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Cubic phases of amphiphilic molecular aggregates

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Abstract. Stability and geometry of the lyotropic periodic cubic mesophases are considered in the framework of a general symmetry based phenomenological approach. A limited number of cubic structural types is shown to be formed by amphiphilic molecular aggregates due to the specific nature of self-organizing units. The related thermodynamic models predict topology of phase diagrams and specific features of transitions between isotropic, lamellar, cubic bicontinuous and cubic micellar phases.

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1 Introduction

Over the few past decades, considerable efforts have been expended to clarify the structures of various translationally-ordered lyotropic cubic liquid-crystalline phases as well as their location in phase diagrams. Collected data confirm not only the existence of such structures but allow us to discuss the cubic polymorphism for different complex fluids [1]. However it is still unclear how many structures there are and where they are located in the phase diagrams. The cubic phases exhibit different structures and there are two fundamentally different classes: i) the *bicontinuous* cubic, consisting of a single, continuous bilayers of amphiphilic molecules that divide space into two interwoven, continuous networks of water and amphiphile; ii) the *micellar* structures composed of discrete aggregates of "oil in water" or "water in oil" type. The basic structures of bicontinuous cubic phases are now well established as being of space groups $O_h^4(Pn3m)$, $O_h^9(Im3m)$ and $O_h^{10}(Ia3d)$ and corresponding to the Diamond (D), Schwarz-P or I-WP, and Schoen Gyroid (G) minimal surfaces, respectively. In the micellar systems the cubic structure types A15, A1, C15 and A2 corresponding to the space groups $O_h^3(Pm3n)$, $O_h^5(Fm3m)$, $O_h^7(Fd3m)$, and O_h^9 , respectively, were found (see [2–4] and references there). Nevertheless, the structure of many possible candidates remains unresolved because lyotropic cubic phases often form relatively large microcrystalline domains which makes small-angle X-ray (SAXS) studies on these materials difficult. Samples also posses a finite and unknown distribution of microcrystalline orientations rather than a uniform powder. Scattering data from lyotropic cubic phases generally contain only a small number of reflections which makes indexing and space group determination very difficult. However, one should remember that amphiphilic molecular aggregates, self-organized in cubic crystalline structures, possess some properties that are fundamentally different from those formed by molecules in ordinary crystals. These structures are not solid-like because both water and surfactant molecules are in the liquid state. Due to these specific features, molecular aggregates can be spatially arranged only in a *limited number* of structures and the principal aim of this paper is, using natural and experimentally confirmed properties of complex fluids, to derive all possible types of cubic periodic organization for the micellar and bicontinuous phases which one can use then as probe structures for X-ray experiments in the search for new phases.

The paper is organized as follows. After an introduction, the formation of the periodically ordered lyotropic mesophases from the isotropic solution is considered in the framework of a general phenomenological scheme. Thermodynamical arguments, as well as specific features of the aggregated amphiphilic molecules and their interactions, are then used to select the allowed space groups for the cubic structures formed by amphiphilic aggregates. The final discussion compares our theoretical predictions with known experimental results.

2 Phenomenological consideration

2.1 Stable anisotropic phases

Since this paper does not intend to analyze in detail thermodynamical aspects of isotropic to cubic phase transformations only results allowing to restrict a number of cubic crystal classes under consideration are of interest. The phenomenological approach introduced by Landau [5] which treats phase transitions on the basis

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of symmetry considerations and needs no structural data but only information about the *symmetry group* of the system and symmetry of transformation mechanism (*i.e.* relevant *irreducible representation*) is well adopted for such a goal. We will follow this approach in the beginning, and only in the final stage will the specific properties of the self-organization of the amphiphilic molecules with cubic structure be discussed.

Let us start from the full space symmetry of the phases. The symmetry group of an isotropic state is the *extended Euclidean group* $\tilde{E}_3$ which is a semi-direct product of the continuous three-dimensional translation group R_3, and orthogonal group $O(3)$ consisting of all continuous proper and improper rotations in the 3D-space [6]. We are considering the segregation type transformation which appears as initial density distribution $\rho_0(\mathbf{r}) = \text{const.}$ to be modulated periodically with undulation function $\delta\rho(\mathbf{r}) = \rho_d(\mathbf{r}) - \rho_0(\mathbf{r})$. This periodic deviation of density $\delta\rho$ can be expanded using $\Phi^m_{k_j}(\mathbf{r})$ basis functions of an relevant irreducible representation (IR) of $\tilde{E}_3$ group:

$$\delta\rho(\mathbf{r}) = \sum_{k_j, m} \eta^m_{k_j} \Phi^m_{k_j}(\mathbf{r}), \tag{1}$$

where $\eta^m_{k_j}$ are the *order parameter* (OP) components and $\mathbf{k}_j$ are the reciprocal space vectors, m specifies an irreducible representation. The functions $\Phi^m_{k_j}(\mathbf{r})$ span infinite-dimensional irreducible representations (IRs) of $\tilde{E}_3$ group which will be denoted hereafter by $D^{m,k_j}_{\pm}$. The lower index indicates symmetry properties with respect to the inversion center. In order to construct IRs $D^{m,k_j}_{\pm}$ the method of induced representation can be used in which irreducible representations (small representations) of the invariant point group $G_{k_j} = C_{\infty v}$ of the $\mathbf{k}_j$ vector that is isomorphous to $SO(2)$ group induce IRs for $\tilde{E}_3$ space group [6].

The "unit cell" of the parent isotropic state is reduced to a single subunit (molecular or micellar center of mass) which is invariant under all symmetry operations of $\tilde{E}_3$. Since the ordering process can be fully specified by the *scalar* parameter which is a probability density variation, and due to the invariance of the structure just mentioned, the $\{\eta^m_{k_j}\}$ necessarily transforms as the IR denoted D^{0,k_j}_{+}, *i.e.* the IR induced by the identity (totally symmetric) small irreducible representation of $C_{\infty v}$.

The variational free energy $F(T, p, \eta^m_{k_j})$ (Landau potential) is invariant by the symmetry transformations of the parent structure. Thus it can be expanded in Taylor series by invariant homogeneous polynomials of OP components. The general form of such a polynomial is

$$\begin{aligned} I_n &= \sum_s C_s \eta_1 \cdots \eta_{n_s} \\ &= \sum_s C_s \mathrm{e}^{\mathrm{i}(\mathbf{k}_1 + \cdots + \mathbf{k}_{n_s})\mathbf{r}} \left|\eta_{k_1}\right| \cdots \left|\eta_{k_{n_s}}\right|. \end{aligned} \tag{2}$$

Since the free energy $F(T, p, \eta^0_{k_j})$ must be a function of modulus $|\mathbf{k}_j|$ but not their orientation, exponential multipliers in equation (2) have to be equal to unity. The $\{\mathbf{k}_j\}$ vector star consists of an infinite number of arms and for any n_s, the corresponding low symmetry star can be chosen such that $(\mathbf{k}_1 + \cdots + \mathbf{k}_{n_s}) = 0$ and the above condition is satisfied. This means that, considering segregation process, the variational free-energy $F(T, p, \eta^0_{k_j})$ expansion contains invariant polynomials of all degrees, excluding the linear one.

In order to find the stable anisotropic phases one needs to minimize the variational free energy (Landau potential) $F(T, p, \eta^m_{k_j})$ with respect to the OP components:

$$\frac{\partial F(T, p, \eta^m_{k_j})}{\partial \eta^m_{k_j}} = 0. \tag{3}$$

Despite the infinite number of equations in (3) the problem can be solved geometrically in the order-parameter space ε for which the set of OP components $\{\eta^m_{k_j}\}$ forms the basis [7,8]. The $\delta\rho$ variation of probability density associated with a phase transition can be considered as a vector in the ε-space, and the components of $\{\eta^m_{k_j}\}$ vector are the values of the OP which minimize the thermodynamic potential. Minimization conditions (3) determine in ε-space $\{\eta^{\mathrm{eq}}_{k_j}\}$ *stationary vectors* which are invariant with respect to different subgroups of OP symmetry group, formed by the matrices of the relevant IR.

Matrices of the relevant D^{0,k_j}_{+} IR corresponding to the rotation subgroup of $\tilde{E}_3$ group are unity ones permuting the arms of $\{\mathbf{k}_j\}$ vector star. Matrices corresponding to the elements of translation subgroup are diagonal ones, the elements of these matrices are exponentials $\exp(\mathrm{i}\mathbf{k}_j\mathbf{a}_i)$. For any crystal group, a homomorphous subgroup of the L-group can be found and the corresponding invariant (stationary) vector can be determined. One can use for this end the obvious idea that only for invariant components of $\{\eta^0_{k_j}\}$, exponential multipliers will be equal to unity ($\exp\{\mathrm{i}\mathbf{k}_j\mathbf{a}_i\} = 1$). Space arrangement of equilibrium $\{\mathbf{k}_{0j}\}$ and $\{\mathbf{a}_{0i}\}$ stars must be consistent also with the point group of the considered crystal class. In the 3D-periodic space only three independent basis vector stars $\{\mathbf{k}_{0j}\}$ are compatible with O_h symmetry of the following structures:

$$\langle A \rangle : \pm\mathbf{k}_{[100]}; \langle \mathbf{B} \rangle : \pm\mathbf{k}_{[111]}; \langle \mathbf{C} \rangle : \pm\mathbf{k}_{[110]}. \tag{4}$$

Consequently, the only relevant sets of OP components are non-zeros and are equal to each other:

$$\eta^0_{\langle k_j \rangle} = \cdots = \eta^0_{\langle k_{j'} \rangle}. \tag{5}$$

Only a pair of representative vectors for each star is presented in (4). Miller indexes $[hkl]$ are used in orientation notation. One can see that in direct space $\langle A \rangle$-star identifies the primitive cubic lattice, $\langle B \rangle$-the face-centered cubic lattice, and $\langle C \rangle$-the body-centered cubic lattice.

In this paper only cubic phases are considered in detail, however it should be mentioned that two non-zero complex conjugate OP components $\eta^0_{[001]} = \eta^0_{[00\bar{1}]}$ correspond to a lamellar phase (L_α). Let us also note that the interlayer spacing in such L_α structure is strictly connected with the periodicity of the cubic structures as the critical $\mathbf{k}_j$ vectors of these phases belong to the same star in the isotropic state. For low symmetry 3D-periodic tetragonal and rhombohedral phases, equilibrium conditions for non-zero components are

$$\begin{aligned}\langle D_{4h}\rangle : P : \eta_1 &= \eta^0_{\pm[100]} = \eta^0_{\pm[010]},\ \eta_2 = \eta^0_{\pm[001]},\\ I:\ \eta_1 &= \eta^0_{\pm[101]} = \eta^0_{\pm[011]},\ \eta_2 = \eta^0_{\pm[110]},\\ \langle D_{3d}\rangle : R : \eta_1 &= \eta^0_{\pm[\bar{1}01]} = \eta^0_{\pm[1\bar{1}0]} = \eta^0_{\pm[01\bar{1}]};\\ \eta_2 &= \eta^0_{\pm[101]} = \eta^0_{\pm[011]} = \eta^0_{\pm[110]},\end{aligned}\tag{6}$$

and the corresponding solutions for the equations of state are two-parametric. It is worthwhile to note that such rhombohedral phase associated with the cubic one was found earlier in the sodiumdecyl sulfate/water system [9].

For the sake of completeness the hexagonal mesophase which is 2D-array of long stiff circular rods should be discussed, since this phase neighbors usually by cubic ones in phase diagrams of lipid-containing or surfactant-water systems (see, for example, [10,11]). Following the above procedure one gets hexagonal phase when the equilibrium values of the relevant OP are $\eta_{k_1} = \eta_{-k_1} = \eta_{k_2} = \eta_{-k_2} \neq 0$ and $\eta_{k_j} = 0$ $(j \neq 1, 2)$ for an angle between $\mathbf{k}_1$ and $\mathbf{k}_2$ of 120°. However, by analyzing the experimental data on epitaxial relationships between hexagonal and cubic structures extensively studied by Clerc *et al.* [10] one can conclude that hexagonal and cubic phases are induced by different order parameters. Following reference [10] the repeat distance d_{10} between (10) planes in the hexagonal phase is continuous with the repeat distance d_{211} between the (211) planes in the cubic phase ($d_{10} \approx d_{211}$). As demonstrated in [10], the (10) planes of hexagonal phase are parallel to the (211) planes of the cubic phase: both are the planes of highest density in the two phases. The minimal lattice vectors relate to the single interplane distance in the hexagonal structure and to the double interplane distance in the cubic structure. One may derive the corresponding OP critical vectors whose modulus are $|\mathbf{k}_{\mathrm{H}}| = 1/d_{10}$ and $|\mathbf{k}_{\mathrm{C}}| = 1/2d_{211}$, respectively for hexagonal and cubic structure. Inequality of the critical vectors clearly indicates that the different OPs induce these phases.

2.2 Thermodynamic model

In the preceding section the lowest degree invariants in the integrity basis for IR D_{+}^{0,k_j} of $\tilde{E}_3$ group were shown to be of 2, 3, 4th degree. Taking into account the equilibrium conditions (5) and (6) for low symmetry phases, one has the integrity basis for the effective three-component OP $\{\eta_{k_1}, \eta_{k_2}, \eta_{k_3}\}$

$$I_1 = \eta_{k_1}^2 + \eta_{k_2}^2 + \eta_{k_3}^2,\ I_2 = \eta_{k_1}\eta_{k_2}\eta_{k_3},\ I_3 = \eta_{k_1}^4 + \eta_{k_2}^4 + \eta_{k_3}^4,\tag{7}$$

where $\mathbf{k}_1$, $\mathbf{k}_2$ and $\mathbf{k}_3$ belong to any vector star from (4).

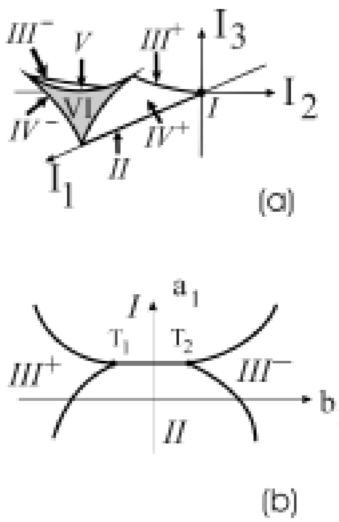

Fig. 1. Location of the phases corresponding to the image group defined by equation (7). (a) Topology of phases in the orbit space (I_1, I_2, I_3). (b) Equilibrium diagram, corresponding to the thermodynamic potential (8) with the limiting conditions (9). Full lines are first-order transition lines. T_1 and T_2 are triple points.

The full set of stable states corresponding to the irreducible L-group contains eight phases [7,8,12]: (I) $\eta_{k_1} = \eta_{k_2} = \eta_{k_3} = 0$; (II) $\eta_{k_1} \neq 0$, $\eta_{k_2} = \eta_{k_3} = 0$; (III$^+$) $\eta_{k_1} = \eta_{k_2} = \eta_{k_3} \neq 0$; (III$^-$) $-\eta_{k_1} = \eta_{k_2} = \eta_{k_3} \neq 0$; (IV$^+$). $\eta_{k_1}, \eta_{k_2} = \eta_{k_3}$ $(\eta_1 > \eta_2)$; (IV$^-$). $-\eta_{k_1}, \eta_{k_2} = \eta_{k_3}$ $(\eta_1 > \eta_2)$; (V) $\eta_{k_1}, \eta_{k_2} = \eta_{k_3}$ $(\eta_1 < \eta_2)$ and (VI) $\eta_{k_1}, \eta_{k_2}, \eta_{k_3}$. One can see that phase I in our model corresponds to the isotropic state. Phase II has $D_{\infty h}$ symmetry with translational symmetry broken in one direction and corresponds to a lamellar structure. The III$^\pm$ are cubic phases (different lattices are not distinguishable). Solutions IV$^\pm$, in the chosen model, correspond to uniaxial phases, but one can not distinguish between tetragonal and rhombohedral symmetry. Phases V and VI are orthorhombic and monoclinic. The location of the phases pertaining to the phase diagram in the orbit space (I_1, I_2, I_3), are shown in Figure 1a. The phase diagram in orbit space not only reveals the full set of possible stable states for the corresponding L-group but also provides an indication of the topological properties of the phases in the real (*e.g.* temperature-pressure) phase diagram. The phase I (non-parametric solution) is located at the origin point $I_1 = I_2 = I_3 = 0$. The stability regions of one-parametric solutions II and III$^\pm$ are represented by the edges of a pyramid, the faces correspond to the two-parametric solutions IV$^\pm$ and V and with the body filled by the phase VI. The number characterizing reduction of dimensionality of the phase stability region in the orbit space is known to be equal to the dimensionality of the corresponding interphase border. From Figure 1a one can deduce that, when undergoing a phase transition from the isotropic state (origin point in the phase diagram, zero-parametric solution) to a phase associated with single-parametric solution of equations of state (II or III$^\pm$), the dimensionality is reduced by one. This means that phases II and III$^\pm$ can be reached *directly* from the phase I across a first-order transition *line* in contrast to the phases IV^+ and V which can touch phase I only at an *isolated point* in the two-dimensional (for example, temperature-concentration) phase diagram. For the lyotropic system this means that only lamellar and cubic phases (among mentioned above) can be expected to border an isotropic phase in the phase diagram. Although two-dimensionally periodic structures are not considered here due to the specific goals of the paper one can see that there are no principal difficulties, following the procedure of Section 2.1, to get corresponding equilibrium conditions for OP components.

The thermodynamic model based on the order-parameter expansion restricted to six-degree terms

$$\begin{aligned} F = a_1 I_1 + a_2 I_1^2 + a_3 I_1^3 + b_1 I_2 + b_2 I_2^2 + c_1 I_3 \\ + f_{12} I_1 I_2 + f_{13} I_1 I_3 \end{aligned} \tag{8}$$

is sufficient to prove the stability of cubic and lamellar phases. However, to have a transition *line* between phases I and II, that would correspond to the experimentally observed situation when isotropic and lamellar phases are neighboring through the line of first-order transitions, additional special conditions for phenomenological coefficients have to be satisfied. These special conditions are:

$$a_2 = a_3 = b_2 = f_{12} = 0,\ c_1 < 0,\ f_{13} > 0. \tag{9}$$

Figure 1b shows a part of equilibrium phase diagram of the model (8) with special conditions (9) for the phenomenological coefficients in the plane of thermodynamic parameters (a_1, b_1). The I-II phase boundary is the straight line parallel to b_1 axis: $a_1 = c_1^2/4f_{13}$. The equations in parametric form of the first-order transition lines between phases I and $\mathrm{III}^{\pm}$ are

$$\begin{cases} 9f_{13}\eta^4 + 3c_1\eta^2 \pm b_1\eta + 3a_1 = 0 \\ 18f_{13}\eta^4 + 4c_1\eta^2 + b_1\eta + 2a_1 = 0 \end{cases} \tag{10}$$

whilst the transition lines from $\mathrm{III}^{\pm}$ to II are

$$\begin{cases} f_{13}\eta_1^6 + c_1\eta_1^4 + a_1\eta_1^2 = 9f_{13}\eta_2^6 + 3c_1\eta_2^4 \pm b_1\eta_2^3 + 3a_1\eta_2^2 \\ \eta_1^2 = \dfrac{-c_1 \pm \sqrt{c_1^2 - 3a_1 f_{13}}}{3f_{13}} \\ 18f_{13}\eta_2^4 + 4c_1\eta_2^4 + b_1\eta_2 + 2a_1 = 0. \end{cases} \tag{11}$$

One can see that the low symmetry phases can be reached from the isotropic state across *lines of first-order phase transitions*. The phase diagram of Figure 1b is symmetric with respect to b_1, or equivalently, with respect to change in sign of η_i. Such a change means an exchange of the population of amphiphilic and solvent molecules. In other words the two symmetric phases can be interpreted as corresponding to a *direct* cubic phase (III^+) and its *reversed* analog (III^-). The setup of a more complete phase diagram associated with different OPs and incorporated hexagonal and other observed phases is beyond the scope of this paper and will be subject of a forthcoming report.

Our results on the phase diagram topology look contradictive with the conclusion of Alexander and McTague [13]. Following the latter only phases in which an equilibrium cubic invariant does exist can border the parent phase. However, such a conclusion clearly is not rigorous since the model used in [13] operates with a single-component effective OP and only single section of the phenomenological phase diagram has been analyzed.

To finalize this section let us note that conditions (9) reduce the anisotropy of the Landau potential (8). This property of the segregating lyotropic system will be discussed in Section 3.

2.3 Partially and fully segregated states

We did not mention up to now the very important problem of description in segregating and self-organizing systems. This problem results from the intrinsic limitation of phenomenological theory of phase transitions in the symmetry form introduced by Landau [5]. Strictly speaking the ordinary phenomenological scheme does not include the stable fully segregated state which is characterized by the probability for molecules to be inside periodically arranged aggregates equal to unity and equal to zero in inter-aggregate space. The variational free energy $F(T, p, \eta)$ considered above has no minima for a state with OP, independent of the thermodynamical parameters. Thus, the Landau theory in its classical form is applicable to the *initial stages* of a segregation process, where OP is varying from zero to unity but does not reach the latter ($0 \leq \eta < 1$). The probability for amphiphilic molecules to be in interaggregate space is still non-zero and this theory is sufficient to consider only transformation from an isotropic state to partially segregated ones, *i.e.* to mesophases in which the segregated and solvent regions are not fully separated (*e.g.* bicontinuous mesophases).

In order to complete an approach by a possibility to consider fully segregated states a semiphenomenological scheme using a density-wave formalism was introduced for displacive and ordering type phase transitions [8,14] and, in the frame-work of such modified theory, OP was shown to be a transcendental function of relevant microscopic parameters ξ_i:

$$\eta_j = \eta_{0j} \sin f(\xi_i),$$

here η_j is the phenomenological OP and $f(\xi_i)$, a linear function of microscopic parameters ξ_i. The explicit form of $f(\xi_i)$ is specified by the transformation mechanism type. The minimization of F has to be performed with respect to the variational parameters ξ_i

$$\frac{\partial F}{\partial \eta_j} \frac{\partial \eta_j}{\partial \xi_i} = 0. \tag{12}$$

In addition to the classical solutions of Landau theory $(\partial F/\partial \eta_j) = 0$ equation (12) yields new ones $(\partial \eta_j/\partial \xi_i) = 0$ ($\eta_j = \text{const.}$).

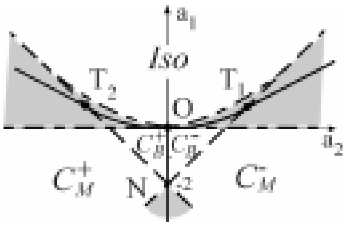

Fig. 2. Phase diagram associated with the one-component order-parameter expansion (14). Full, dashed and dotted-dashed lines are, respectively, first-order, second-order transitions and limit of stability lines. The regions of phase coexistence are shadowed. T_1 and T_2 are triple points, N is the four-phase point.

For the segregation phase transitions function $\eta_j(\xi_i)$ was shown to have form

$$\eta = \eta_0 \sin \frac{\pi}{2}\xi, \tag{13}$$

where ξ is a normalized variation of population by molecules of segregated subspaces, and η_0 conventionally equal unity [14].

In order to describe the transformations from the isotropic state to cubic bicontinuous and to cubic micellar structures one can use a model with non-linear single-component OP (13). The variational free energy in this model can be restricted to the fourth power

$$F(T,p,\eta(\xi)) = a_1(T,p)\eta^2 + a_2\eta^3 + a_3\eta^4. \tag{14}$$

Introducing the function $\eta(\xi)$ given by equation (13) in the effective free-energy $F(T,p,\eta(\xi))$ one gets by minimizing $F(T,p,\eta(\xi))$ with respect to the ξ variable, the equation of state:

$$\left(\sin\frac{\pi}{2}\xi\right)\left(\cos\frac{\pi}{2}\xi\right)\left\{2a_1 + 3a_2\sin\frac{\pi}{2}\xi + 4a_3\sin^2\frac{\pi}{2}\xi\right\} = 0 \tag{15}$$

which yields three possible stable states:

1) Iso: $\sin\frac{\pi}{2}\xi = 0,\ \ \xi = 0$ - initial isotropic state;

2) C_{M}: $\cos\frac{\pi}{2}\xi = 0,\ \ \xi = \pm 1$ - micellar cubic phase;

3) C_{B}: $\sin\frac{\pi}{2}\xi = \frac{-3a_2 \pm \sqrt{9a_2^2 - 32a_1a_3}}{8a_3}$ - bicontinuous cubic phase.

Figure 2 shows the phase diagram of the model (14) in the plane of the phenomenological parameters (a_1, a_2). One can see that the low symmetry phases can be reached from the isotropic phase across lines of first-order phase transitions. Bicontinuous and micellar phase regions are separated by lines of second-order *topological transition*, which are determined by the property that the OP magnitude reaches its maximal value $\eta = 1$.

The phase diagram in Figure 2 (as in Fig. 1b) is symmetric with respect to change in sign of η. Again, this means an exchange of amphiphilic and solvent molecules. In other words, the two symmetric phases can be interpreted as corresponding to the direct micellar or bicontinuous phases (C_{M}^+ and C_{B}^+) and to their reversed analogs (C_{M}^- and C_{B}^-). A direct-reversed phase transition of first-order can easily be observed in this diagram.

3 Crystal structures

The standard scheme of phenomenological theory of phase transitions would imply as a next step, after enumeration of the stable low-symmetry states (Sect. 2.1), the determination of their space groups and, for concrete systems, the prediction of the related structural deformation of the parent phase or positions for molecules in the low-symmetry structures [7,8,12]. Such a procedure applied to crystalline structures of discrete symmetry possesses strict predictive ability, reducing the variety of low-symmetry superstructures. However, this is not the case for the initial isotropic state with continuous translational and rotational symmetry. Various types of crystal lattices and space groups have corresponding solutions for the equations of state due to the infinite dimensionality of the relevant IR or, equivalently, infinite number of arms in the $\{\mathbf{k}_j\}$ vector star. Different solutions of the equations of state as well as different numbers of order parameters (*i.e.* reducible OP), induce the onset of different discrete structures. In order to restrict to a reasonable number the varieties of possible discrete low-symmetry structures for lyotropic liquid crystals and ensure predictive ability of our theory, we will complete standard group-theoretical procedure by some physical and crystallographic arguments.

3.1 Crystal field and micellar shape

Periodic space arrangement of amphiphilic molecular aggregates is known to be controlled by specific factors originating from the liquid-like nature of packed subunits, specific form of interaction of aggregates and from the specific ratio between long and short-range interactions. For ordinary elemental, ionic or molecular crystals, no limitations exist for the site symmetry of positions occupied by atoms, ions or molecules, or for their spatial organization described by 230 space groups. However, this is not the case for lyotropic crystals and thus, we will analyze briefly such limitations and use them to predict the bicontinuous and the micellar crystalline structures.

The first limitation we are going to use in our consideration is justified by the preceding thermodynamic and phenomenological analysis (Sect. 2.2). It has been shown above that for the relevant single OP, *only cubic O_h phases* border the isotropic state and other multi-parametric low-symmetry solutions for equations of state can be reached only by crossing these cubic phases. Experimentally the situation is that in all known cases the stability regions of cubic phases neighbor on the phase diagrams either with isotropic solution or with a lamellar phase, in complete agrement with the results of the preceding phenomenological analysis (Fig. 1). The same O_h crystal class for possible lyotropic 3D-periodic structures was suggested by Luzzati and coworkers [15], and by Seddon [16] using crystallographic arguments.

Secondly, only *micelles of identical chemical content* exist in lyotropic systems. This assumption can be justified on chemical grounds since the micellization conditions are common for all groups of molecules in solution, and this is supported experimentally by the existence of a unique critical micelle concentration. Hypothetical aggregation of amphiphilic molecules in micelles of different chemical contents under the same conditions imply a strong non-equilibrium situation with gradients in the chemical potential. Consequently, due to the chemical identity of micelles, multiple sublattice micellar structures can be formed mainly by micelles of different shape. In the isotropic solution the micellar shape is controlled exclusively by the minimization of surface energy with respect to a *scalar* parameter (curvature). Thus, the point symmetry of the initial minimal surface coincides with the point symmetry of the parent isotropic phase, *i.e.* the micelles are *spherical*. The homogeneous deformations changing the shape of the micelle with the good accuracy are components of a *symmetrical* second-rank tensor. Such a deformation can change the micellar shape from isotropic spherical to *uniaxial* (oblate or prolate), or to *biaxial* (rounded matchbox) but *it can not induce an inversion center loss*. The same conclusion can be reached for a system of non-spherical micelles considering statistical or dynamical *average* symmetry and correspond *effective* shape, due to the identical transformation properties of orientational and deformation OPs.

One could suggest that the shape and the proper symmetry of micelles aggregated in a cubic structure can be affected by the crystal field, as in site symmetry of ions or molecules in ordinary crystals. However two important features of the lyotropic crystal field, compared to an ordinary one, should be stressed. The first is that the character of the inter-micellar interaction is essentially isotropic, in contrast to the simplest inter-atomic interactions in metallic crystals, which are known to have a anisotropic tensorial character. Let us recall here the isotropization of Landau potential (Sect. 2.2, Eq. (9)) that has been justified by experimental arguments. Since the initial state is isotropic, the potential of undulative forces reflects mainly the character of interactions in the *low-symmetry periodic* state. For the segregation (probabilistic) phase transition mechanism, the phenomenological coefficients a_i, b_i, c_i and f_{ij} have meaning as a linear combination of N-body interaction potentials, where N is equal to the degree of the corresponding invariant. The special conditions (9) show that, despite the fact that interactions in a segregated lyotropic system cannot be reduced simply to pairwise terms (when only the $a_i \neq 0$), the anisotropic part is extremely limited. The second point is related to the ratio between bonding and deformation energy of crystallizing units. For an ordinary crystal these energies can be considered approximately as the latent heat of crystallization and as the distance between atomic energy levels correspondingly, and they have either the same order of magnitude or the deformation energy is one order more. In micellar systems, the deformation energy is related essentially to the bending surface energy and is of the order of 10^{-11} ergs, that is, at least, three orders higher than the bonding energy (10^{-14} ergs). The same ratio could be calculated if the deformation energy is identified as that of micellar formation which is on the order of 10^{-10} ergs as, for example, in the dodecylammonium octanoate system. This means that there is no reason to consider the possibility of micellar shape deformation by the crystal field. Thus, in the search for possible crystallographic positions of the micelles, only chemically identical spherical, uni- or biaxial centrosymmetric micelles will be considered.

In bicontinuous structures two chemically nonidentical subspaces of amphiphilic molecules and solvent are known to exist. Amphiphilic molecules form continuous passages linking the volumes surrounding high-symmetry points in the structure. The minimization conditions for the passage surface energy determine, as well, the geometry of the corresponding skeletal graphs, which tend to be lines of maximal symmetry. These latter belong in the space groups to the (x00), (xx0) and (xxx) type Wyckoff positions. The existence of a single free parameter for this type of position ensures the stability of corresponding bicontinuous structures as its geometry suppresses destructive transverse fluctuations.

3.2 Lattice complexes

In crystal structures with different space groups, the relative locations of symmetrically equivalent atoms may be the same (*e.g.* Cl in CsCl and F in CaF_2). Such a set of points is called a point configuration. Point configurations have been grouped into types called *lattice complexes*, each type referring to a Wyckoff position. Following the definition in reference [17], a lattice complex is the set of all point configurations that may be generated within one type of Wyckoff sets. Let us stress that the same lattice complexes may occur in different space-group types. For example, the complex "cubic primitive lattice" may be generated on O_h^1 - Wyckoff positions 1(a) and 1(b), O_h^5 - 8(c). All Wyckoff positions, Wyckoff sets and types of Wyckoff sets are assigned to the 402 lattice complexes listed in [17].

The existence of a restricted number of possible aggregate types in the cubic mesophases makes important the characteristic space-group type of the lattice complex; that is, one stands out because its corresponding Wyckoff position exhibits the highest site symmetry. This latter is called the *characteristic position* of the lattice complex.

The concept of lattice complex is very useful when considering crystal structures with a limited number of sublattices, such as those found in micellar and bicontinuous cubic crystals. We should take into account that only the characteristic positions being occupied provide experimental possibility to distinguish between space groups. For example, analyzing probable space group O_h^5 for a crystal structure, one can not localize single type micelles in the 8(c) position mentioned above. This is due to the fact that it belongs to the primitive cubic lattice and so will be identified as O_h^1 space group in the X-ray diffraction experiment. In our analysis we have checked all such possibilities.

Table 1. Micellar (M) and bicontinuous (B) cubic structures. Note: Upper index * marks the characteristic positions for micellar structures. Lower index notes a shape of micelle: s, spherical; u, uniaxial; b, biaxial.

Space Group	Type	Position
O_h^1	M	$a_{\mathrm{s}}^{*}, b_{\mathrm{s}}^{*}, c_{\mathrm{u}}^{*}, d_{\mathrm{u}}^{*}$
	B	e, f, h, i, j
O_h^3	M	$a_{\mathrm{s}}, b_{\mathrm{b}}, c_{\mathrm{u}}^{*}, d_{\mathrm{u}}^{*}$
	B	j
O_h^4	B	e, i, j
O_h^5	M	$a_{\mathrm{s}}^{*}, b_{\mathrm{s}}^{*}, c_{\mathrm{s}}, d_{\mathrm{b}}$
	B	h, i
O_h^7	M	$a_{\mathrm{s}}^{*}, b_{\mathrm{s}}^{*}, c_{\mathrm{u}}^{*}, d_{\mathrm{u}}^{*}$
	B	h
O_h^8	B	g
O_h^9	M	$a_{\mathrm{s}}^{*}, b_{\mathrm{s}}^{*}, c_{\mathrm{u}}, d_{\mathrm{u}}^{*}$
	B	e, f, h, i
O_h^{10}	B	f, g

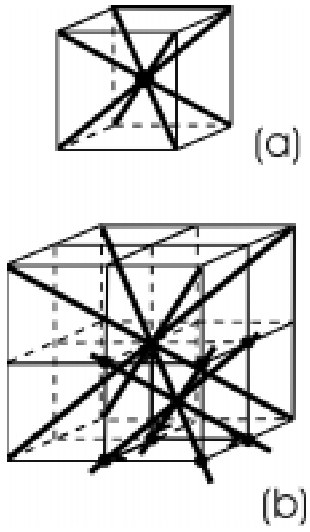

Fig. 3. Transformation of primitive cubic arrangement of Schwarz I-WP-surfaces to the body-centered cubic one. (a) Skeletal graph of I-WP surface. (b) Eight cubic unit cells. One can see an additional intersectial nodes in the center of the cubic unit cell.

3.3 Space groups selection

Now we apply the selection procedure for all space groups belonging to the O_h crystal class. For micellar systems it consists of direct examination of all non-parametric Wyckoff positions in the space group with respect to their site symmetry and characteristic properties. The bicontinuous structures, in addition, must be revised from the point of view of possible intersections of passages that can change the crystal lattice or its periodicity.

To show the procedure for *micellar crystals* let us apply the criteria above to two space groups. The first one, O_h^2, has no centrosymmetric positions and so, it is ruled out. The second one, O_h^3, has four centrosymmetric non-parametric positions. Two of them, $2(a)$: (000) and $6(b)$: (0 1/2 1/2) are not characteristic following the table in reference [17] and being occupied, will produce diffraction patterns identified as O_h^9 space group with positions $1(a)$ and $3(b)$ correspondingly filled. This means that a set of single type micelles can be arranged like position points $2(a)$ and $6(b)$, but it has no O_h^3 symmetry. Positions $6(c)$: (1/4 0 1/2) and $6(d)$: (1/4 1/2 0) are characteristic ones for O_h^3 space group, and micelles being distributed among them, show corresponding space symmetry. One can conclude that for the single-type micellar crystal of O_h^3 space symmetry, the positions $6(c)$ or $6(d)$ must be filled. For complex micellar structures these positions can be completed by $2(a)$ and/or $6(b)$ positions. Table 1 summarizes results of such an analysis of space groups belonging to the O_h symmetry class and indexes all allowed positions. The characteristic positions that have to be occupied are marked as well.

The specific feature of the *bicontinuous structures* is that all points of their corresponding skeletal graphs (*i.e.* axial lines along which amphiphilic layers are organized), excluding intersects, belong to the single-type Wyckoff positions in the space group. Despite this fact, each bicontinuous network has to be examined for a possible intersection of passages. For example, surface which organized along the straight lines belonging to $8(g)$: (xxx) position of O_h^1 space group is I-WP Schwarz minimal surface (Fig. 3a). However, being arranged on a primitive cubic lattice, the corresponding skeletal graphs will have identical intersection nodes in the positions (000) and (1/2 1/2 1/2) (Fig. 3b). Such a space organization of identical nodes identifies the body-centered cubic lattice and the O_h^9 space group. Thus, diffraction experiment will show spacings corresponding to the latter. It should be stressed that, in the case of ordinary crystal with discrete packing of objects, the $8(g)$ position is characteristic of O_h^1 group, and one can conclude that for bicontinuous structures, the concept of lattice complexes should be applied with some modifications.

4 Discussion

Two approaches, being in fact complementary, were used earlier to predict the stable structures in the lyotropic liquid-crystalline systems. The first approach, due to Charvolin and Sadoc [18], formulates the problem of description of these structures in purely geometrical terms and reduces it to the search for geometrical elements, points, lines or surfaces, around which, or along which, the amphiphilic layers may be organized in order to conciliate optimal distances and symmetric interfacial curvatures. In such an approach the polymorphism of amphiphilic systems is associated with the set of geometrical configurations which optimize the frustration between forces perpendicular to the interfaces, maintaining them at constant distances, and forces parallel to the interfaces, controlling their curvature. In the framework of this approach, *three* principal types of spatial organization of the amphiphilic layers or, equivalently, three types of bicontinuous structures have been generated, and it has been shown that the corresponding surfaces are related to infinite periodic minimal surfaces (IPMS). These are the Schoen Gyroid G, the Schwarz F surface (or diamond surface D) and the Schwarz P surface [18]. Three cubic structures with space groups O_h^{10}, O_h^4 and O_h^9 are actually known to correspond to these IPMS.

The second approach, presented mostly in the papers of Anderson, Hyde and coworkers, uses the elegant formalism of differential geometry in order to derive IPMS [19]. The same list of bicontinuous structures corresponding to different IPMS has been worked out showing the consistency of those two approaches. Nevertheless, evidence is mounting that many more IPMS exist than those so far discovered, and many solutions exist within each space group ([20] and references there).

Keeping in mind such actual indeterminacy, our analysis, following the spirit of Landau type theory, allows us to determine an upper limit for the variety of anisotropic low symmetry structures. This means that structures not contained in Table 1 can not be formed in lyotropic systems but the stability conditions for the possible ones should be located in the framework of the corresponding thermodynamic model formulated on the basis of general considerations (see in Sect. 2). The special positions in the space groups belonging to the crystal class O_h were examined with respect to their compatibility with the micellar or bicontinuous organization. Structures predicted within a such approach, due to the purely symmetry basis of the latter, will be stable even if their stability is not controlled exclusively by the topological factors or, by the minimization conditions for the corresponding surface. Table 1 lists the limited number of space groups and allowed positions for amphiphilic aggregates that essentially restricts the variety of structures showing the same spacings in X-ray diffraction.

It is of interest also to examine the relation between predicted bicontinuous and micellar structures. Semiphenomenological considerations predict a possibility for disruption of passages of any bicontinuous structure and its *topological* transformation to the micellar one (see, Sect. 2.3, Fig. 2). A direct test of predicted structures from Table 1 has shown that, in full agreement with the results of the above procedure, bicontinuous structures with O_h^4, O_h^8 and O_h^{10} space symmetry have *no related micellar structures of the same symmetry* since the discrete positions appearing in the disrupted variants are not characteristic. The corresponding micellar structures then have O_h^5 and O_h^9 symmetries. This fact is important for experimental identification of phases in the phase diagrams because there are no purely phenomenological reasons for a topological phase transition to change the symmetry of the system. Predicted bicontinuous structures of other symmetries follow the latter rule and their related micellar structures keep the space group unchanged.

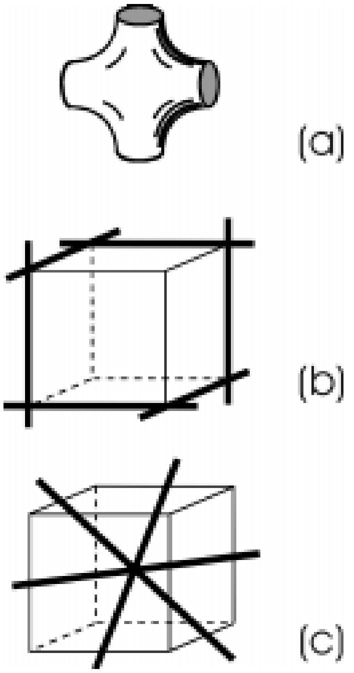

Fig. 4. Geometry of passages in some cubic bicontinuous structures. (a) Cross-like element. (b) Skeletal graph showing cross-like intersections of passages. Only eight's part of cubic unit-cell is presented. (c) Hexagonal intersection of infinite passages in the cubic structure. Eight's part of the unit-cell is shown.

Among the possible types of spatial bicontinuous organization of bilayers summarized in Table 1, several types correspond to the well-known IPMS, but there are still two new types of surfaces that have not been used before in the interpretation of diffraction data. The first one, cross-like, is generated by the (h)-position of O_h^1 space group. Figures 4a and 4b shows the basic element of such a surface and its spatial arrangement in the cubic structure. This latter is usually referred as Petrie's hexagon [18]. The second one, is the hexagonal interwoven nets (Fig. 4c) that are formed by passages belonging to the positions (j) in O_h^3, (h) in O_h^7, (g) in O_h^8 and (i) in O_h^9, but spatial organization of such flat hexagonal grids is different in all mentioned space groups.

It is worthwhile to mention an intermediate between micellar and bicontinuous form of cubic organization which is not presented in Table 1. A structure formed by nonintersective orthogonal infinite rods can be realized on the positions (g) and (h) of O_h^3 group. The corresponding structure of defect lines was found in the molecular liquid-crystalline "blue phase II" [21].

The structure of seven cubic phases listed in Table 1 are now well established. Four direct and reversed micellar structures belonging to the space groups $O_h^3(Pm3n)$, $O_h^7(Fd3m)$, $O_h^5(Fm3m)$ and O_h^9 $(Im3m)$ have been found for different amphiphilic molecular aggregates [2–4]. The two latter structures are formed by the single type of micelle while the remaining are two-sublattice. Three bicontinuous cubic phases of $O_h^4(Pn3m)$, O_h^9 and $O_h^{10}(Ia3d)$

symmetry are also well established at present [2]. Some compounds provide examples of really rich cubic polymorphism. In the dodecaoxyethylene mono-*n*-dodecyl ether ($C_{12}EO_{12}$)/water system, the first three of just mentioned above micellar cubic phases were identified [22]. Another impressive example is the poly(oxybutylene)-*b*-poly(oxyethylene)-water-xylene system, in which not only all known bicontinuous structures are present, but also three more micellar phases were found [23].

Despite an auxiliary character of the thermodynamic consideration presented herein some of its predictions could be related directly to experimental data. In particular, the first-order character of all “isotropic-periodic cubic” and “lamellar-cubic” transitions is undoubtedly proved experimentally by the existence of biphasic metastable regions between mentioned states on “temperature-concentration” or on concentration triangle diagrams. However, more detailed comparison with existing experimental data (for example, the form of the phase boundaries) is difficult as a phenomenological theory operates with *intensive* parameters (temperature and pressure) that provides a *linear* transformation of phenomenological coefficients and mapping of the theoretical phase diagrams to $p{-}T$ diagrams. The concentration is an *extensive* parameter generally showing no analytical relation to the variational parameters of phenomenological theory. The indicative property of the corresponding temperature-concentration phase diagram is the bell-shaped stability domains of anisotropic phases that is the case, for example, for the surfactant-water and lipid-containing systems mentioned in Section 2.1 [10,11]. Nevertheless, it does not exclude the possibility for the concentration to play the role of an intensive parameter through the coupling with true intensive variables, as that shown to occur in some lyotropic systems [24,25].

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