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New Results in Weak Segregation Limit Theory of Block Copolymers

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Summary: Some theoretical results recently obtained in papers with participation of the author in the field of statistical thermodynamics of block copolymers are briefly discussed.

Keywords: block copolymers; morphology; nanotechnology; phase diagrams; theory

Introduction

A peculiar feature of block copolymers is the appearance in their melts of equilibrium spatially periodic mesophases whose period falls within the nanometer range.[1] This unique property of block copolymers opens up fresh possibilities for their application in nanotechnology[2] and, particularly, in designing advanced polymer materials based on photon crystals.[3] This circumstance motivates the importance of a theoretical investigation of the dependence of the thermodynamic behavior of block copolymer liquids on the chemical structure of their macromolecules.

One of the main approaches commonly used for this purpose is the Weak Segregation Limit (WSL) theory.[1] It rests on the ideas of the Landau theory of phase transitions extensively employed in theoretical physics of condensed matter under the description of the phase transitions in liquids magnetics and crystals.[4–6] According to this theory, the nonequilibrium free energy $\mathcal{F}$ is written down as several first terms of the functional series in powers of order parameters $\{\psi_\alpha(\mathbf{r})\}$ whose equilibrium values are found by minimization of functional $\mathcal{F}\{[\psi_\alpha]\}$. The coefficients of such an expansion, referred to as the vertex functions, are governed by the chemical structure of macromolecules of a specimen of the block copolymer under examination. Finding of this dependence, performed in the framework of the microscopic approach, constitutes the main challenge for the weak segregation theory of heteropolymer liquids.

A special emphasis should be placed on two fundamental peculiarities of such liquids owing to which the Landau theory of phase transitions in such systems differs qualitatively from that traditionally used in condensed matter physics. So, in the traditional Landau theory of low-molecular weight liquids the order parameter $\psi_\alpha(\mathbf{r})$ is proportional to the deviation of local density $\Delta\rho_\alpha(\mathbf{r})$ of α-type particles at point $\mathbf{r}$ from its average value $\overline{\rho}_\alpha$. When this theory is invoked to describe polymers, the role of particles is played by monomeric units. These latter, however, unlike the former are not true thermodynamic components, because they are linked to one another by stable chemical bonds which normally remain unbreakable for the operational use of polymer materials.

The second fundamental distinction of heteropolymer liquids from low-molecular ones consists in their polydispersity. In fact, any specimen of real heteropolymer represents a mixture of an enormous number of macromolecules differing in configuration, i.e., in length, chemical composition and struc-

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ture of polymer chains. The configuration of each macromolecule is formed in the course of the synthesis of a heteropolymer to remain later on unaltered. The thermodynamic behavior of any polydisperse heteropolymer liquid is, apparently, dependent on the distribution of its macromolecules for configurations. Problems of finding of this molecular structure distribution have been solved by the methods of statistical chemistry[7] for many processes of the obtaining of synthetic heteropolymers.

To calculate the free energy of polydisperse heteropolymer, one is supposed to average over both conformations of macromolecules and their configurations. In other words, averaging should be necessarily performed over two types of disorder, i.e., over heat disorder and quenched structure one.[8] To cope with this sort of problems, the methods of statistical physics of disordered systems are usually engaged, being the ''replica trick'' the most popular among them.[9,10] Its application to polydisperse heteropolymer liquids offers new opportunities for deriving expressions for vertex functions in the expansion of the free energy of such liquids. A remarkable feature of this expansion resulting from averaging over macromolecules' configurations is the appearance in these vertices of so-called ''non-local'' terms. These, unlike local ones, tend to infinity in the long-wave limit, when the momenta approach zero. In the expansion of the Landau free energy of monodisperse heteropolymers, all macromolecules of which have, by definition, identical configuration, the non-local terms are, evidently, absent.

The first to present the expression for the non-local term in the forth order vertex function were Shakhnovich and Gutin[11] who considered a melt of binary random heteropolymer. Later, these results were extended[12–15] to heteropolymers whose molecular structure distribution is described by a Markov chain. Such markovian heteropolymers are synthesized in the processes of free-radical copolymerization and copolycondensation,[16–17] that conditions the importance of the theoretical investigation of their thermodynamic behavior. Of particular value here are papers by Panyukov and Potemkin[18,19] where for the first time two-phase states of an incompressible melt of binary markovian copolymer have been considered in the framework of the WSL theory.

A substantial drawback of all the above-cited publications consists in ignoring the contributions into the free energy of the terms in which the order parameters enter in degree $n > 4$. It has been recently shown,[20] that there exists a certain sixth order non-local term, the neglect of which can be responsible for erroneous results under consideration of the thermodynamic behavior of an incompressible melt of binary markovian heteropolymer. To carry out such a consideration for melts of markovian copolymers whose macromolecules consist of m types of monomeric units, it is necessary to find the fifth and sixth order vertex functions at arbitrary m. This problem has been solved[21] making use of a diagrammatic algorithm that is a modification of the general algorithm of finding of the n-th order vertex functions for a m-component heteropolymer with arbitrary molecular structure distribution.[22]

Although any copolymer specimen is actually polydisperse, its degree of polydispersity can markedly vary depending on the method by which this specimen was synthesized. So, polydispersity of multiblock copolymers obtained by polycondensation of oligomers is substantially controlled by the width of their molecular weight distribution whose quantitative characteristic is the polydispersity coefficient. For oligomers prepared by polycondensation and ''living'' anionic polymerization the values of this coefficient are close to unity and zero, respectively. Hence, under a theoretical consideration of the phase behavior of multiblock copolymers obtained by polycondensation of the first type oligomers the role of polydispersity is of utmost importance. However, under an analogous examination of multiblock copolymers with molecules comprising the second type blocks the polydispersity may well be neglected. This approximation enables to substantially simplify the theoretical analysis, since it excludes the necessity of averaging over configurations of macromolecules.

The most developed is the WSL theory of an incompressible melt of binary monodisperse heteropolymers because here the Landau free energy represents a functional of a sole order parameter $\psi(\mathbf{r})$. At given chemical structure of macromolecules the phase behavior of their melt in the framework of this model is governed exclusively by the Flory parameter χ. Leibler[23] was the first to invoke the formalism of the WSL theory for the description of such behavior of melt of diblock copolymer. The phase diagrams constructed by him for macromolecules of different length and chemical composition comprise regions of the existence of three mesophases, i.e., Body-Centered Cubic (BCC), Hexagonal (HEX) and Lamellar (LAM). These classical mesophases, as well as the Gyroid mesophase found later, were believed for a while to be the only possible in melts of binary block copolymers. This inference was repeatedly supported by results of the consideration of triblock and multiblock copolymers with macromolecules of trivial one-scale architecture. However, recently the authors of papers[24,25] employ the WSL theory to study the phase behavior of melts of binary linear block copolymers with the two-scale architecture (Figure 1) found the conditions of the thermodynamic stability of some other mesophases, such as Simple Cubic, Face-Centered Cubic and that known as BCC2.

Along with mesophases whose morphology is characterized by the only scale of space periodicity, it is possible to imagine complex mesophases with two different scales. Examples of these latter are Hexagonally Modulated Lamellae (HML) and Hexagonally Perforated Layers (HPL) mesophases. The possibility of their existence was thoroughly investigated both theoretically and experimentally (See[1] pp. 46–52 and references therein). The results of the investigations revealed that in melts of diblock copolymers such mesophases do not exist as stable equilibrium ones, but the HML may be a transient, and the HPL a long-lived metastable mesophase. The first of them corresponds to a saddle point in the free energy hypersurface, whereas the second one is associated with its local minimum.

A challenging problem facing statistical thermodynamics of heteropolymer liquids is to explore theoretically the possibility of the existence of some mesophases characterized by two scales of spatial periodicity. It seems to be natural to look for such mesophases among block copolymers with the two-scale architecture similar to that presented in Figure 1. A specific feature of the melts of such two-scale macromolecules is that their structure factor $\tilde{S}(q^2)$ can have two maxima (Figure 2) associated with two branches of nontrivial spinodal.[26] Of particular interest are Double Spinodal Points (DSPs) belonging to both such branches since at these points the loss of absolute thermodynamic stability of the spatially homogeneous state occurs simultaneously on the wave vectors of two different lengths. For this reason there are serious grounds to expect the emergence in the vicinity of the DSP line of thermodynamically stable mesophases characterized by two scales of spatial periodicity.

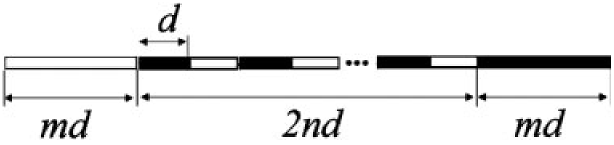

Figure 1.
Example of the architecture of a block copolymer with two intrinsic length scales.

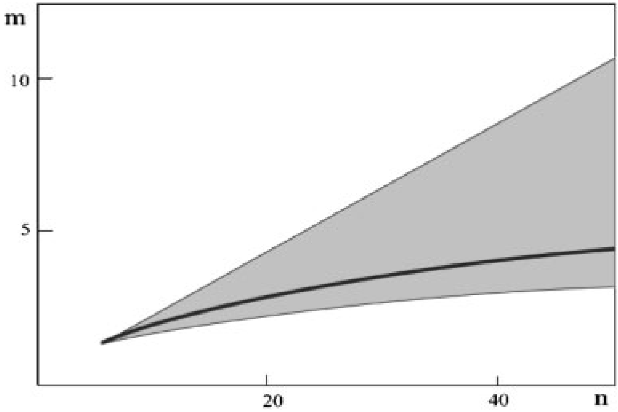

Figure 2.
Classification diagram of structure factor $\tilde{S}(q^2)$ for the melt of a block copolymer with the architecture depicted in Fig. 1. In gray region function $\tilde{S}(q^2)$ has two maxima whose heights are equal on the heavy (DSP) line.

One of the central problems of the WSL theory arising under the description of such mesophases consists in deriving expressions that relate the coefficients of the amplitude expansion of the Landau free energy with the vertex functions. The first who presented such expressions for three particular two-scale mesophases was Nap.[27] Later a diagram algorithm was suggested[28] enabling one to write down analogous expressions for any mesophases with two scales of spatial periodicity. Using this algorithm to consider a melt of two-scale macromolecules the authors of paper[29] managed to reveal for the first time the possibility of the existence on the phase diagram of a region of thermodynamic stability of some two-scale mesophase.

Of prime importance for the thermodynamics of block copolymers is finding the dependence of their phase behavior on chemical structure of macromolecules. This is characterized for a monodisperse specimen by the sequence of types of blocks (i.e., by architecture) and by their lengths. Binary copolymers like segmented polyurethanes or segmented copolyesters, provided their molecules consist of a considerable number of monodisperse blocks, have, evidently, periodic architecture. In a sense such a polymer chain may be thought of as a certain one-dimensional ‘‘pseudo-crystal’’ in a configurational space of macromolecules. The elementary cell of such a pseudo-crystal is a pair of neighboring blocks of different types.

Because a periodic multiblock copolymer can be obtained by polycondensation of a macromonomer with the chemical structure of an elementary cell, it is interesting to compare to which extent the scattering and phase diagrams of melts of the macromonomer and the products of its polycondensation will differ. In the simplest case, when macromonomer is a monodisperse diblock copolymer, such distinctions are of quantitative rather than qualitative character.[30,31] The correctness of this assertion for macromolecules, whose chemical structure is characterized by two intrinsic length scales, remained an open question till the appearance of paper.[32] It was recognized there that angular dependences of scattering intensity of these two systems differ only quantitatively. Conversely, the distinction in their phase behavior was found[32] to be of qualitative character.

Upon pointing out some novel problems of the statistical physics of multiblock copolymers, which we managed to solve recently in the framework of the WSL theory, let us survey briefly the results achieved.

The Landau Theory of Phase Transitions with Two-Component order Parameter

The dimensionless Landau free energy $\mathcal{F}_L$ of an incompressible melt of a binary multiblock copolymer in the momentum representation can be presented as follows

$$\mathcal{F}[\tilde{\psi}] \equiv \frac{\mathcal{F}_L[\tilde{\psi}]}{TM} = \sum_{n=2}^{4} \frac{1}{n!} \mathcal{F}_n[\tilde{\psi}]$$

$$\mathcal{F}_n[\tilde{\psi}] = \sum_{\{\mathbf{q}_i\}} \tilde{\Gamma}^{(n)}(\mathbf{q}_1, \dots \mathbf{q}_n) \prod_{i=1}^{n} \tilde{\psi}(\mathbf{q}_i) \tag{1}$$

Here M denotes the overall number of monomeric units, T stands for absolute temperature in energetic units, and $\tilde{\psi}(\mathbf{q})$ represents the Fourier transform of the order parameter $\psi(\mathbf{r})$. Vertex functions $\tilde{\Gamma}^{(3)}$ and $\tilde{\Gamma}^{(4)}$ are controlled exclusively by the parameters of the chemical structure of a macromolecule, whereas $\tilde{\Gamma}^{(2)}(q) = \tilde{S}^{-1}(q^2) - 2\chi$ depends additionally on temperature that governs the Flory parameter χ.

Minimizing functional (1), it is possible to find the Fourier transforms of the equilibrium densities of monomeric units of different types. This, particularly, provides a possibility to specify the spatial symmetry group of an equilibrium mesophase. In order to construct a phase diagram, the consideration is usually restricted to a set of several candidate mesophases among which only one should be chosen afterwards whose free energy is minimal.

When developing the WSL theory of a melt of block copolymers, whose molecules have architecture like that given in Figure 1, the traditional approach fails in the vicinity of DSP line (See Figure 2). Indeed, at every its point the structure factor $\tilde{S}(q^2)$ has at q_L^* and q_S^* two maxima of the same height. That is why on this line the homogeneous state of a melt looses the absolute thermodynamic stability simultaneously with respect to the fluctuations along arbitrary directed wave vectors $\mathbf{q}^{(L)}$ and $\mathbf{q}^{(S)}$ whose lengths q_L^* and q_S^* are fixed at each point of DSP line. Therefore, in its vicinity the traditional WSL theory with one-component order parameter turns out to be incorrect. To make up this deficiency it was suggested[28] to introduce the two-component order parameter, which in the first-harmonic approximation reads

$$\begin{aligned} \tilde{\psi}(\mathbf{q}) = {} & \frac{A}{\sqrt{k}} \sum_{j_1=1}^{k_1} \Big[\exp\left(i\varphi_{j_1}\right) \delta_K\left(\mathbf{q} - \mathbf{q}_{j_1}^{(L)}\right) \\ & + \exp\left(-i\varphi_{j_1}\right) \delta_K\left(\mathbf{q} + \mathbf{q}_{j_1}^{(L)}\right) \Big] \\ & + \frac{B}{\sqrt{k}} \sum_{j_2=1}^{k_2} \Big[\exp\left(i\varphi_{j_2}\right) \delta_K\left(\mathbf{q} - \mathbf{q}_{j_2}^{(S)}\right) \Big] \\ & + \exp\left(-i\varphi_{j_2}\right) \delta_K\left(\mathbf{q} + \mathbf{q}_{j_2}^{(S)}\right) \Big] \end{aligned} \tag{2}$$

where the summation in the first and the second terms is over all $k = k_1 + k_2$ wave vectors of the first coordination spheres having radii q_L^* and q_S^*, respectively. Formula (2) can be employed to describe any block copolymer, provided the difference in values $\chi_{sp}^{(1)} = [2\tilde{S}(q_L^{*2})]^{-1}$ and $\chi_{sp}^{(2)} = [2\tilde{S}(q_S^{*2})]^{-1}$ of parameter χ on two spinodal branches is small enough in comparison with each of these values.

The substitution of expression (2) into formula (1) results in the amplitude expansion of the Landau free energy

$$\begin{aligned} \mathbf{F} = {} & \nu_1 \tau_1 A^2 + \nu_2 \tau_2 B^2 \\ & - \sum_{i=0}^{3} \sum_{j=0}^{3} C_3^{(ij)} A^i B^j \delta_{i+j,3} \\ & + \sum_{i=0}^{4} \sum_{j=0}^{4} C_4^{(ij)} A^i B^j \delta_{i+j,4} \end{aligned} \tag{3}$$

where the following designations are used

$$\tau_\alpha = \chi_{sp}^{(\alpha)} - \chi \quad \nu_\alpha = k_\alpha / k \quad (\alpha = 1, 2) \tag{4}$$

Minimizing polynomial (3) with respect to variables A and B, it is possible to construct a phase diagram, provided the values of coefficients $C_3^{(ij)}$ and $C_4^{(ij)}$ are known for all candidate mesophases. Any of these coefficients represents a sum, each item of which is the product of two factors. One of them being governed by the space symmetry group of the mesophase under consideration does not depend on the chemical structure of block copolymer macromolecules. The second factor represents vertex function $\tilde{\Gamma}^{(3)}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3)$ or $\tilde{\Gamma}^{(4)}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4)$, taken at values of arguments controlled by q_L^* and q_S^* as well as by the spatial symmetry of the mesophase of interest. A diagram technique was developed[28] which permits writing down complete sets of coefficients $C_3^{(ij)}$ and $C_4^{(ij)}$ of the amplitude expansion (3) for any mesophase of an incompressible melt of arbitrary binary monodisperse block copolymer. Expressions for the coefficients of polynomial (3), which can be derived by means of the diagram technique,[28] are valid for arbitrary dependencies of the vertex functions on the wave vectors. The determination of these dependencies for block copolymers of given chemical structure, falling outside the limits of the Landau theory, is a problem of the microscopic theory. A diagram algorithm developed for the solution of this problem will be discussed below.

Diagram technique for finding of vertex functions

Fundamental for the WSL theory of heteropolymer liquids is the expression for the Landau free energy

$$\mathcal{F}\{[\tilde{\psi}_\alpha]\} = \sum_{n=2}^{\infty} \frac{1}{n!} \mathcal{F}_n\{[\tilde{\psi}_\alpha]\} \tag{5}$$

where the n-th order contribution is described by expression

$$\mathcal{F}_n\{[\tilde{\psi}_\alpha]\} = \sum_{\{\alpha_i\}} \sum_{\{\mathbf{q}_i\}} \tilde{\Gamma}^{(n)(+)}_{\alpha_1 \ldots \alpha_n}(\mathbf{q}_1, \ldots, \mathbf{q}_n) \prod_{i=1}^{n} \tilde{\psi}_{\alpha_i}(\mathbf{q}_i) \tag{6}$$

Formula (5) is of general character, being reduced to expression (1) in a particular case of an incompressible melt of binary copolymer.

Obviously, functional (6) is completely specified by the vertex functions, each being, in accordance with the Lifshitz ideas,[33] a sum of two items

$$\tilde{\Gamma}^{(n)(+)}_{\alpha_1 \ldots \alpha_n}(\mathbf{q}_1, \ldots, \mathbf{q}_n) = \tilde{\Gamma}^{(n)}_{\alpha_1 \ldots \alpha_n}(\mathbf{q}_1, \ldots, \mathbf{q}_n) + \Gamma^{(n)(*)}_{\alpha_1 \ldots \alpha_n} \delta_K\left(\sum_{i=1}^{n} \mathbf{q}_i\right) \tag{7}$$

The first of them is the vertex function in an auxiliary subsystem of ‘‘chemical bonds’’, representing a heteropolymer liquid with no physical interactions between monomeric units. The entropy of such a hypothetic liquid is termed the Lifshitz entropy.[33] The second item in expression (7) describes the auxiliary subsystem of ‘‘separate units’’ that would form from the system under consideration as a result of the cleavage of all chemical bonds in macromolecules. Values of components $\Gamma^{(n)(*)}_{\alpha_1 \ldots \alpha_n}$ of tensor $\Gamma^{(n)(*)}$ are taken to be independent of the wave vectors $\mathbf{q}_1, \ldots, \mathbf{q}_n$. These components can be found by considering some model of low-molecular weight liquid. For example, for the simplest ‘‘lattice liquid’’ model they look as follows[22]

$$\begin{aligned} \Gamma^{(2)(*)}_{\alpha_1 \alpha_2} &= \frac{\Phi}{1-\Phi} - \Phi \frac{\varepsilon_{\alpha_1 \alpha_2}}{T} \\ \Gamma^{(n)(*)}_{\alpha_1 \ldots \alpha_n} &= \frac{(n-2)!\Phi^{n-1}}{(1-\Phi)^{n-1}} \quad n \geq 3 \end{aligned} \tag{8}$$

Here Φ denote the volume fraction of monomeric units of all m types, whereas $\varepsilon_{\alpha_1 \alpha_2}$ stands for the energy of physical interactions between units of types α_1 and α_2. If a polymer melt is considered to be incompressible, all those contributions (6) to the free energy (5), which are proportional to the components of tensors $\Gamma^{(n)(*)}$ at $n \geq 3$, disappear. As for tensor $\Gamma^{(2)(*)}$, its components in this limiting case are reduced to

$$\Gamma^{(2)(*)}_{\alpha_1\alpha_2} = -\chi_{\alpha_1\alpha_2}, \text{ where } \chi_{\alpha\beta} = \frac{1}{2T}\left(\varepsilon_{\alpha\alpha} + \varepsilon_{\beta\beta} - 2\varepsilon_{\alpha\beta}\right) \qquad (9)$$

The Flory parameters, $\chi_{\alpha\beta}$, are actively engaged in thermodynamics of polymers, and their values are tabulated for many particular polymer systems.[34–36]

Components $-\tilde{\Gamma}^{(n)}_{\alpha_1\cdots\alpha_n}(\mathbf{q}_1, \ldots, \mathbf{q}_n)$ of tensor-function $-\tilde{\Gamma}^{(n)}(\mathbf{q}_1, \ldots, \mathbf{q}_n)$ represent the vertex functions of the expansion of partial Lifshitz entropy in powers of the order parameter. A general algorithm has been put forward[22] permitting to express any of these vertex functions for an arbitrary specimen of a linear m-component heteropolymer through the generating functions of its chemical correlators. The simplest among them is one-point correlator $Y^{(1)}_{\alpha}$, equal to the probability for a monomeric unit chosen at random to be of type α. As for n-point correlator $Y^{(n)}_{\alpha_1\ldots\alpha_n}(j_1, \ldots, j_n)$, it represents a joint probability to find $n \geq 2$ units of given types $M_{\alpha_1}, \ldots, M_{\alpha_n}$ separated along a polymer chain by arbitrary sequences, each containing $j_1, \ldots, j_n$ units. The generating function of such a n-point chemical correlator (*gfcc-n*)

$$W^{(n)}_{\alpha_1\cdots\alpha_n}(x_1, \ldots, x_{n-1}) = \sum_{j_1=0}^{\infty} \cdots \sum_{j_{n-1}=0}^{\infty} Y^{(n)}_{\alpha_1\ldots\alpha_n}(j_1, \ldots, j_{n-1}) \prod_{i=1}^{n-1} x_i^{j_i+1} \qquad (10)$$

is at fixed values of indices $\alpha_1, \ldots, \alpha_n$ is one of the components of tensor-function $W^{(n)}(x_1, \ldots, x_{n-1})$ of $(n-1)$ independent dummy variables $\{x_i\}$.

The concept of the chemical correlator has been first introduced in monograph[37] for the statistical description of the molecular structure of heteropolymer chains. The complete set of such correlators or their generating functions exhaustively characterizes the chemical structure of any specimen of linear heteropolymer. The relation of the vertex functions with the chemical correlators revealed in paper[13] predetermines the importance of these latter for the statistical thermodynamics of heteropolymer liquids. In order to use the WSL theory for the construction of the phase diagram of such a liquid, it is necessary to have *gfcc-n* (10) specified at values n not exceeding the order of terms retained under the truncation of series (1). Since the chemical structure of macromolecules forms in the course of their synthesis, the task of finding chemical correlators is relevant to the statistical chemistry[7] rather than statistical physics of polymers. This problem is solved by now for many varieties of heteropolymers, obtained in different ways.

To have analytical expressions for the vertex functions $\tilde{\Gamma}^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1, \ldots, \mathbf{q}_n)$ derived through the *gfcc-n* (10), it is convenient to resort to the diagram technique,[22] whose elements are presented in Figure 3. Each apex of the polygon presented in this figure is supplied by label $\zeta = (\alpha, \mathbf{q})$ where α stands for the type of a monomeric unit, whereas $\mathbf{q}$ is the momentum ascribed to it.

Elements 1 and 3 have been used in diagram technique,[38] developed earlier to determine the vertex functions in the traditional Landau theory of phase transitions in low-molecular weight liquids. The

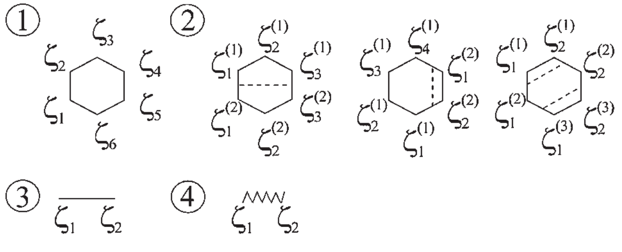

Figure 3.
Elements of the diagram technique developed in paper.[22] Corresponding explanation is provided in the text.

first of these elements represents the Fourier transform of a regular reducible correlation function of the densities of monomeric units $X^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1,\ldots,\mathbf{q}_n)$, while the second one is the element of the matrix inverse to that with elements

$$X^{(2)}_{\alpha_1\alpha_2}(\mathbf{q}_1,\mathbf{q}_2) \equiv X_{\alpha_1\alpha_2}(\mathbf{q}_1,\mathbf{q}_2) \\ \equiv X_{\alpha_1\alpha_2}(\mathbf{q}_1)\delta_K(\mathbf{q}_1+\mathbf{q}_2) \qquad (11)$$

As for elements 2 and 4, missing from the traditional diagram technique,[38] their appearance is due to the polydispersity of block copolymers. Element 2 represents an n-gon partitioned by $(\omega-1)$ dashed lines into ω parts (replicas), each containing not less than two apices. Label $\zeta^{(\nu)}$ of each of them specifies the belonging of the apex to the ν-th replica. Partitioning $J = (a_1^{(1)}\ldots a_{m_1}^{(1)}),\ldots,(a_1^{(\omega)}\ldots a_{m_\omega}^{(\omega)})$ containing in each ν-th replica m_ν apices is associated with the Fourier transform of the replica correlation function of the densities of monomeric units, *FTRC-n*, $X_J^{(n,\omega)}$ $(\mathbf{q}_1^{(1)}\ldots\mathbf{q}_{m_1}^{(1)};\ldots;\mathbf{q}_1^{(\omega)}\ldots\mathbf{q}_{m_\omega}^{(\omega)})$. Essentially, the sum of the apices' momenta in each replica equals zero. Zigzag line 4 corresponds to element $X^{(-1)}_{\alpha_1\alpha_2}$ of matrix which is inverse to that with elements $X_{\alpha_1\alpha_2} \equiv X_{\alpha_1\alpha_2}(0)$.

To obtain vertex functions, one should perform the coupling of polygons by linking some of their apices by lines 3 or 4.[39] We will call these lines, as well as the apices adjacent to them, internal lines to distinguish them from the external ones (3) which are attached to the remaining apices. An apex of a polygon can be joined to any line's end only if their labels $\zeta^{(\nu)}$ coincide. Subsequent summation over indices and momenta of all internal apices of polygons, corresponding in diagram language to "erasing" of the labels of these apices, results in a family of labeled cactus-like graphs. Each of them consists of a certain set of fragments separated by dashed and zigzag lines. The sum of momenta of all apices of any such a fragment is zero. It was shown[22] that the algebraic sum of all such cactus-like graphs with n external lines is a diagram representation of vertex function $\tilde{\Gamma}^{(n)}_{\alpha_1\ldots\alpha_n}$ $(\mathbf{q}_1,\ldots,\mathbf{q}_n)$. Figure 4 provides an example of such a representation for $n = 4$. Diagrams inside the first and the second braces in this figure make a contribution into local and nonlocal parts of the vertex function, respectively.

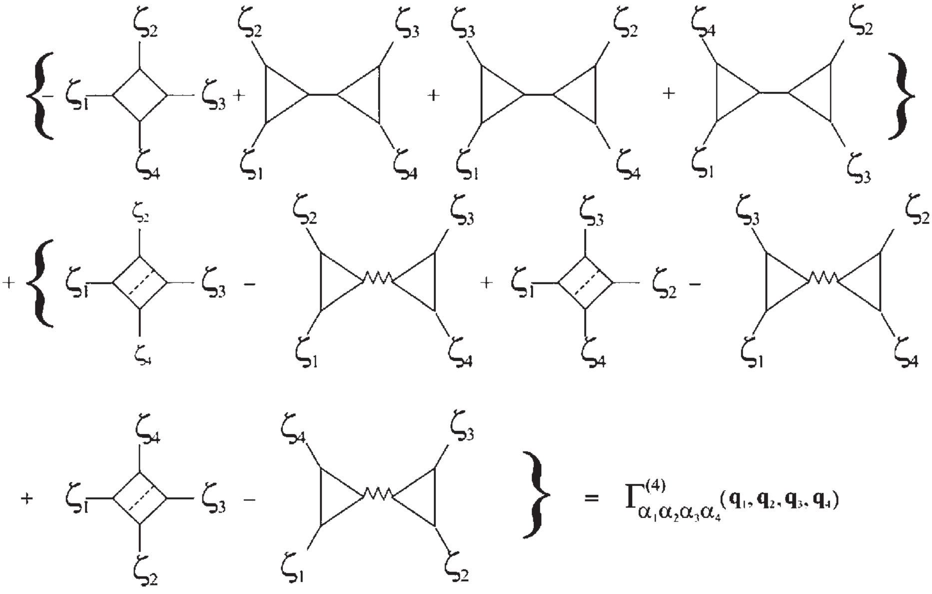

Figure 4.
Diagrammatic representation of vertex function $\tilde{\Gamma}^{(4)}_{\alpha_1\alpha_2\alpha_3\alpha_4}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4)$. Corresponding explanation is provided in the text.

To find the contribution (6) into the Landau free energy, it is necessary to conduct the convolution of the vertex functions with the Fourier transforms of the order parameters making use of the symmetry property of the tensor-function (7) with respect to some permutations of the apices' labels inside each fragment. Complete sets of cactus-like diagrams for finding local $\mathcal{F}_5^{loc}, \mathcal{F}_6^{loc}$ and non-local $\mathcal{F}_5^{nl}$, $\mathcal{F}_6^{nl}$ contributions have been first reported in review[40] and paper,[22] respectively.

Since the elements of the diagram technique (Figure 3) are analytically expressed in terms of the correlation functions of the monomeric units' densities, the relationship should be established between these physical correlators and chemical ones. The solution of this problem implies the necessity to specify a conformational model of polymer chains. Ordinarily they proceed from the simplest of such models in which the vectors of all chemical bonds between neighboring monomeric units are taken to be statistically independent and to have the same length α. In the framework of this "freely joint" model the probability of any conformation of a macromolecule, representing a sequence of vectors of all its bonds, equals the product of the probabilities of these statistically independent vectors. Fourier-transform $\tilde{\lambda}(\mathbf{q})$ of the distribution $\lambda(\mathbf{r})$ of random vector $\mathbf{r}$ with length $|\mathbf{r}| = a$ as well as its asymptotics at $qa \ll 1$

$$\tilde{\lambda}(\mathbf{q}) = \frac{\sin(aq)}{aq} \approx 1 - \frac{a^2q^2}{6} \approx \exp\left(-\frac{a^2q^2}{6}\right) \tag{12}$$

enter into expressions for the vertex functions.

Any *FTRC-n* is the sum of $n!$ functions (10), differing in indices' sequence (each being one of $n!$ permutations in the sequence $(\alpha_1 \ldots \alpha_n)$) and in values of arguments $x_1, \ldots, x_{n-1}$. These latter are expressed in a specific way through the momenta of the apices of an n-gon under its given partitioning J. In the case of single-replica partitioning, the setting of arguments in every of $n!$ items is trivial. So, at $\omega = 1$ any item in *FTRC-n,* referred to as "principal function", is obtained from "base function"

$$W^{(n)}_{\alpha_1 \cdots \alpha_n}(e_1, \ldots, e_{n-1}), \quad \textit{where} \qquad e_i \equiv \tilde{\lambda}(\mathbf{Q}_i), \quad \mathbf{Q}_i = \sum_{j=1}^{i} \boldsymbol{q}_j \tag{13}$$

as a result of one of $n!$ permutations of labels $\zeta = (\alpha, \mathbf{q})$. This assertion partially holds when considering polygons presented in Fig. 3 (2) at an arbitrary partitioning $J = (a_1^{(1)} \ldots a_{m_1}^{(1)}), \ldots, (a_1^{(\omega)} \ldots a_{m_\omega}^{(\omega)})$ of their apices.

In fact, any *FTRC-n* representing the sum $n!$ of n-point principal functions, is partitioned into $N = n!/m_1! \ldots m_\omega!$ groups, each containing $m_1! \ldots m_\omega!$ items. All items, constituting any group are obtained from its base function as a result of the *intrareplica* transpositions of labels of a polygon's apices. That is why the tensor-function $X_J^{(n,\omega)}$ associated with the polygon is symmetric with respect to any permutations of labels of its apices, provided these belong the same replica. However, such a symmetry is broken under the permutations of the labels of apices belonging to different replicas. As the base function of each group any its representative can be chosen. A general diagrammatic algorithm has been proposed[22] to realize such a choice for any *FTRC-n* to which the n-gon corresponds with an arbitrary partitioning J of its n apices. For example, for partitioning $J = (\alpha_1^{(1)}\alpha_2^{(1)})(\alpha_1^{(2)}\alpha_2^{(2)})$ of a tetragon into two replicas the following expressions are obtained for $4!/2!2! = 6$ base functions

$$\begin{array}{llll} 1) & W^{(4)}_{a_1^{(1)}a_2^{(1)}a_1^{(2)}a_2^{(2)}}\left(e_1^{(1)}, 1, e_1^{(2)}\right) & 4) & W^{(4)}_{a_1^{(2)}a_2^{(2)}a_1^{(1)}a_2^{(1)}}\left(e_1^{(2)}, 1, e_1^{(1)}\right) \\ 2) & W^{(4)}_{a_1^{(1)}a_1^{(2)}a_2^{(1)}a_2^{(2)}}\left(e_1^{(1)}, e_1^{(1)}e_1^{(2)}, e_1^{(2)}\right) & 5) & W^{(4)}_{a_1^{(2)}a_1^{(1)}a_2^{(2)}a_2^{(1)}}\left(e_1^{(2)}, e_1^{(2)}e_1^{(1)}, e_1^{(1)}\right) \\ 3) & W^{(4)}_{a_1^{(1)}a_1^{(2)}a_2^{(2)}a_2^{(1)}}\left(e_1^{(1)}, e_1^{(1)}e_1^{(2)}, e_1^{(1)}\right) & 6) & W^{(4)}_{a_1^{(2)}a_1^{(1)}a_2^{(1)}a_2^{(2)}}\left(e_1^{(2)}, e_1^{(2)}e_1^{(1)}, e_1^{(2)}\right) \end{array} \tag{14}$$

The designations used here are

$$e_i^{(\nu)} = \tilde{\lambda}\left(\mathbf{Q}_i^{(\nu)}\right) \quad \mathbf{Q}_i^{(\nu)} = \sum_{j=1}^{i} \mathbf{q}_j^{(\nu)} \tag{15}$$

where $\mathbf{q}_j^{(\nu)}$ is j-th momentum in ν-th replica. It's easy to see that the base functions 4,5,6 result, respectively, from functions 1, 2, 3 under the inversion of superscripts labeling the replicas.

Using the above mentioned algorithm analytic expressions have been found for vertex functions $\tilde{\Gamma}^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1,\ldots,\mathbf{q}_n)$ at $2 \le n \le 6$ for random[22] and markovian[21] heteropolymers whose macromolecules consist of an arbitrary number m of types of monomeric units.

A peculiar feature distinguishing polydisperse polymer liquids from monodisperse ones is the possibility of the coexistence in their solutions and melts of $s \ge 2$ macroscopic phases with volume fractions $\phi_1,\ldots,\phi_s$. When considering such s-phase states in the framework of the WSL theory, any order parameter $\psi_\alpha(\mathbf{r})$ is supposed to have s components. Each of them, $\psi_\alpha^\lambda(\mathbf{r}) \quad (\lambda = 1,\ldots,s)$, describes the density distribution of α-th type units in phase λ. That is why any apex of the polygon depicted in Fig. 3 is supplied by label $\zeta^{(\nu)(\lambda)}$, indicating that this apex belongs to ν-th replica associated with phase λ. Let us conventionally consider such an apex to be painted with color λ. It was theoretically established[41] that all apices belonging to one and the same replica will necessarily be of identical color. Such a property is apparently peculiar to the apices entering in any fragment. This can be inferred from the fact that under coupling of two arbitrary polygons their apices linked by a line should be of the same color.

A rigorous examination of s-phase systems by means of the WSL theory[41] enabled the formulation of a general algorithm for finding the vertex functions in the expansion of the Landau free energy when number s of phases is supposed to be arbitrary. This algorithm is based on a simple modification of the diagrammatic representation of vertex function $\tilde{\Gamma}^{(n)}_{\alpha_1\ldots\alpha_n}\left(\mathbf{q}_1^{\lambda_1},\ldots,\mathbf{q}_n^{\lambda_n}\right)$ of expansion (6) describing a monophase system. Such a modification implies first of all that the cactus-like diagrams of this diagrammatic representation should be colored in such a way that every fragment of a diagram is painted with one of s colors. As a result, any white ω-replica diagram splits into s^ω colored diagrams, some of which can coincide by virtue of a symmetry condition. Secondly, fragment painted with λ color is ascribed weight ϕ_λ, and the weight of colored diagram is taken to be equal to the product of weights constituting its fragments. Up to this weight factor the contributions into the vertex function of all diagrams obtained by the procedure of coloring of a certain white diagram are described by a unified function. These contributions differ from one another just by the set of its arguments. Essentially, this function controlled exclusively by the appearance of white diagram is found from consideration of a homophase system.

The convolution of the vertex functions $\tilde{\Gamma}^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1^{\lambda_1},\ldots,\mathbf{q}_n^{\lambda_n})$ with the order parameters leads to the expression for the contribution $\mathcal{F}_n$ into the Landau free energy of s-phase system, representing a sum of contributions of all colored diagrams with n external lines. Substitution of $\mathcal{F}_n$ in formula (5) results upon resummation procedure in the following expression

$$\begin{aligned}\mathcal{F}\{[\tilde{\psi}_\alpha^\lambda]\} &= \sum_{\lambda=1}^{s} \phi_\lambda \mathcal{F}_\lambda^{loc}\{[\tilde{\psi}_\alpha^\lambda]\} \\ &\quad + \sum_{1\le\lambda_1\le}\sum_{\lambda_2\le s} \phi_{\lambda 1}\phi_{\lambda 2}\mathcal{F}^{nl}_{\lambda_1\lambda_2}\{[\tilde{\psi}_\alpha^{\lambda_1}],[\tilde{\psi}_\alpha^{\lambda_2}]\} \\ &\quad + \ldots\end{aligned} \tag{16}$$

The first item of the infinite series (16) comprises contributions of all orders $n \ge 2$ into the Landau free energy from diagrams composed from a single fragment. This item differs qualitatively from the remaining ones which represent contributions from diagrams consisting, respectively, from two, three and so on fragments. Because all these contribution vanish when considering monodisperse polymers, the free energy written down in terms of monomeric units will be phase-additive. In melts and solutions of polydisperse polymers such an additivity is broken due to nonlinear dependence (16) of function $\mathcal{F}$ on volume fractions of phases. This may be conventionally interpreted as some nonlocal interaction of units involved in macromolecules situated in different phases. Of course, such an interpretation is formal one since it is connected with the transition in the description of a system in terms of macromolecules to that in terms of their units. These latter, unlike low-molecular compounds, are not, however, true thermodynamic components because they are incorporated into polymer chains. Averaging over macromolecules' configurations leads to the emergence of nonlocal terms in the expression (16) for the Landau free energy.

Long-Wave Limit

The diagram technique discussed in the preceding section permits to write down the expressions for all vertex functions of any order. However, only some of them are indispensable for practical implementation of the WSL theory in the thermodynamics of heteropolymer liquids. Below such an implementation will be briefly considered as applied to a melt of binary markovian multiblock copolymer. For simplicity sake the theoretical description can be carried out in the asymptotic limit by letting to infinity both the lengths of macromolecules and the numbers of blocks at fixed values $\bar{l}_1$ and $\bar{l}_2$ of their average lengths. Although in this limit the possibility of the separation of a melt into two macroscopic homogeneous phases is ignored, analytical formulas are substantially simplified. If average lengths of both blocks are large enough, the scale l_c (17) of the decay of chemical correlations along macromolecules is large as well. In this case, $l_c \gg 1$, it is enough to retain in expressions for vertex functions only terms which are linear in the small parameter $1/l_c$. Noteworthy, all these terms are controlled only by moduluses q_i of vectors $\mathbf{q}_i$ since the arguments of any vertex function in this approximation are dimensionless variables y_i

$$
\begin{aligned}
&y_i = R_G^2 q_i^2, \quad \textit{where} \quad R_G^2 = \frac{l_c a^2}{6}, \\
&\frac{1}{l_c} = \frac{1}{\bar{l}_1} + \frac{1}{\bar{l}_2} = \nu_{21} + \nu_{12} \ll 1
\end{aligned}
\tag{17}
$$

where ν_{21}, ν_{12} are nondiagonal elements of the transition matrix of the Markov chain, whereas R_G^2 stands for the average square of the gyration radius of a macromolecule's fragment composed of l_c monomeric units.

Being interested only in mesophases with periodicity scales far exceeding R_G, it will suffice to consider in the expressions for vertex functions their asymptotic behavior in the long-wave limit $y_i \to 0$. Expanding these functions into power series of variables $y_i \ll 1$ and retaining the main terms gives the following expression for the Landau free energy (1)

$$
\begin{aligned}
l_c \mathcal{F}\left[\tilde{\psi}\right] \quad &= \tfrac{1}{2!} \sum_{\mathbf{q}} \left(K_{2d}^{loc} + K_{2s}^{loc} y\right) \tilde{\psi}(\mathbf{q}) \tilde{\psi}(-\mathbf{q}) \\
&\quad - \tfrac{K_{3d}^{loc}}{3!} \sum_{\{\mathbf{q}_i\}} \delta_K \left(\sum_{i=1}^{3} \mathbf{q}_i \right) \prod_{i=1}^{3} \tilde{\psi}(\mathbf{q}_i) \\
&\quad + \tfrac{K_{4d}^{loc}}{4!} \sum_{\{\mathbf{q}_i\}} \delta_K \left(\sum_{i=1}^{4} \mathbf{q}_i \right) \prod_{i=1}^{4} \tilde{\psi}(\mathbf{q}_i) \\
&\quad + \tfrac{1}{4!} \sum_{\{\mathbf{q}_i\}} \delta_K(\mathbf{q}_1 + \mathbf{q}_2) \delta_K(\mathbf{q}_3 + \mathbf{q}_4) \left(\tfrac{K_{4d}^{nl}}{y_1 + y_3} + K_{4s}^{nl} \right) \prod_{i=1}^{4} \tilde{\psi}(\mathbf{q}_i) \\
&\quad + \tfrac{K_{6d}^{nl}}{6!} \sum_{\{\mathbf{q}_i\}} \tfrac{\delta_K(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3) \delta_K(\mathbf{q}_4 + \mathbf{q}_5 + \mathbf{q}_6)}{(y_1 + y_4) \quad (y_3 + y_6)} \prod_{i=1}^{6} \tilde{\psi}(\mathbf{q}_i)
\end{aligned}
\tag{18}
$$

This expression differs from that presented in paper[20] only by the designations of vertices. A superscript stands to distinguish local vertices from nonlocal ones, whereas the destination of a subscript, d or s, is to show whether this particular term is dominant or subdominant in the asymptotic expansion of the vertex function of corresponding order. Among all vertices only one, $K_{2d}^{loc} \equiv \tau = 2l_c(\chi_s - \chi)$, is temperature dependent. The rest of the vertices as well as quantity $l_c\chi_s$ are governed exclusively by copolymer composition, i.e., by either of fractions X_1, X_2 of monomeric units belonging to type 1 or 2.

$$\begin{aligned}&l_c\chi_s = \frac{1}{4\xi}, \quad K_{2s}^{loc} = \frac{1}{2\xi}, \quad K_{3d}^{loc} = \frac{3\sqrt{1-4\xi}}{4\xi^2}, \quad K_{4d}^{loc} = \frac{3(5-16\xi)}{8\xi^3},\\ &K_{4d}^{nl} = \frac{3}{\xi^2}, \quad K_{4s}^{nl} = \frac{3(3-8\xi)}{8\xi^3}, \quad K_{6d}^{nl} = \frac{45}{\xi^3}, \quad where\ \xi = X_1X_2\end{aligned} \tag{19}$$

The first four items in expression (18) are similar to those which enter in the expansion of the Landau free energy of monodisperse heteropolymers. The remaining items owe their existence to the polydispersity of a markovian block copolymer. The first of them is traditionally taken into account when calculating phase diagrams of such copolymers.[11–15,18–19,31,42–45] It is concerned with the partitioning of the quadruple of vectors $\{\mathbf{q}_i\}_4$ into two replicas, ($\mathbf{q}_1$, $\mathbf{q}_2$) and ($\mathbf{q}_3$, $\mathbf{q}_4$). Evidently, apart from this dominant item the subdominant one should be also retained in the asymptotic limit $y_i \to 0$. This is because its order of magnitude is just the same as that of the fourth term in expansion (18).

The question may arise why the right hand part of this expansion does not contain the fifth order nonlocal contributions, and among the sixth order contributions only one is retained. The answer to this question stems from the analysis of the expression for the amplitude expansion F of the free energy, which is obtained in the first harmonic approximation. Minimizing this function F with respect to variables y and A, it is possible to find the period and the amplitude of equilibrium mesophase, that has been performed in all papers except for[20] in disregard of contributions of two last items in expression (18). However, ignoring these items is incorrect, since both of them are of order A^4. This conclusion is arrived at because in thermodynamic equilibrium $y \sim A$. Thus, the fifth and the seventh items in (18) whose vertex functions have the first and the second order poles, respectively, upon minimization with respect to y will be of order A^3 and A^4, respectively. A rigorous analysis revealed[21] that all vertex functions $\tilde{\Gamma}^{(5)nl}_{\alpha_1\cdots\alpha_5}(\mathbf{q}_1,\ldots,\mathbf{q}_5)$ remain finite in the long-wave limit $y_i \to 0$. This explains the absence of the contribution $\mathcal{F}_5[\tilde{\psi}]$ in expansion (18). Because of the above stated reasons when finding contribution $\mathcal{F}_6[\tilde{\psi}]$ one should restrict himself to the dominant item of the asymptotic expansion of the vertex function $\tilde{\Gamma}^{(6)nl}_{\alpha_1\cdots\alpha_6}(\mathbf{q}_1,\ldots,\mathbf{q}_6)$ which is associated with the partitioning of the sextuple of vectors $\{\mathbf{q}_i\}_6$ into two replicas, $(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3)$ and $(\mathbf{q}_4, \mathbf{q}_5, \mathbf{q}_6)$. The sixth order subdominant item in the long-wave limit has the first order pole with respect to variables y_i. Consequently the corresponding contribution to the amplitude expansion of the free energy upon the exclusion of variable y will have order A^5. Therefore expression (18) contains all items which upon the minimization with respect to the wave vectors will provide the complete set of terms of the second, third and fourth orders in amplitude expansion of the Landau free energy. In all papers apart from article,[20] where the WSL theory was employed to calculate the phase diagram of polydisperse heteropolymers, the abovementioned set was incomplete, since two last items in expression (18) were missed. The idea about the importance of their allowance is possible to get from the inspection of Fig. 5. A comparison of the phase diagrams (a) and (b) in this figure demonstrates that the account of the sixth order nonlocal term in expression (18), leaving the sequence of the phase transitions

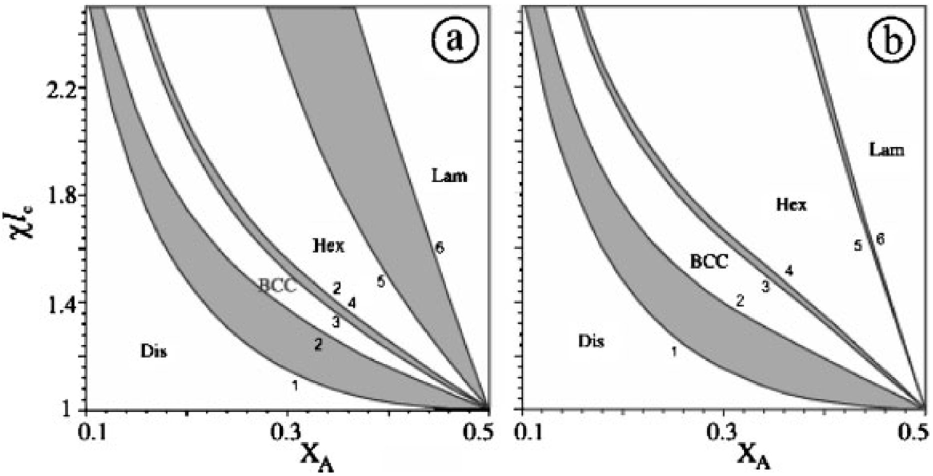

Figure 5.
Phase diagram of the melt of binary markovian copolymers presented in papers[18,19] (a) and[20] (b), respectively. Lines in this figure separate homophase regions (colored white) from two-phase ones (colored gray).

between mesophases unaltered, exerts a significant influence on the appearance of the phase diagram. Of central importance here is the considerable expansion of the region of coexistence of hexagonal and lamellar mesophases.

Conclusion

Efficiency of novel theoretical approaches based on current ideas of the statistical physics of disordered systems is shown as applied to description of the phase behavior of melts and solutions of block copolymers.

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