A correct account of the non-local terms in the Landau theory of phase transitions in

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LETTER TO THE EDITOR

A correct account of the non-local terms in the Landau theory of phase transitions in polydisperse heteropolymers

S I Kuchanov[1] **and S V Panyukov**[2]

[1] Keldysh Institute of Applied Mathematics, Miusskaya Square, 4, 125047, Moscow, Russia
[2] Theoretical Department, PN Lebedev Physics Institute, Russian Academy of Sciences, Leninskiy prospekt, 53, Moscow, 117924, Russia

E-mail: kuchanov@orc.ru

Abstract
The non-local terms previously disregarded in the Landau free energy expansion of a melt of polydisperse heteropolymers are shown to dramatically change the appearance of the phase diagram of a heteropolymer liquid.

1. Introduction

One of the most intriguing phenomena observed in heteropolymer liquids is the formation in these systems of thermodynamically stable mesophases where the densities of monomeric units periodically change in space [1]. Such mesophases are conveniently described using the main approaches of the weak crystallization theory [2]. It was Leibler who pioneered this idea [3], but, like the authors of many subsequent publications (see reviews [4–6] and references therein), he considered only monodisperse block copolymers. However, most commercial synthetic copolymers are polydisperse, i.e. they consist of macromolecules differing in length, chemical composition and sequence distribution. Later it was shown [7, 8] that the traditional Landau theory describing the phase behaviour of such polydisperse systems needed to be substantially modified. Namely, the set of the ordinary regular terms of the free energy expansion must be complemented by the so-called 'non-local' terms [9–13]. The incorporation of these terms stems from the need to take into account the 'quenched' disorder in the chemical structure of the macromolecules of a polydisperse heteropolymer. The derivation of such terms suggests averaging of the free energy of a system over this structural disorder. To this purpose, recourse can be made to the replica trick, widely used in the statistical physics of disordered systems [14, 15]. The authors of all works published so far invoking the Landau theory to describe the thermodynamic behaviour of polydisperse heteropolymer systems (see, for instance, [9–13, 16–23]) retained only the fourth-order non-local term in the free energy

expansion. In the present letter it will be shown that the neglect in these articles of some non-local terms of sixth order is responsible for the erroneous results reported. The problem is that their contribution is of the same order of magnitude as the contribution of the terms traditionally retained in the Landau free energy expansion of polydisperse heteropolymer liquids.

The vertex functions corresponding to the non-local terms are largely controlled by the wavevector of the mesophase under consideration. That is why the minimization of the free energy must be carried out not only with respect to the amplitude of the order parameter but also with respect to its wavevector. Once the latter has been performed, the amplitude expansion of the Landau free energy is obtained. Some of the fourth-order terms of this expansion originate from the sixth-order non-local terms of the initial expansion of the Landau free energy functional. All such terms are taken into consideration in the present letter, and this is shown to considerably change the phase diagram.

The key feature peculiar to polydisperse heteropolymers is the presence on their phase diagram of two-phase regions [18, 22, 23]. It will be shown below that the location and size of some of these essentially depends on whether the relevant sixth-order terms in the free energy expansion are accounted for.

2. Main results

Let us study the phase behaviour of the melt of a binary copolymer composed of macromolecules in which the pattern of arrangement of monomeric units A and B is described by a Markov chain. For the sake of simplicity the calculations will be restricted to an asymptotic limit. This can be obtained when the length of a macromolecule as well as the number of constituent blocks A and B tend to infinity, provided their average lengths are fixed. The chemical structure of a Markovian copolymer is completely defined by the transition matrix. Its element ν_{ij} has a meaning of the probability for the jth type unit to be found immediately after a unit of type $i = A, B$ for the conventional movement along a macromolecule. Due to two normalization conditions of these probabilities, the chemical structure of a copolymer is fully characterized by a couple of independent parameters. It is convenient to choose as such parameters the fraction X_A of units A (the fraction of units B equals $X_B = 1 - X_A$) and the characteristic length of block l_a connected with the probabilities ν_{AB} and ν_{BA} by the relationships

$$X_A = \frac{\nu_{BA}}{\nu_{AB} + \nu_{BA}}, \qquad l_a = \frac{1}{\nu_{AB} + \nu_{BA}}. \tag{1}$$

The Landau theory of phase transitions is based on the expansion of the free energy functional in powers of the order parameter. A general algorithm of the calculation of these expansion coefficients (i.e. vertex functions) in the case of polydisperse heteropolymer liquids was formulated in [6]. This algorithm was thereafter used [24] to state the rules of a diagrammatic technique that permits finding explicit expressions for the vertex functions. In the limit $l_a \gg 1$, it is sufficient to retain in these expressions the terms which are proportional to the first power of the small parameter $1/l_a$. The vertex functions thus obtained depend exclusively on dimensionless variables $y_i = l_a a^2 q_i^2/6$ with a standing for the size of the monomeric unit. Of concern to us here are the mesophases whose spatial period substantially exceeds the gyration radius R_G ($R_G^2 = l_a a^2/6$) of the longer block. In this case all variables y_i are much less than unity. Expanding the vertex functions in their arguments y_i and retaining only the principal terms in this expansion we get in the momentum representation the following expression for

the functional of the Landau free energy

$$\frac{l_a \mathcal{F}[\tilde{\psi}]}{MT} = \sum_{\mathbf{q}} \frac{\tau + cy}{2!} \left| \tilde{\psi}(\mathbf{q}) \right|^2 - \frac{\lambda}{3!} \sum_{\{\mathbf{q}_i\}} \delta_K \left(\sum_{i=1}^{3} \mathbf{q}_i \right) \prod_{i=1}^{3} \tilde{\psi}(\mathbf{q}_i)$$

$$+ \frac{g}{4!} \sum_{\{\mathbf{q}_i\}} \delta_K \left(\sum_{i=1}^{4} \mathbf{q}_i \right) \prod_{i=1}^{4} \tilde{\psi}(\mathbf{q}_i)$$

$$+ \frac{1}{4} \sum_{\{\mathbf{q}_i\}} \delta_K (\mathbf{q}_1 + \mathbf{q}_2) \, \delta_K (\mathbf{q}_3 + \mathbf{q}_4) \left(\frac{k}{y_1 + y_3} + \frac{\gamma}{24} \right) \prod_{i=1}^{4} \tilde{\psi}(\mathbf{q}_i)$$

$$+ \frac{\eta}{12} \sum_{\{\mathbf{q}_i\}} \frac{\delta_K (\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3)}{(y_1 + y_4)} \frac{\delta_K (\mathbf{q}_4 + \mathbf{q}_5 + \mathbf{q}_6)}{(y_3 + y_6)} \prod_{i=1}^{6} \tilde{\psi}(\mathbf{q}_i), \qquad (2)$$

where M is the overall number of monomeric units in a system, while T denotes the temperature in the energetic units. In expression (2), $\tilde{\psi}(\mathbf{q})$ has the sense of the dimensionless Fourier transform of the order parameter

$$\psi(\mathbf{r}) = \Delta\rho_A(\mathbf{r}) / M = -\Delta\rho_B(\mathbf{r}) / M. \qquad (3)$$

Here $\Delta\rho_\alpha(\mathbf{r}) = \rho_\alpha(\mathbf{r}) - \bar{\rho}_\alpha$ stands for the deviation of local density $\rho_\alpha(\mathbf{r})$ at point $\mathbf{r}$ of type $\alpha = A, B$ units from its average value $\bar{\rho}_\alpha$, while $\delta_K(\mathbf{q})$ is the dimensionless Kronecker symbol. Among all vertex functions entering in the expansion (2) only one, $\tau = 2l_a(\chi_s - \chi) \ll 1$, is temperature dependent. The reason for this is the dependence on temperature of the Flory–Huggins parameter, χ, characterizing the intensity of the pair interaction between different types of units. The free energy expansion (2) is valid only near the critical point, $(X_A = X_B = 1/2, \chi l_a = 1)$, where the coefficient λ in the cubic term vanishes. All other dimensionless coefficients of this functional are governed exclusively by the copolymer composition

$$\chi_s = \frac{1}{4l_a\xi}, \qquad c = \frac{1}{2\xi}, \qquad \lambda = \frac{3}{4\xi^2}(X_B - X_A), \qquad g = \frac{3}{8\xi^3}(5 - 16\xi),$$

$$k = \frac{1}{2\xi^2}, \qquad \eta = \frac{3}{4\xi^3}, \qquad \gamma = \frac{3}{2\xi^3}(3 - 8\xi), \qquad \text{where} \quad \xi = X_A X_B. \qquad (4)$$

The first three items in expression (2) are identical to those constituting the traditional expansion of the Landau free energy of low-molecular systems and monodisperse heteropolymers. The remaining items, known as the non-local terms, owe their existence to the polydispersity of a Markovian copolymer. The first of them is normally taken into consideration when calculating the phase diagrams of such copolymers [9–13, 16–23]. This term is associated with partitioning of the quadruple of vectors $\{\mathbf{q}_i\}_4$ into two groups (replicas), $(\mathbf{q}_1, \mathbf{q}_2)$ and $(\mathbf{q}_3, \mathbf{q}_4)$, each having vanishing momentum. Clearly, along with this term it is also necessary to retain in the asymptotic limit $y_i \to 0$ the term proportional to γ, since the order of magnitude of its contribution is just the same as that of the third term in expansion (2). The analysis shows that although the last term in expansion (2) is of the sixth order, its contribution needs to be accounted for as well. This term is associated with the partitioning of the sextuple of vectors $\{\mathbf{q}_i\}_6$ into two groups, $(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3)$ and $(\mathbf{q}_4, \mathbf{q}_5, \mathbf{q}_6)$. The contribution of other non-local terms is negligible in the approximation at hand. This is because the expression (2) incorporates all terms, which upon the minimization of the free energy with respect to the wavevector form the complete set of the second-, third- and fourth-order terms of the amplitude expansion of the Landau free energy. In all preceding works in which the Landau theory was used to calculate the phase diagrams of polydisperse heteropolymers, this set was incomplete since it did not

contain the last two terms in expansion (2). When treating the phase behaviour of a system, for the sake of simplicity we will confine the consideration to three classical mesophases with the spatial symmetry of lamellar (Lam), hexagonal (Hex) and body-centred cubic (BCC) lattices [5]. In the framework of a one-harmonic approximation, when the Fourier transform of the order parameter (3) is taken to be equal to the sum of n pairs of harmonics with identical quantity q_n, but with opposite directions of the wavevectors

$$\tilde{\psi}\,(\mathbf{q}) = \frac{A_n}{\sqrt{n}} \sum_{k=1}^{n} \left[e^{i\varphi_k} \delta_K(\mathbf{q} - \mathbf{q}_n^{(k)}) + e^{-i\varphi_k} \delta_K(\mathbf{q} + \mathbf{q}_n^{(k)}) \right], \tag{5}$$

where $n = 1, 3$ and 6 for Lam, Hex and BCC mesophases, respectively. All harmonics have the same amplitude A_n, whereas their phases $\{\varphi_k\}$ for all mesophases under consideration are equal to zero. The amplitude expansion of the Landau free energy of every mesophase is obtainable by substitution of the expression (5) into the expansion (2):

$$\frac{l_a F_n}{T} = (\tau + cy_n) A_n^2 - \frac{\lambda \alpha_n}{6} A_n^3 + \frac{g\beta_n}{24} A_n^4 + \frac{k}{2} \frac{A_n^4}{y_n} + \frac{\gamma}{24} A_n^4 + \frac{\eta \alpha_n^2}{48} \frac{A_n^6}{y_n^2}. \tag{6}$$

Here the coefficients α_n and β_n are controlled exclusively by the symmetry of the mesophases ($\alpha_1 = 0, \alpha_3 = 4/\sqrt{3}, \alpha_6 = 8/\sqrt{6}$ and $\beta_1 = 6, \beta_3 = 10, \beta_6 = 15$). The expression for the free energy of a two-phase state with the volume fractions $\phi_n = \phi$ and $\phi_m = 1 - \phi$, occupied by phases n and m, respectively, can be found in the same way as reported earlier [22, 23]. In the case of the transition from a disordered phase with $m = 0$ into a mesophase with $n \neq 0$, substituting $q_0 = 0, A_0 = 0$, we will get

$$\frac{l_a F_{0n}}{T} = \phi \left[(\tau + cy_n) A_n^2 - \frac{\lambda \alpha_n}{6} A_n^3 + \frac{g\beta_n}{24} A_n^4 \right] + \phi^2 \left[\frac{k}{2} \frac{A_n^4}{y_n} + \frac{\gamma}{24} A_n^4 + \frac{\eta \alpha_n^2}{48} \frac{A_n^6}{y_n^2} \right]. \tag{7}$$

The free energy of coexisting mesophases $m \neq 0$ and n can be written as

$$\mathsf{F}_{mn}(\phi) = (1 - \phi)\,\mathsf{F}_m + \phi \mathsf{F}_n + \phi\,(1 - \phi)\,\Delta \mathsf{F}_{nm} \tag{8}$$

where the following designation is used

$$\frac{l_a \Delta \mathsf{F}_{nm}}{T} = k \left(\frac{2A_n^2 A_m^2}{y_n + y_m} - \frac{A_n^4}{2y_n} - \frac{A_m^4}{2y_m} \right) - \frac{\gamma}{24} \left(A_n^2 - A_m^2 \right)^2$$
$$+ \frac{\eta}{6} \left[\frac{\alpha_n \alpha_m A_n^3 A_m^3}{(y_n + y_m)^2} - \frac{\alpha_n^2}{8} \frac{A_n^6}{y_n^2} - \frac{\alpha_m^2}{8} \frac{A_m^6}{y_m^2} \right]. \tag{9}$$

A specific feature of expression (8) is the absence of the additivity of the free energy with respect to two coexisting phases. In the thermodynamics of low-molecular liquids, the violation of such an additivity is known to be caused exclusively by the surface energy of the interphase boundary. In expression (8) this contribution to the free energy is neglected, and the presence of the last term characterizing its deviation from additivity is due to the polydispersity inherent in a Markovian copolymer. Note that the volume free energy of a two-phase monodisperse heteropolymer represents the sum of contributions of the coexisting phases. The variables A_n, y_n and ϕ_n, characterizing the nth phase, are obtained via minimization of the corresponding free energies (6)–(8). This procedure results in the phase diagram shown in figure 1(a). The phase diagram of this system found in [22, 23] is presented in figure 1(b). A comparison of these figures demonstrates that the allowance for the sixth-order non-local terms in expansion (2), leaving the sequence of the phase transitions 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 the mesophases Hex and
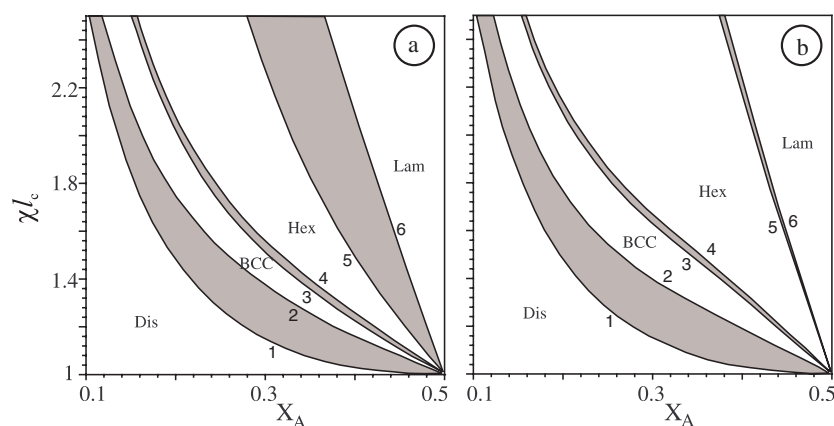
Figure 1. Phase diagram of the melt of binary Markovian copolymers: (a) calculated in this work and (b) reported earlier [22, 23]. Lines in figure separate homophase regions (coloured white) from two-phase ones (coloured grey).

(This figure is in colour only in the electronic version)

Lam. Absolute values of the initial slope of curves 1–6 in figures 1(a) and (b) are presented in the following table:

	1	2	3	4	5	6
(a)	0	1.363	2.011	2.327	4.303	10.164
(b)	0	1.847	3.111	3.405	9.479	10.164

As evident from this table, the slopes of all curves (except for 1 and 6) in figures 1(a) and (b) differ markedly. This distinction is the most strongly pronounced for curve 5.

Accounting for the last two terms in expression (2) for the Landau free energy enabled us to reveal an important qualitative peculiarity of the two-phase state of the melt of polydisperse heteropolymers. In the absence of these two terms the previous theory [22, 23] predicted the equality of the periods of the coexisting mesophases, which is violated upon the inclusion of the above-mentioned terms in the expression for the Landau free energy (2). Our calculations showed that such a distinction in the periodicity scales is especially strongly pronounced in the region of coexistence of hexagonal and lamellar mesophases.

3. Conclusion

The results outlined in this letter convincingly prove that when considering the phase behaviour of polydisperse heteropolymers it is critically important to take into account the non-local terms in the Landau free energy expansion in a more accurate manner than has been done before. In particular we have shown that the addition of two such terms, ignored in all preceding publications, is indispensable. This assertion stems from the inspection of the phase diagram we managed to calculate for the melt of binary Markovian multiblock copolymers. It differs markedly from the phase diagram constructed earlier without regard for these terms (see figure 1). Key results obtained in this letter for Markovian heteropolymers can be verified for other polydisperse multiblock copolymers, since formulae (6)–(9) hold at arbitrary values of the parameters of the vertex functions in expansion (2). Obviously, its applicability suggests

the fulfilment of inequalities $\tau \ll 1$ and $\lambda \ll 1$, identical to those employed in the traditional Landau theory of phase transitions [7, 8].

It is worth emphasizing that the central idea of this letter far exceeds the limits of the construction of the phase diagram of heteropolymer liquids. This idea may well find application when considering the thermodynamic behaviour of various systems with 'quenched' structural disorder in terms of the Landau theory of phase transitions.

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