}(k)$, $\forall\,a,b$.

3. Mean-field phase diagram

We are interested in properties and phase boundaries of the homogeneous phase. To calculate the phase diagram we proceed as follows. We first pass to new field variables in eqs. (2.3) and (2.5), defined via a transformation: $\phi_i(\mathbf{r}) = \sum_a T_{ia}^{-1}\,\varphi_a(\mathbf{r})$. Here $a = 1, 2$ corresponds to particles A and B, and $a = 3, 4$ correspond to particles S_A and S_B, respectively. The matrix T is given by

$$
T^{-1} = \begin{pmatrix} 1 & -1 & 1 & -1 \\ 1 & 1 & 1 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}\,. \tag{3.1}
$$

This defines

$$
\phi_1(\mathbf{r}) = \varphi_A(\mathbf{r}) + \varphi_{S_A}(\mathbf{r}) - [\varphi_B(\mathbf{r}) + \varphi_{S_B}(\mathbf{r})] \tag{3.2a}
$$

and

$$
\phi_2(\mathbf{r}) = \sum_a \varphi_a(\mathbf{r})\,. \tag{3.2b}
$$

The field $\phi_2(\mathbf{r})$ is related to the total number density. We note that there is an "intrinsic" total number density $\tilde{\varrho} = \sum_a \varrho_a = \varrho_A + \varrho_B + 2\varrho_S$ and an "observable" total number density $\varrho = \varrho_A + \varrho_B + \varrho_S$. In the local incompressibility condition $\phi_2(\mathbf{r}) = \tilde{\varrho}$ at any space point, hence, $\mathcal{M}[\phi_{2,\mathbf{k}}] = \delta(\phi_{2,\mathbf{k}} - \tilde{\varrho}\,\delta_{\mathbf{k},\mathbf{0}})$. The field $\phi_1(\mathbf{r})$ is related to an order parameter. In the homogeneous phase $\langle\phi_1(\mathbf{r})\rangle = \phi_1^{(0)} = \varrho_A - \varrho_B$, therefore, it is instructive to define

$$\phi_1(\mathbf{r}) = \phi_1^{(0)} + \psi(\mathbf{r})\,, \tag{3.3}$$

where $\psi(\mathbf{r})$ describes fluctuations (note that $\langle\psi(\mathbf{r})\rangle = 0$). Then, from eqs. (2.5) and (2.3), and using eq. (3.3), one finds for the grand partition function (the terms linear in $\phi_{i,\mathbf{0}}$ in the exponent have been dropped since they are irrelevant for further analysis):

$$\Xi_G \propto \int \mathcal{D}\psi_{\mathbf{k}} \exp\left\{-\frac{1}{2(2\pi)^3} \int d\mathbf{k}\,\psi_{\mathbf{k}}\,A(k)\psi_{\mathbf{k}}^*\right\} \int \prod_{i\neq 1} \mathcal{D}\phi_{i,\mathbf{k}}\,\mathcal{M}[\phi_2]$$

$$\times \exp\left\{-\frac{1}{2(2\pi)^3} \int d\mathbf{k}\left[\sum_{i,j\neq 1}\phi_{i,\mathbf{k}}A_{ij}(k)\phi_{j,\mathbf{k}}^* + 2\sum_{i\neq 1}\phi_{i,\mathbf{k}}A_{i1}(k)\psi_{\mathbf{k}}^*\right]\right\}\,,$$

where

$$A(k) \equiv A_{11}(k) = \frac{\beta}{4}\left[v_A(k) + v_B(k) - 2v_{AB}(k)\right] + \frac{\varrho_A + \varrho_B}{4\varrho_A\varrho_B}\,, \tag{3.4a}$$

$$A_{ij}(k) = A_{ji}(k) = \left(T^T\left[\beta\hat{v}(k) + V\hat{u}^{-1}(k)\right]T\right)_{ij}\,. \tag{3.4b}$$

Note that in the small wave-vector limit there are Coulomb-like terms in eq. (3.4b):

$$A_{ij}(k) \sim z_i z_j/k^2\,, \quad i,j = 3,4\,, \tag{3.5}$$

where $z_3 = -z_4 = (3/\varrho_S\ell)^{1/2}$ is a "frustrating charge". These terms originate from the *intra*-molecular structure factors of the surfactant molecules (see eqs. (2.8) and (2.9), see also Ref. [16]). It is worthwhile to mention that electrostatic terms have been adopted in a number of models of microemulsions, both (lattice) microscopic and field-theoretical [4–7, 13–15].

When all fields but $\psi_{\mathbf{k}}$ are removed altogether we find

$$\Xi_G \propto \int \mathcal{D}\psi_{\mathbf{k}} \exp\left\{-\frac{1}{2(2\pi)^3} \int d\mathbf{k}\,\psi_{\mathbf{k}}\,a(k)\psi_{\mathbf{k}}^*\right\}\,, \tag{3.6}$$

where

$$a(k) = A(k) - W(k) \cdot B^{-1}(k) \cdot W^T(k)\,, \tag{3.7}$$

where $W^T(k) = \big(A_{13}(k), A_{14}(k)\big)$ and $B(k)$ is a 2×2 matrix with the elements $\{A_{33}(k), A_{34}(k); A_{43}(k), A_{44}(k)\}$. Expanding $a(k)$ up to the forth order in k one finds

$$\Xi_G \propto \int \mathcal{D}\psi_{\mathbf{k}} \exp\left\{-\mathcal{H}_{TS}[\psi_{\mathbf{k}}]\right\}\,; \tag{3.8}$$

$$\mathcal{H}_{TS} = \frac{\pi d^3}{6(2\pi)^3} \int d\mathbf{k}\,\psi_{\mathbf{k}}\left\{a_2 + c_1\,(\ell k)^2 + c_2\,(\ell k)^4\right\}\psi_{\mathbf{k}}^*\,. \tag{3.9}$$

Functional $\mathcal{H}_{TS}[\psi_{\mathbf{k}}]$ of the form (3.9) was introduced by Teubner and Strey [9] to explain typical features of scattering curves of microemulsions. We note also that a similar functional was employed by Lifshitz [21] to study spatially modulated structures.

The coefficients of the expansion read:

$$a_2\left(\{\bar{\varrho}_a\},\bar{\beta}\right) = -\Lambda\bar{\beta} + \left(\bar{\varrho}_A + \bar{\varrho}_B + 4\bar{\varrho}_S\right)/4D\,, \tag{3.10a}$$

$$c_1\left(\{\bar{\varrho}_a\},\bar{\beta}\right) = 3\Lambda\bar{\beta}p_2/10 - \bar{\varrho}_S(\bar{\varrho}_A + 2\bar{\varrho}_C)(\bar{\varrho}_B + 2\bar{\varrho}_C)/3D^2\,, \tag{3.10b}$$

$$c_2\left(\{\bar{\varrho}_a\},\bar{\beta}\right) = -\Lambda\bar{\beta}p_4/56 + (\bar{\varrho}_S/180D^3)\big\{80\bar{\varrho}_S^4 \tag{3.10c}$$
$$+ P(\bar{\varrho}_A,\bar{\varrho}_B,\bar{\varrho}_S) + P(\bar{\varrho}_B,\bar{\varrho}_A,\bar{\varrho}_S)\big\}\,,$$

where we have introduced dimensionless quantities: $\bar{\varrho}_a = 4\pi d^3\varrho_a/3$ and $\bar{\beta} = \bar{T}^{-1} = \beta\epsilon_A$. In eqs. (3.10),

$$D\left(\bar{\varrho}_A,\bar{\varrho}_B,\bar{\varrho}_S\right) = \bar{\varrho}_A\bar{\varrho}_B + \bar{\varrho}_S\left(\bar{\varrho}_A + \bar{\varrho}_B\right)\,, \tag{3.11}$$

$$P(\bar{\varrho}_A,\bar{\varrho}_B,\bar{\varrho}_S) = 11\bar{\varrho}_A^2\bar{\varrho}_S^2 + 72\bar{\varrho}_S^3\bar{\varrho}_A + 14\bar{\varrho}_S\bar{\varrho}_A^2\bar{\varrho}_B$$
$$+ 3\bar{\varrho}_A^2/2 + 37\bar{\varrho}_S^2\bar{\varrho}_A\bar{\varrho}_B\,, \tag{3.12}$$

and p_n is related to the n-th moment of the function $v_A(r) + v_B(r) - 2v_{AB}(r)$:

$$p_n = \frac{n+3}{4\pi d^3\epsilon_A\Lambda\ell^n} \int_V d\mathbf{r}\,r^n\big\{v_A(r) + v_B(r) - 2v_{AB}(r)\big\}\,, \tag{3.13}$$

with $p_0 = 1$.

Some comments are in order at this stage. First, notice that the direct correlation function $c_{hs}(k)$ does not appear in eqs. (3.10) and that the long-range potentials appear only in the combination $v_A + v_B - 2v_{AB}$ (see eqs. (2.2c) and (3.13)), and, as a consequence, eqs. (3.10) are symmetric with respect to the interchange of ϱ_A with ϱ_B. Of course these

assertions would not hold if a more general case of the model was considered. On the other hand, the direct correlation function c_{hs} is present in eqs. (3.4b), namely, it contributes to the matrix element $A_{22}(k)$. However, because integration over the field ϕ_2 is covered by the local incompressibility condition, i.e., by $\mathcal{M}[\phi_2] = \delta(\phi_{2,\mathbf{k}} - \tilde{\varrho})$, the direct correlation function does not enter expressions (3.10). The same concerns the function $\upsilon_{\mathrm{A}}(k) - \upsilon_{\mathrm{B}}(k)$ which contributes to $A_{12}(k) = A_{21}(k)$; it does not enter eqs. (3.10) either. Next, we emphasize that the last terms on the right-hand side of eqs. (3.10b) and (3.10c) are entirely due to the intra-molecular structure factor of the surfactant molecules (see eq. (2.8), cf. also eq. (3.5)). Thus, these terms are new as to compare to a simple n-component fluid; evidently they vanish when $\varrho_{\mathrm{S}} = 0$. Further, because effects we are going to study are due to the presence of these terms, hereafter we assume $p_4 = 0$ in eq. (3.10c) for simplicity. This assumption is also supported by the following observation. At small surfactant concentration ($\varrho_{\mathrm{S}}/\varrho \approx 0$) the coefficient c_2 is small comparing to the coefficient c_1 (in fact, one expects, in analogy with a simple fluid, that the ratio $c_2/c_1 \ll 1$ for $\varrho_{\mathrm{S}} = 0$), hence, for small values of k the term $\sim k^2$ dominates over the k^4 term, and the latter term can at all be neglected. The k^4 term *is* however important at a large surfactant concentration, for which c_1 vanishes or becomes negative (cf. Fig. 2 below). However, because the second term on the right-hand side of eq. (3.10c) increases with increasing ϱ_{S} (cf. Fig. 2), while the first term ($\sim p_4$) does not depend on ϱ_{S}, the ϱ_{S}-dependent term dominates over the term $\sim p_4$ at large $\varrho_{\mathrm{S}}/\varrho$. We note that a similar assumption has also been made in Refs. [4, 5] (see section 5 for a discussion on these works).

On the mean-field level the homogeneous phase is unstable with respect to fluctuations with the wave-vector k_c when the coefficient at $\psi_{\mathbf{k}}\psi_{\mathbf{k}}^*$ vanishes. If $c_1 > 0$ it gives $k_c = 0$ and $a_2\left(\{\bar{\varrho}_a\}, \bar{T}\right) = 0$, which corresponds to the phase separation (the solid line in Fig. 1). This line is continued for $c_1 \leq 0$ by the line $c_1 = -2(c_2 a_2)^{1/2}$. On this line the homogeneous phase is unstable with respect to fluctuations with the wave-vector $k_c = \left(-c_1/2c_2\right)^{1/2}$ (the long dashed line in Fig. 1). For temperature $\bar{T}$ below this line one would expect an occurrence of lamellar or other lyotropic phases. We emphasize, however, that in the framework of the present analysis we merely determine the limit of *stability* of the homogeneous phase, whereas the actual transition can be discontinuous and occur at the higher temperature $\bar{T}$. Indeed, there are arguments in the literature that a continuous (order-disorder) phase transition predicted by a mean-field approximation can become a first order transition if fluctuations are taken into account [22, 23]. It is worthwhile to note
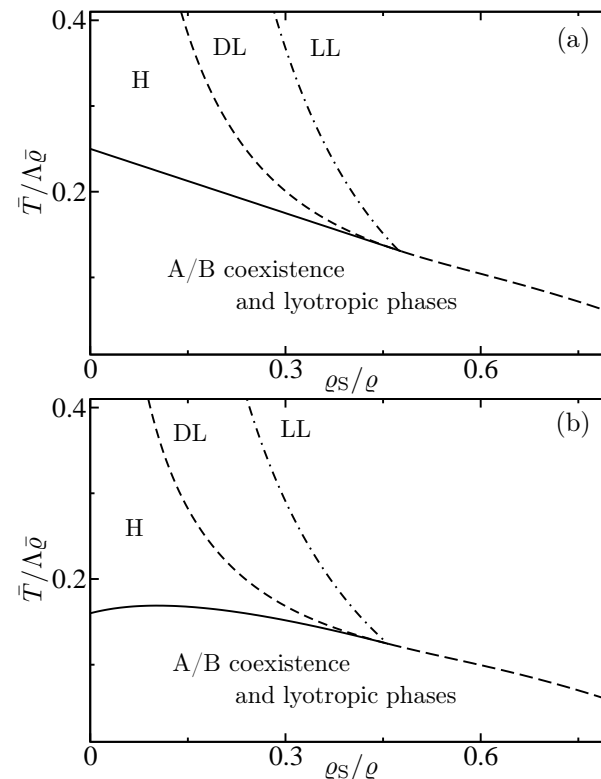
Figure 1. Mean-field phase diagram for $p_2 = 1$, $p_4 = 0$, and (a) for symmetric mixture ($\varrho_{\mathrm{A}} = \varrho_{\mathrm{B}}$) and (b) for $\varrho_{\mathrm{B}}/\varrho_{\mathrm{A}} = 4$. The lines where the homogeneous phase (H) is unstable with respect to the phase separation ($k_c = 0$) is denoted by the solid line. It is continued for $c_1 \leq 0$ by the line where the H-phase is unstable with respect to fluctuations with the wave-vector $k_c = \left(-c_1/2c_2\right)^{1/2}$ (long dashed line). The short dashed line and the dot-dashed line denotes the disorder line (DL) and the Lifshitz line (LL), respectively (see section 4, cf. also Fig. 2).

that an essential ingredient of such a consideration is the presence of quartic (or higher order) terms in $\psi_{\mathbf{k}}$ in the functional (3.9), which, in turn, means that one must go beyond the harmonic approximation in calculation of the Jacobian (2.4); studies of this kind are deferred for future works.
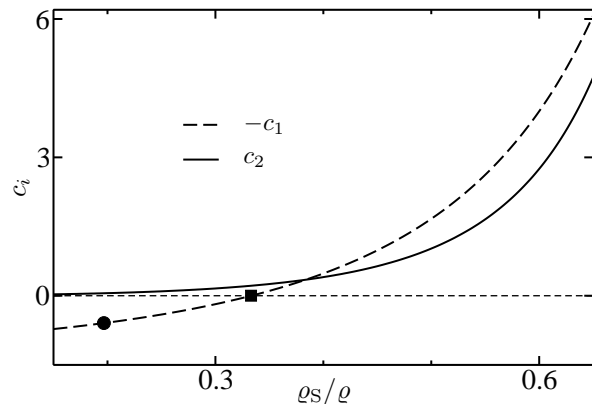
Figure 2. The coefficients $-c_1$ and c_2 (see eqs. (3.10)) of the functional (3.9) as functions of the surfactant concentration ϱ_S/ϱ for symmetric mixture ($\varrho_A = \varrho_B$), and for $\bar{T} = 3\Lambda\bar{\varrho}/10$, $p_2 = 1$ and $p_4 = 0$. The stright dashed line corresponds to $c_i = 0$, and the circle and the square corresponds to the disorder line ($c_1 = c_1^{(DL)}$) and the Lifshitz line ($c_1 = 0$), respectively (cf. Fig. 1).

In Fig. 1 we also show the disorder line (DL) and the Lifshitz line (LL). Beyond the disorder line (toward larger values of ϱ_S) there are oscillations in the real-space order parameter–order parameter correlation function, and at yet higher surfactant concentration, beyond the Lifshitz line, the peak of the (order parameter–order parameter) structure factor is at non-zero wave-vector. This is discussed in more detail in the next section.

4. Structure factor

The order parameter–order parameter correlation function can be deduced from the following generating functional:

$$\mathcal{Z}[J] = \Xi^{-1} \int \mathcal{D}\psi_{\mathbf{k}} \, \exp\left\{ -\mathcal{H}_{TS}[\psi_{\mathbf{k}}] + \frac{1}{(2\pi)^3} \int d\mathbf{k} \, J_{\mathbf{k}}\psi_{\mathbf{k}}^* \right\}, \quad (4.1)$$

which is normalized such that $\mathcal{Z}[0] = 1$. Thus, the two-point correlation function is

$$\langle \psi_{\mathbf{k}} \, \psi_{\mathbf{k}}^* \rangle = V^2 \left. \frac{\delta^2 \, \mathcal{Z}[J]}{\delta J_{\mathbf{k}} \delta J_{\mathbf{k}}^*} \right)_{J=0}, \quad (4.2)$$

where V is the volume. Using eqs. (4.2) and (3.9), one finds, after simple calculations,

$$\langle \psi_{\mathbf{k}} \, \psi_{\mathbf{k}}^* \rangle = \frac{3V}{\pi d^3} \left[a_2 + c_1(k\ell)^2 + c_2(k\ell)^4 \right]^{-1}. \quad (4.3)$$

Fourier transformation of eq. (4.3) gives the real-space correlation function; simple evaluation yields [1]

$$G(r) \propto \frac{1}{r} \, \sin(r/\lambda) \exp(-r/\xi), \quad (4.4)$$

where

$$\lambda = \left[\frac{1}{2} \left(\frac{a_2}{c_2} \right)^{1/2} - \frac{c_1}{4c_2} \right]^{-1/2} \quad (4.5a)$$

and

$$\xi = \left[\frac{1}{2} \left(\frac{a_2}{c_2} \right)^{1/2} + \frac{c_1}{4c_2} \right]^{-1/2}. \quad (4.5b)$$

The correlation function (4.4) shows two characteristic features of microemulsions: oscillations, indicating alternating arrangement of molecules of the A and B sorts, and an exponential decay, indicating the absence of long-range order [1]. In other words, the wavelength λ gives the domain size of coherent A and B regions, while ξ characterizes the decay of the local order. The line

$$c_1 = c_1^{(DL)} = 2(c_2 a_2)^{1/2}, \quad (4.6)$$

called the *disorder line* (the short dashed line in Fig. 1), separates the region where $G(r)$ decays monotonically (that is, where $c_1 > c_1^{(DL)}$, whence, where $\varrho_S < \varrho_S^{(DL)}$, see Fig. 2) and the region of oscillatory behaviour of the correlation function, i.e., it is the line at which the oscillatory behaviour first appears upon increasing the surfactant concentration ϱ_S/ϱ; notice that λ diverges at the disorder line if we think of decreasing ϱ_S/ϱ. Note, incidentally, that the correlation length ξ diverges on the line $c_1 = -c_1^{(DL)}$ (the long dashed line in Fig. 1). As noted in section 3, this line corresponds to a continuous phase transition between the homogeneous (disordered) and ordered phases.

From eq. (4.3) one easily finds that the maximum of the order parameter–order parameter structure factor $\langle \psi_{\mathbf{k}} \, \psi_{\mathbf{k}}^* \rangle$ occurs at the wave-vector k_m given by
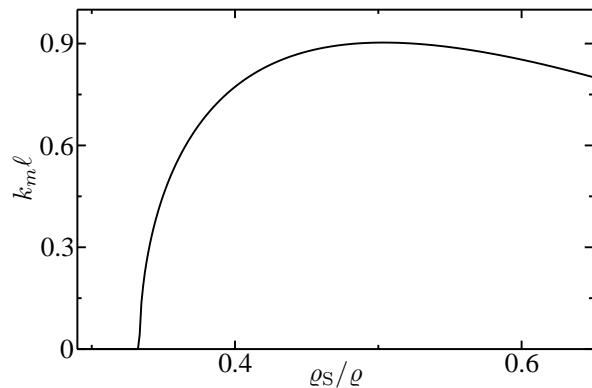
$$(k_m\ell)^2 = -c_1/2c_2, \quad (4.7)$$

Figure 3. The peak's position k_m of the order parameter–order parameter structure factor as a function of the surfactant concentration ϱ_S/ϱ for symmetric mixture ($\varrho_A = \varrho_B$), and for $\bar{T} = 3\Lambda\bar{\varrho}/10$, $p_2 = 1$ and $p_4 = 0$.

hence, the peak in the structure factor moves off $k_m = 0$ when c_1 decreases to zero (cf. Fig. 2). The line $c_1 = 0$ defines the *Lifshitz line* (the dot-dashed line in Fig. 1). At the Lifshitz line the ratio $\lambda/\xi = 1$ (see eqs. (4.5)), which means that the correlation function (4.4) becomes dominated by oscillatory behaviour. In Fig. 3 the peak's position k_m is plotted against the surfactant concentration ϱ_S/ϱ. We observe that k_m increases starting from zero at the Lifshitz line. This trend inverses, however, when ϱ_S/ϱ is further increased, and k_m begins to decrease. We recall that the length $\sim k_m^{-1}$ is a measure of the domain size in a micro(meso)-phase separated structure. Therefore, such a behaviour of k_m at large ϱ_S/ϱ would suggest the formation of complex structures with the fundamental wavelength larger than the length of a surfactant molecule ($\sim \ell$ in our model). It should be noted, however, that the coefficients c_1 and c_2 increase rapidly with increasing the surfactant concentration (see Fig. 2) and, probably, simple gradient expansion (3.9) is insufficient in this region of the model parameters.

Finally, in Fig. 4 we present examples of the order parameter–order parameter structure factor $\langle\psi_{\mathbf{k}}\psi_{\mathbf{k}}^*\rangle$ plotted as a function of the wavevector k, for the homogeneous phase and for a few values of the surfactant concentration ϱ_S/ϱ. It is known that the structure factor is proportional to the scattering intensity which can be measured, for instance, in a small angle neutron scattering experiment [1]. In Fig. 4(a) $\langle\psi_{\mathbf{k}}\psi_{\mathbf{k}}^*\rangle$ is shown for relatively small values of ϱ_S. In accord with the experimental
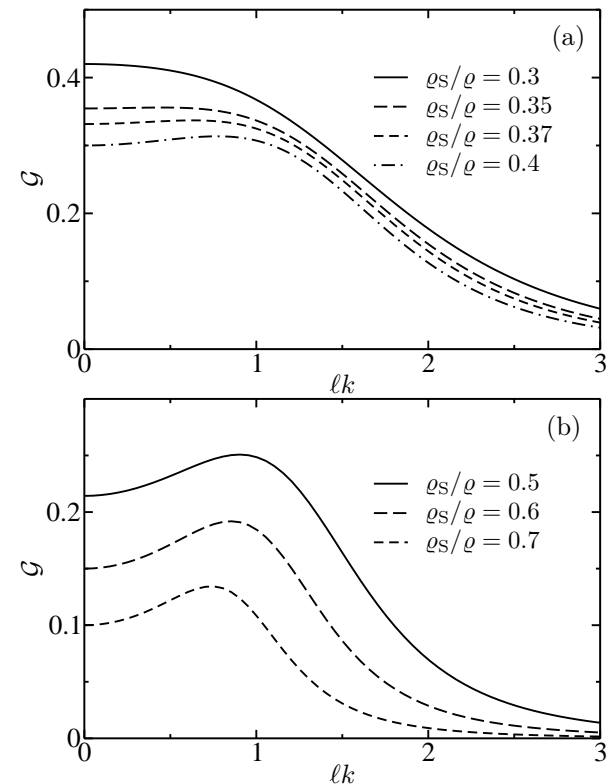

Figure 4. The order parameter–order parameter structure factor $\mathcal{G} = (\pi d^3/3V)\langle\psi_{\mathbf{k}}\psi_{\mathbf{k}}^*\rangle$ (see eq. (4.3)) for (a) small and (b) large values of the surfactant concentration ϱ_S/ϱ. In this plot $\varrho_A = \varrho_B$, $\bar{T} = 3\Lambda\bar{\varrho}/10$, $p_2 = 1$ and $p_4 = 0$.

observations (see, e.g., Refs. [9, 24, 25]), the magnitude of the structure factor decreases as the surfactant concentration increases, and the peak's position k_m moves off zero wave-vector and goes toward larger values of k (cf. Fig. 3). However, as discussed above, for large ϱ_S/ϱ the peak's position goes toward small k, though the magnitude of $\langle\psi_{\mathbf{k}}\psi_{\mathbf{k}}^*\rangle$ continues to decrease, which is shown in Fig. 4(b).

5. Summary

We have considered a simple microscopic continuous model of (weak) surfactant solutions. The model consists of four sorts of particles: two sorts of particles represent the oil-like (A) and water-like (B) molecules, and the two remaining components (S_A and S_B) form a dimer representing the surfactant molecule. Using a simple modification of the collective variables method, we have derived (in the Gaussian approximation) an effective Landau–Ginsburg–Wilson hamiltonian for microemulsions, functional form of which was first proposed by Teubner and Strey [9]. In such a way we have linked the phenomenological parameters appearing in the Teubner–Stray functional with the microscopic parameters of our model (see eqs.(3.10)). Using a mean-field approximation, we have calculated the phase diagram, namely, the phase boundary of a homogeneous phase. Our calculations show that the homogeneous phase can be unstable with respect to fluctuations with zero as well as a non-zero wave-vector. The latter instability indicates the existence of spatially modulated phases in our simple model. We note, however, that more elaborate calculations must be carried out in order to study the structure of such phases (as well as the order of the transition, see section 3). In order to study the structure of the homogeneous phase we have calculated the order parameter–order parameter correlation function. It is shown, in particular, that there are oscillations in the real space correlation function, and that for a sufficiently large concentration of surfactants the peak of the order parameter–order parameter structure factor occurs at a non-zero wave-vector, which is characteristic for microemulsions (see Figs. 3 and 4). This effect is related to the fact that the coefficient c_1 at the k^2 term can change sign, depending on the temperature and the surfactant concentration (see Fig. 2).

It is interesting to point out certain similarity of our model and the *lattice* model of Woo et al. [4, 5]. The authors of these works have derived the functional (3.9) (albeit to higher orders in $\psi_{\mathbf{k}}$) from the "frustrated" Ising model with spin ± 1, where each value of the spin represents an oil and water molecule. Some of the sites, representing surfactant components, are endowed with the "frustrating charges" and interact via the Coulombic potential (cf. eq. (3.5)). The fact that the spin takes only the values ± 1 merely indicates that there is always a molecule on the site, and this corresponds roughly to our local incompressibility condition $\mathcal{M}[\phi_2]$. The parameters σ, Δ and the lattice spacing a of Refs. [4, 5] are, in a certain sense, analogous to our parameters Λ, ℓ and d, respectively. Furthermore, our order parameter (the field ϕ_1, see eqs. (3.2a))

is in fact equivalent to the order parameter used is Refs. [4, 5]. In the above-mentioned works it emerges naturally as an average value of the spin, hence, it corresponds to the oil–water concentration difference, *including* also the surfactant's components concentration difference. It is therefore no surprising that the phase diagram presented in our work (Fig. 1) is very similar to the phase diagram calculated in Ref. [4].

Acknowledgments

A. Grand partition function with density constraints

The approach discussed here has a rather strong resemblance with the collective variable method introduced by Zubaryev [26] and further developed by Yukhnovskii and co-workers [19, 20, 27–29]. The difference is merely due to density constrains which we impose on a system. Because of these constraints it is more convenient to introduce a "collective" variable in R-space instead of k-space, as it is conventionally done in the collective variables approach.

We consider an M-component system whose particles interact via a pairwise additive potential $U_{ab}(\mathbf{r}_i, \mathbf{r}_j)$. The potential function is

$$U = \frac{1}{2} \sum_{a,b}^{M} \sum_{i,j}^{N_a, N_b} U_{ab}(\mathbf{r}_i, \mathbf{r}_j), \qquad (A.1)$$

where the absence of the terms with $i = j$ for the same sort of particles is understood. For further purposes it is convenient to divide the interaction potential $U_{ab}(\mathbf{r}_i, \mathbf{r}_j)$ into a short-range and long-range part, $\xi_{ab}(\mathbf{r}_i, \mathbf{r}_j)$ and $v_{ab}(\mathbf{r}_i, \mathbf{r}_j)$, respectively; the former is usually referred to as a reference system. The kinetic part of the hamiltonian is assumed to be of the usual quadratic form. The integration over the momenta yields the standart de Broglie thermal wavelength factors Λ_a (for a-th component). Consequently, the grand partition function is

$$\Xi = \mathrm{Sp}\, e^{-\beta U} = \prod_a \sum_{N_a} \frac{e^{\beta \mu_a N_a}}{\Lambda_a^{3N_a} N_a!} \int (\mathrm{d}\Gamma)\, e^{-\beta U_R}\, e^{-\beta U_1} , \qquad (A.2)$$

where

$$U_R = \frac{1}{2}\sum_{a,b}\sum_{i,j}\xi_{ab}(\mathbf{r}_i,\mathbf{r}_j)\,, \tag{A.3a}$$

$$U_1 = \frac{1}{2}\sum_{a,b}\sum_{i,j}\upsilon_{ab}(\mathbf{r}_i,\mathbf{r}_j)\,. \tag{A.3b}$$

In eq. (A.2), β is inverse of the temperature multiplied by the Boltzmann constant k_B, and $(\mathrm{d}\Gamma) = \prod_a\prod_i(\mathrm{d}\mathbf{R}_i^a/V)$, where V is the volume and $\mathbf{R}_i^a$ is the position of the i-th particle (of sort a) in coordinate space. The chemical potential μ_a is determined by the equation $\bar{N}_a = \partial\ln\Xi/\partial(\beta\mu_a)$, provided $\bar{N}_a$ (an average number of particles of a-th sort) is known. We present the grand partition function as follows

$$\Xi = \Xi_R\,\Xi_1\,, \tag{A.4}$$

where

$$\Xi_R = \prod_a\sum_{N_a}\frac{\mathrm{e}^{\beta\mu_a^{(R)}N_a}}{\Lambda_a^{3N_a}N_a!}\int(\mathrm{d}\Gamma)\,\mathrm{e}^{-\beta U_R} \tag{A.5}$$

is the grand partition function of the reference system and

$$\Xi_1 = \left\langle \mathrm{e}^{\beta\sum_a\mu_a'N_a}\mathrm{e}^{-\beta U_1}\right\rangle_R\,. \tag{A.6}$$

Here $\left\langle\cdots\right\rangle_R$ means averaging over the reference system,

$$\left\langle\cdots\right\rangle_R = \Xi_R^{-1}\prod_a\sum_{N_a}\frac{\mathrm{e}^{\beta\mu_a^{(R)}N_a}}{\Lambda_a^{3N_a}N_a!}\int(\mathrm{d}\Gamma)\bigl(\cdots\bigr)\mathrm{e}^{-\beta U_R}\,, \tag{A.7}$$

$\mu_a^{(R)}$ is the chemical potential of the reference system, determined by the equation $\bar{N}_a^{(R)} = \partial\ln\Xi_R/\partial(\beta\mu_a^{(R)})$, and $\mu_a' = \mu_a - \mu_a^{(R)}$; it is convenient to divide μ_a so that $\bar{N}_a = \bar{N}_a^{(R)}$.

Let us introduce a local density operator $\hat{n}_{N_a}(\mathbf{r}) = \sum_i^{N_a}\delta(\mathbf{r} - \mathbf{r}_i^a)$, where $\delta(\mathbf{r})$ is the (three dimensional) Dirac delta function. Note that $N_a \equiv n_{N_a} = \int_V\mathrm{d}\mathbf{r}\,\hat{n}_{N_a}(\mathbf{r})$. We want to calculate the partition function (A.2) with *local density constraints*. By those we mean that at any phase-space point a linear combination $\mathcal{L}\left(\{\hat{n}_{N_a}\}\right)$ of the density operators $\hat{n}_{N_a}(\mathbf{r})$ is fixed in the sense that $\int_{V_G}\mathrm{d}\mathbf{r}\,\mathcal{L}\left(\{\hat{n}_{N_a}(\mathbf{r})\}\right) = \mathcal{C}V_G$ for an arbitrary volume V_G, where $\mathcal{C}$ is a constant. Note that $\mathcal{C}$ must have the dimension of number density. A generalization to what can be called an

integral density constraint, i.e., the constraint for a linear combination of n_{N_a}, is straightforward. To introduce constraints into the partition function Ξ we proceed as follows. First, we pass to field variables in eq. (A.6) by introducing functional integrals $\int\mathcal{D}\varphi_a(\mathbf{r})$ together with the Dirac delta functions $\delta\bigl(\varphi_a(\mathbf{r}) - \hat{n}_{N_a}(\mathbf{r})\bigr)$. One easily finds

$$\Xi_1 = \int\prod_a[\mathrm{d}\varphi_a\mathcal{D}\varphi_a(\mathbf{r})]\exp\left\{\beta\sum_a\mu_a^{(1)}\varphi_a - \beta\,\Phi[\{\varphi_a(\mathbf{r})\}]\right\}\\ \times\mathcal{J}_1[\{\varphi_a,\varphi_a(\mathbf{r})\}]\,, \tag{A.8}$$

where

$$\Phi[\{\varphi_a(\mathbf{r})\}] = \frac{1}{2}\sum_{a,b}\int_V\mathrm{d}\mathbf{r}_1\int_V\mathrm{d}\mathbf{r}_2\,\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2)\upsilon_{ab}(\mathbf{r}_1,\mathbf{r}_2), \tag{A.9a}$$

$$\mu_a^{(1)} = \mu_a' + \frac{1}{2}\upsilon_{aa}(\mathbf{0}) = \mu_a' + \frac{1}{2V}\sum_{\mathbf{k}}\upsilon_{aa}(\mathbf{k})\,. \tag{A.9b}$$

The last term in $\mu_a^{(1)}$ is due to the absence of the $i = j$ (for $a = b$) terms in eq. (A.1); $\mathcal{J}_1$ reads

$$\mathcal{J}_1 = \left\langle\prod_a\delta(\hat{n}_{N_a}(\mathbf{r}) - \varphi_a(\mathbf{r}))\,\delta(n_{N_a} - \varphi_a)\right.\\ \left.\times\delta\left(n_{N_a} - \int_V\mathrm{d}\mathbf{r}\,\hat{n}_{N_a}(\mathbf{r})\right)\right\rangle_R \tag{A.10a}$$

$$= \prod_a\delta\left(\varphi_a - \int_V\mathrm{d}\mathbf{r}\,\varphi_a(\mathbf{r})\right)\mathcal{J}[\{\varphi_a,\varphi_a(\mathbf{r})\}]\,, \tag{A.10b}$$

where the last delta function in eq. (A.10a), which ensures a correct relation between $\hat{n}_{N_a}(\mathbf{r})$ and n_{N_a}, has been taken out of $\left\langle\;\right\rangle_R$ by using the integral representation of the Dirac delta function. In eq. (A.10b),

$$\mathcal{J}[\{\varphi_a,\varphi_a(\mathbf{r})\}] = \left\langle\prod_a\delta(\hat{n}_{N_a}(\mathbf{r}) - \varphi_a(\mathbf{r}))\,\delta(n_{N_a} - \varphi_a)\right\rangle_R\,. \tag{A.11}$$

The aforementioned constraints can now be easily taken into account by inserting the corresponding delta functions into eq. (A.11). By taking

similar steps as in (A.10) one obtains

$$
\Xi = \Xi_R \int \prod_a \left[\mathrm{d}\varphi_a \mathcal{D}\varphi_a(\mathbf{r})\, \delta\left(\varphi_a - \int_V \mathrm{d}\mathbf{r}\, \varphi_a(\mathbf{r})\right)\right]
$$
$$
\times \prod_\alpha \delta\big(\mathcal{L}_\alpha(\{\varphi_a(\mathbf{r})\}) - \mathcal{C}_\alpha\big) \tag{A.12}
$$
$$
\times \exp\left\{ \beta \sum_a \mu_a^{(1)} \varphi_a - \beta\, \Phi[\{\varphi_a(\mathbf{r})\}]\right\} \mathcal{J}[\{\varphi_a, \varphi_a(\mathbf{r})\}]\,.
$$

It is now convenient to pass to Fourier space. Due to the linearity of our constraints, and because Fourier series has a unit Jacobian, eq. (A.12) simply becomes

$$
\Xi = \Xi_R \int \prod_a \mathcal{D}\varphi_{a,\mathbf{k}} \prod_\alpha \delta\big(\mathcal{L}_\alpha(\{\varphi_{a,\mathbf{k}}\}) - \mathcal{C}_\alpha \delta_{\mathbf{k},\mathbf{0}}\big)\, \mathcal{J}[\{\varphi_{a,\mathbf{k}}\}]
$$
$$
\times \exp\left\{ \beta \sum_a \mu_a^{(1)} \varphi_{a,\mathbf{0}} - \frac{\beta}{2V}\sum_{a,b}\sum_{\mathbf{k}} \varphi_{a,\mathbf{k}} v_{ab}(\mathbf{k}) \varphi_{b,\mathbf{k}}^* \right\}, \tag{A.13}
$$

where, because $\varphi_a(\mathbf{r})$ is a real field, the integration over $\varphi_{a,\mathbf{k}}$ is restricted to $\varphi_{a,\mathbf{k}} = \varphi_{a,\mathbf{k}}^*$, i.e., $\mathbf{k} \in \Omega = \left\{ \mathbf{k} \in \mathbb{R}^3 \mid k_z > 0; k_x, k_z = 0, k_y \geq 0; k_z = 0, k_x, k_y > 0 \right\}$, and

$$
\mathcal{J}[\{\varphi_{a,\mathbf{k}}\}] = \left\langle \prod_a \prod_{\mathbf{k} \in \Omega} \delta\big(\hat{\rho}_{N_a}(\mathbf{k}) - \varphi_{a,\mathbf{k}}\big)\right\rangle_R, \tag{A.14}
$$

where $\hat{\rho}_{N_a}(\mathbf{k})$ is the Fourier amplitude of the density operator $\hat{n}_{N_a}(\mathbf{r})$, i.e.,

$$
\hat{\rho}_{N_a}(\mathbf{k}) = \int_V \mathrm{d}\mathbf{r}\, \hat{n}_{N_a}(\mathbf{r}) \exp\left(i\mathbf{k}\mathbf{r}\right) = \sum_i^{N_a} \exp\left(i\mathbf{k}\mathbf{r}_i\right). \tag{A.15}
$$

In eq. (A.13) we have integrated out over $\mathrm{d}\varphi_a$ using $\hat{\rho}_{N_a}(\mathbf{0}) = n_{N_a} = N_a$. Using the integral representation of the delta function we rewrite eq. (A.14) as follows

$$
\mathcal{J}[\{\varphi_{a,\mathbf{k}}\}] = \int \prod_a (\mathrm{d}\nu_{a,\mathbf{k}}) \exp\left\{ i \sum_a \sum_{\mathbf{k}} \nu_{a,\mathbf{k}}^* \varphi_{a,\mathbf{k}} \right\} \mathcal{K}[\{\nu_{a,\mathbf{k}}\}]. \tag{A.16}
$$

Here

$$
(\mathrm{d}\nu_{a,\mathbf{k}}) = \frac{\mathrm{d}\nu_{a,\mathbf{0}}}{2\pi} \prod_{\mathbf{k} \in \Omega_0} \frac{\mathrm{d}\nu_{a,\mathbf{k}}^{(\Re)}}{2\pi} \frac{\mathrm{d}\nu_{a,\mathbf{k}}^{(\Im)}}{2\pi}, \tag{A.17}
$$

where $\Omega_0 = \Omega \backslash \{\mathbf{k} = \mathbf{0}\}$, and

$$
\mathcal{K}[\{\nu_{a,\mathbf{k}}\}] = \left\langle \exp\left\{ -i \sum_a \sum_{\mathbf{k}} \nu_{a,\mathbf{k}}^* \hat{\rho}_{N_a}(\mathbf{k}) \right\} \right\rangle_R \tag{A.18}
$$
$$
= \exp\left\{ \sum_{n>0} \frac{(-i)^n}{n!} \sum_{a_1,\ldots,a_n} \sum_{\mathbf{k}_1,\ldots,\mathbf{k}_n} u_{a_1\cdots a_n}(\mathbf{k}_1,\ldots,\mathbf{k}_n) \nu_{a_1,\mathbf{k}_1}^* \cdots \nu_{a_n,\mathbf{k}_n}^* \right\},
$$

where we have used the cumulant expansion theorem [30]. In eq. (A.18),

$$
u_{a_1\cdots a_n}(\mathbf{k}_1,\ldots,\mathbf{k}_n) = \left\langle \hat{\rho}_{N_{a_1}}(\mathbf{k}_1) \cdots \hat{\rho}_{N_{a_n}}(\mathbf{k}_n) \right\rangle_c^{(R)}, \tag{A.19}
$$

where $\left\langle \cdots \right\rangle_c^{(R)}$ means cumulant avaraging over the reference system; $u_{a_1\cdots a_n}(\mathbf{k}_1,\ldots,\mathbf{k}_n)$ is the n-particle cumulant of the reference system, i.e., the n-particle structure factor (of the reference system) times $\bar{N}_a$. In the thermodynamic limit $\sum_{\mathbf{k}} \mapsto V/(2\pi)^3 \int \mathrm{d}\mathbf{k}$, and eq. (A.17) defines the measure of functional integral $\mathcal{D}\nu_{a,\mathbf{k}}/2\pi$.

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Мирослав Федорович Головко
Святослав Васильович Кондрат

Проста мікроскопічна модель для опису мезоскопічних кореляцій в тернарній амфіфільній системі