Non-Conventional Structural Phase Transitions and Amphiphobic Matter

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Abstract. – The order-disorder and order-order transitions in the ternary $ABC$ block and graft copolymers are analyzed via a Leibler-like microscopic approach. We show that simple cubic, face-centered cubic, well known double gyroid as well as some other phases could be stable in these systems in a vicinity of the critical point, equally with the conventional phases (body-centred cubic, hexagonal planar and lamellar). In particular, the ternary linear $ABC$ block copolymers with a long middle block non-selective with respect to the side blocks are especially inclined to form the gyroid phase. A new cubic non-centrosymmetric phase and some other cubic phases are also first predicted to exist as the most stable low temperature phase instead of the lamellar one. Such a phase behavior is suggested to be common for a new class of materials we call amphiphobic since their (macro)molecules consist at least of three mutually incompatible types of monomers.

A number of systems undergo order-disorder and order-order phase transitions due to the fact that their uniform state becomes unstable with respect to certain spatial fluctuations of the corresponding order parameter $\Phi(\mathbf{r})$ having a finite period $L$ and, respectively, wave number $q^* = 2\pi/L$. For instance, addition of an ionic solute to a solvent in its critical region may result in charge-density waves generation [1, 2], similar behavior was predicted and observed in weakly charged polyelectrolytes [3–6]. Microphase separation in solutions and melts of copolymers is also due to instability with respect to spatial fluctuations of the polymer concentration having a finite period [7–9]. The various morphologies emerging as a result of these transitions have attracted much interest [10] due to both numerous possible technological applications and interesting physics underlying their formation.

A common theoretical framework for these systems is provided by the weak crystallization theory [8, 11–13]. As consistent with the mean field approximation of this theory [8], the typical succession of the 1st order phase transitions occurring with decrease of temperature is as follows: the uniform (disordered) phase (DIS) - body-centred cubic lattice (BCC) - hexagonal planar lattice (HEX) - lamellar structure (L). Further we refer to the phases BCC, HEX and LAM as the conventional ones. For some special sets of parameters, all these phase transitions merge in the critical point where the 2nd order phase transition from the disordered to lamellar phase occurs. For $A_fN B_{(1-f)}N$ diblock copolymers such a parameter is just the composition $f$ and the critical point corresponds to the symmetric diblock copolymer
\( f_c = 0.5 \) in case the repeated units of both blocks have the same excluded volumes \( v \) and Kuhn lengths \( a \). Other phases usually could exist as metastable only, even though simple cubic (SC) and face-centered cubic (FCC) were shown to become stable for some special models [19].

One more equilibrium phase commonly encountered in lipid-water and surfactant systems [14] has been observed in weakly segregated molten diblock copolymers [15, 16]. It is characterized by \( Ia3d \) space group symmetry and often called the double gyroid (G). The bicontinuous morphology characteristic of this phase has attracted much interest during the last decade and a few of theoretical papers has been published to explain and describe this phase. In particular, for the aforementioned copolymer systems the mean-field phase diagrams were first theoretically calculated in the works [17]. A specific feature of these phase diagrams is the existence of two triple points \( f_{tr1} < f_c \) and \( f_{tr2} > f_c \) in which three phases HEX, G and LAM coexist. Therewith, the conventional sequence DIS-BCC-HEX-LAM and non-conventional one DIS-BCC-HEX-G-LAM would hold for compositions within and out of the interval, respectively. (For simplicity we do not address in this paper the fluctuation-caused changes of the mean-field phase diagrams discussed in detail in [18–23].)

A general analysis carried out by the author [24] within the mean-field approximation of the weak crystallization theory led to conclusion that the existence of triple point(s) different from the critical one is not a necessary feature of the phase diagrams of the systems capable of forming the thermodynamically stable bicontinuous gyroid morphology. The phase G as well as other phases different from the conventional ones were predicted to be stable, at certain conditions, around the critical point. However, this behavior was not reported, basing on microscopic calculations, for any real systems yet.

In this Letter we demonstrate that the real systems revealing the non-conventional morphologies G, SC, FCC and defined below BCC \(_2\) and G \(_2\) in the close vicinity of the critical point in accordance with our prediction [24] do exist. In particular, we show that the systems especially inclined to form the G phase are the ternary ABC block copolymers with a long non-selective middle block.

We start with a general phenomenological analysis. Being interested in the phase behavior close to the critical point, we write down the free energy related to emergence of a non-uniform scalar order parameter profile \( \Phi(\mathbf{r}) \) a Landau expansion in powers of \( \Phi \) up to the 4th order:

\[
\Delta F = \int \frac{\tau + \Gamma_2(q) - \Gamma_2(q_*)}{2} |\Phi_0| \frac{d\mathbf{q}}{(2\pi)^3} + \Delta F_3 + \Delta F_4
\]

\[
\frac{\Delta F_n}{(2\pi)^3} = \frac{1}{n!} \int \delta \left( \sum_{i=1}^{n} \mathbf{q}_i \right) \Gamma_n(\mathbf{q}_1...\mathbf{q}_n) \prod_{l=1}^{n} \Phi(\mathbf{q}_l) \frac{d\mathbf{q}_l}{(2\pi)^3} 
\]

The coefficients \( \Gamma_i \) appearing in the free energy expression (1), depend on the structure of the system, the function \( \Gamma_2(q) \) has a minimum at \( q = q_* \) and \( \tau \) is an effective dimensionless temperature measured from the instability point.

The system morphology is described by the order parameter \( \Phi(\mathbf{r}) \) (or its Fourier transform \( \Phi_0(\mathbf{q}) \)) providing the minimum of this free energy.

In general, it can be expanded in an infinite series in the Fourier harmonics corresponding to the set \( \{\mathbf{n}_i\} \) of the points of the inverse lattice conjugated to the chosen spatial lattice. But in the weak segregation approximation (close to the critical point) one takes account only of the 2\( k \) main harmonics belonging to the 1st coordination sphere of the inverse lattice

\[
\Phi_0(\mathbf{r}) = A \sum_{|\mathbf{n}_i|=1} \left( \exp i \left( q_* \mathbf{n}_i \mathbf{r} + \phi_i \right) + c.c. \right)
\]
Therewith, the phases \( \phi_i \) are relevant. Indeed, substituting the trial functions (2) into the r.h.s. of eq. (1) and minimizing the result with respect to \( A \) gives
\[
\Delta F = \tau A_0^2 + \alpha_k A_0^3 + \beta_k A_0^4
\]
where \( A_0 = Ak^{1/2} \), \( \alpha_k = \left( \gamma/k^{3/2} \right) \sum_3 \cos \Omega^{(3)}_j \) and
\[
\beta_k = \frac{\lambda_0(0)}{4k} + \frac{\sum_0 \lambda_0(h) + \sum_4 \lambda(h_1, h_2, h_3) \cos \Omega^{(4)}_{j}}{k^2}
\]
We use the Leibler designations and parameters [8]
\[
h_1 = (q_1 + q_2)^2/q_x^2, \quad h_2 = (q_1 + q_3)^2/q_y^2, \quad h_3 = (q_1 + q_4)^2/q_z^2.
\]
\( \gamma = \Gamma_3(p_1, p_2, p_3) \) (\( |q_i| = q_0 \)), \( \lambda_0(h) = \lambda(0, h, 4 - h) \), \( \lambda(h_1, h_2, h_3) = \Gamma_4(q_1, q_2, q_3, q_4) \) with
\[
\sum_{i=1}^4 q_i = 0, \quad |q_i| = q_0. \quad [25]. \quad \text{The phases } \Omega^{(n)}_{j} \text{ are the algebraic sums of the phases } \phi \text{ for the}
\]
triplets and noncoplanar quartets of the vectors involved in the definition of corresponding \( \gamma \) and \( \lambda \), the symbol \( \sum_n \) designating summation over all sets of such \( n \) vectors. The first summation in eq. (4) is over all pairs of noncollinear vectors \( q_i \) and \( q_j \).

The BCC family. The six main harmonics
\[
\begin{align*}
n_1 & \sim (0, 1, -1), \quad n_2 \sim (-1, 0, 1), \quad n_3 \sim (1, -1, 0), \\
n_I & \sim (0, -1, -1), \quad n_{II} \sim (-1, 0, -1), \quad n_{III} \sim (-1, -1, 0),
\end{align*}
\]
are known to correspond the conventional BCC morphology if all the phases are zero. This set gives also the BCC2 lattice [19] if we choose
\[
\phi_I = \phi_{II} = \phi_{III} = 0, \quad \phi_1 = \phi_2 = \phi_3 = \pi/2
\]
As consistent with the definitions (5), (6), the order parameter (2) for BCC2 reads
\[
\Phi(r) = A(\cos(x + y) + \cos(y + z) + \cos(z + x) - \sin(x - y) - \sin(y - z) - \sin(z - x)),
\]
where the waved coordinates are scaled as compared to the original ones according to the rule \( \tilde{s} = sq_0/\sqrt{2} \). As consistent with the most general symmetry properties [26], BCC2 morphology is non-centrosymmetric. Remarkably, the zero level surface for BCC2 differs from the well known ”gyroid” surface [27] only in a shift of the origin of the co-ordination system.

The G family. The 12 main harmonics
\[
\begin{align*}
n_{01} & \sim (-2, 1, 1), \quad n_{11} \sim (-2, -1, 1), \quad n_{21} \sim (2, 1, -1), \quad n_{31} \sim (2, -1, 1), \\
n_{02} & \sim (1, -2, 1), \quad n_{12} \sim (1, 2, -1), \quad n_{22} \sim (-1, -2, 1), \quad n_{32} \sim (-1, 2, 1), \\
n_{03} & \sim (1, 1, -2), \quad n_{13} \sim (1, -1, 2), \quad n_{23} \sim (-1, 1, 2), \quad n_{33} \sim (-1, -1, 2),
\end{align*}
\]
provide i) the bi-continuous gyroid morphology \( Ia\overline{3}d \) with the phases
\[
\begin{align*}
\alpha_{12} &= \alpha_{23} = \alpha_{31} = \alpha_{01} = \alpha_{02} = \alpha_{03} = 0, \\
\alpha_{21} &= \alpha_{32} = \alpha_{13} = \alpha_{11} = \alpha_{22} = \alpha_{33} = \pi;
\end{align*}
\]
ii) the morphology we call the BCC3 if all the 12 phases equal zero (it is just the ordinary BCC but the dominant harmonics correspond to the 3rd rather than 1st co-ordination sphere);
Fig. 1 – The phase diagrams of the ordered phases whose existence is possible close to the critical point of the order-disorder transitions. a) for the phenomenological angle dependence of the forth vertex on the plane (effective temperature \( \tau_{\text{eff}} \) - structure parameter \( \delta \)); b) for the ternary ABC linear triblock copolymers with the middle non-selective block on the plane (\( \tau_{\text{eff}} - f_B \)); c) for the ABC miktoarm terpolymers with one non-selective block (referred to as B) on the plane (\( \tau_{\text{eff}} - f_B \)). The phases are designated as follows: 1 - BCC, 2 - HEX, 3 - LAM, 4 - G, 5 - BCC, 6 - FCC, 7 - SC, 8 - G2.

and iii) the morphology we call the G2 if \( \alpha_{21} = \alpha_{32} = \alpha_{13} = \pi \) and other 9 phases equal zero (it seems to correspond to the crystallographic symmetry class \( \bar{I}43d \)).

The next step is to take into account the explicit angle dependence of the fourth vertex \( \Gamma_4 \) appearing in the expression (1) rather than to adopt the commonly accepted approximation [20]

\[
\Gamma_4(q_1, q_2, q_3, q_4) \approx \lambda_0(0). \tag{9}
\]

Assuming the angle dependence to be given by the first non-constant term in the expansion of \( \Gamma_4 \) in powers of \( h_i \):

\[
\Gamma_4(h_1, h_2, h_3) = \lambda_0 \left( 1 \frac{3\delta}{32} \left( 4^2 - \sum_{i=1}^{3} h_i^2 \right) \right) \tag{10}
\]

we build the phase diagram shown in fig. 1 on the plane (\( \delta \) - the reduced temperature \( \tilde{\tau} = 32\tau \lambda_0/(9\gamma^2) \)), where only the phase transition lines starting at the very critical point are shown. As seen from fig. 1 for \( \delta > \delta_0 = 0.362 \) the nonconventional sequences occur:

- DIS-BCC-HEX-LAM for \( \delta_{12} > \delta > \delta_0, \delta_{12} = 4/9; \)
- DIS-BCC-HEX-G-BCC for \( \delta_{23} > \delta > \delta_{12}, \delta_{23} = 2/3; \)
- DIS-BCC-HEX-G-FCC for \( \delta_1 > \delta > \delta_{23}, \delta_1 = 0.822; \)
- DIS-BCC-G-FCC for \( \delta_{34} > \delta > \delta_1, \delta_{34} = 5/6; \)
- DIS-BCC-G-SC for \( \delta_{15} > \delta > \delta_{34}, \delta_{15} = 0.891; \)
- DIS-BCC-SC for \( \delta_2 > \delta > \delta_{45}, \delta_2 = 4/3; \)
- DIS-BCC for \( \delta_3 > \delta > \delta_2, \delta_3 = 1.538. \)

The lines \( \delta_2 = 4/3 \) and \( \delta_3 = 1.538 \) are shown in fig. 1 by the dotted lines. At last, for \( \delta > \delta_3 \) the value of \( \beta_{\text{BCC}} \) becomes negative and the weak crystallization theory does not hold anymore even in the vicinity of the critical point. In this region the proper consideration of the ordered phases is possible with due regard for the higher terms of the Landau expansion (1) only.

Thus, to find any non-conventional phase transition sequence it is intrinsically necessary to take into account the angle dependence.
Let us remember now that the phase diagrams calculated for the diblock and star AB block copolymers [8, 28] are quite conventional in the sense that the gyroid phase exists only outside an interval including the critical point [17]. We conclude, therefore, that $\theta > \theta_0$ for these systems and the gyroid phase stability here is due to the "higher harmonics" contribution [29–31]. The same topology is characteristic of the phase diagrams we calculated for some other $AB$ molten copolymers of complex architecture.

The situation changes drastically if we address the ternary $ABC$ copolymers. We analyze them via numerical calculation of the explicit expressions for the vertices $\Gamma_i$, their substitution into (1) and minimization of the obtained free energy expressions with respect to the trial order parameters (2) for all the morphologies described above. Therewith, we employ an approximate reduction of the real 2-order parameter problem to an effective 1-order parameter.

To this end, we introduce a quantitative distinction between strongly and weakly fluctuating order parameters $\Phi(r)$ and $\Psi(r)$, respectively, minimize the free energy with respect to the weakly fluctuating field $\Psi(r)$ given a profile of $\Phi(r)$ and, by doing so, obtain an effective 1-order parameter Hamiltonian in terms of the strongly fluctuating field $\Phi(r)$. The whole procedure is described in detail in refs [29–34].

The last simplification is the approximation of the binary interaction parameters via the solubility parameters: $2\chi_{ij} = v(\delta_i - \delta_j)^2 / (2T)$, where the temperature $T$ is measured in energetic units, $\delta_i$ is the conventional (temperature-independent) solubility parameter of the $i$-th component and $v$ is (the same) excluded volume of the repeating units $A, B, C$. Then there are two independent interaction parameters naturally characterizing the ternary systems:

$$\chi_{AC} = \frac{v(\delta_A - \delta_C)^2}{2T}, \quad x = \frac{2\delta_B - \delta_A - \delta_C}{\delta_A - \delta_C} \tag{11}$$

The first of them characterizes incompatibility of the side blocks in the $ABC$ triblock copolymer whereas the selectivity parameter $x$ describes how much is the middle block $B$ selective with respect to the side blocks [32].

It could be shown via considerations similar to those presented in [32] that for $x = 0$ the cubic term vanishes identically along the line $f_A = f_C$ both for molten $A_lB_mC_n$ triblock and trigrfat copolymers. Thus, this line is the critical one for these systems. Their phase diagrams in the vicinity of this critical line we calculated using the procedure and approximations described above are presented in fig. 4 b, c on the plane $(f_B, \tilde{\tau})$, where the reduced temperature $\tilde{\tau} = 32\tau\lambda_0 / (9\gamma^2(f_B)a^2)$, where the asymmetry parameter $\sigma = |l-n|/(l+n)$ and a scaling factor $\gamma(f_B)$ are introduced.

Whereas $\tilde{\tau}$ describes the distance between the reduced temperatures of different phase transition lines and that of spinodal, location of the spinodal itself is naturally described in terms of the reduced parameter $\tilde{\chi} = \chi_{AC}N$, where $N = l + m + n$ is the total degree of polymerization of the $ABC$ macromolecule. The values of $\tilde{\chi}$ and the reduced value of the critical wave number $Q_c = \left(qav\sqrt{N}\right)/6$ are plotted as functions of the middle block composition $f_B$ on fig. 2. We see clearly that the evolution of the phase diagrams of the linear $ABC$ block copolymers with increase of the middle block fraction $f_B$ closely follows the trend predicted phenomenologically in [24] and shown in fig. 1 h. Namely, a consecutive replacing of the lamellar morphology as the most low-temperature stable phase according to sequence LAM-BCC₂-FCC-SC-G₂ occurs with decrease of the length of the shortest side block. This trend is quite natural and means that it is impossible to form lamellae when the side blocks are short enough. The only topological difference between the phase diagrams shown on fig. 1 h and fig. 1 b is replacing of the BCC phase by a new phase of symmetry G₂ for extremely short (but finite) side blocks with $f_B > 0.96$. This difference is, obviously, due to the fact that the
Fig. 2 – The characteristic scale $Q^2 = (q^*a)^2 N/6$ (a) and location of the spinodal with respect to microphase separation $\tilde{\chi} = \chi N$ (b) as functions of the non-selective block composition $f_B$ for the linear (1) and star (2) ternary block copolymers.

angle dependence of the vertex $\Gamma_4$ cannot be approximated by the simple parabolic form \[11\] if it is strong enough. Some parallels with our predictions could be found in [35, 36].

Even more strong and different is this dependence for the molten $ABC$ miktoarm terpolymers with one arm (referred to as $B$) non-selective with respect to both other as demonstrated by the topology of their phase diagram shown on fig. 1c. The weak segregation theory is intrinsically not applicable for these systems for $f_B > 0.3815$ since the fourth vertex of the BCC phase becomes negative here and, therefore, this phase becomes unstable with respect to strong segregation. In this case the sequence of the most low-temperature stable phases is as follows: LAM-HEX-BCC. A rich phase behavior was found also in our preliminary analysis of the mixtures of ternary and binary block copolymers, the values of $f_B$ corresponding to the phase transitions LAM-BCC$^2$-FCC-SC$^2$ being strongly dependent on the concentration and the polymer length ratio.

Summarizing, in this paper we carried out a microscopic Leibler-like analysis of the ternary triblock copolymers with the middle block non-selective with respect to the side ones. We showed that for the linear ternary triblock copolymers i) a new cubic non-centrosymmetric morphology BCC$_2$ should replace the lamellar one as the most stable low temperature phase for reasonably long middle block ($0.67 < f_B < 0.72$), with further increase of $f_B$ BCC$_2$, in turn, will be replaced by SC, FCC and G$_2$ morphologies; ii) the gyroid phase $Ia\overline{3}d$ becomes stable in the very vicinity of the critical point for $0.38 < f_B < 0.85$. On the contrary, for the ternary miktoarm (star) triblock copolymers we predict increase of the BCC stability and strong segregation with increase of $f_B$. One can expect, in general, that the phase behavior of block copolymers with $n \geq 3$ mutually incompatible sorts of blocks would be not only much richer but also much more architecture dependent than that of the conventional binary block copolymers. We believe this class of materials to deserve a particular generic name of amphiphobic matter.

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