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New statistical approach to the description of spatial inhomogeneous states in heteropolymer solutions

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Abstract. — It is shown that the free energy of polymer systems is a nonlocal functional of the distribution of monomer density, unlike usual low-molecular systems. A general statistical approach is proposed, which takes into account corresponding nonlocal effects for the polymers containing macromolecules of various chemical composition and chemical structure. The phase diagram is set up for solutions of linear heteropolymers, alternation of monomer units in the macromolecules of which obey Markovian statistics. It is shown that a melt of the Markovian multi-block copolymers undergoes a third-order phase transition to superstructure with symmetry of body-centered cubic lattice whose period depends essentially on the parameters of monomer units interactions.

1. Introduction.

The majority of theoretical works [1-8], devoted to the study of spatial inhomogeneous structures in the heteropolymer systems use the density functional method. It is based on the mean field expression for the free energy of the polymer with the given set of numbers \(n(C)\) of macromolecules with chemical structure C and spatial distribution of the densities of monomer units. It is very important that within the framework of traditional consideration the monomer units can not be chosen as independent thermodynamic variables due to the very fact of their connectivity in the macromolecule.

In accordance with the classical Flory approach [9] one can use the individual molecules as such variables, which can be characterized by the chemical potentials \(\mu (C)\). The applicability condition \(n(C) \gg 1\) of this approach is held only for linear homopolymers, their blends and solutions. In the case of the branched polymers as well as heteropolymers the number of different configurations \(\{C\}\) of macromolecules in the concrete sample increases exponentially with the raise of their degree of polymerization \(\ell\). Therefore for the real system of large but finite volume average numbers of macromolecules of the given configuration are small \(n(C) \ll 1\) and they can not strictly speaking be chosen as independent components in the framework of traditional thermodynamic description.
In this paper a more general approach based on the density functional method is proposed, which enables us to describe polymers with an arbitrary set of values \( \{n(C)\} \). The main idea of this approach consists of the consideration of monomer units as effective quasi-components for which the very conception of chemical potentials is meaningless. The chemical potentials of individual molecules \( \mu(C) \) become the functional of the density distributions, which have not been taken into account in the previous investigations [2-8]. This dependence leads to the essential nonlocality of the free energy [10] in spite of the short-range character of the real interactions between monomer units in macromolecules.

This nonlocality has no analogy in the low-molecular systems. To demonstrate its physical nature let us begin with the consideration of the simplest homopolymer system, which consists of the set of macromolecules with \( \ell_i \) monomer units. The entropy of such a system is

\[
S \{n_i, \rho(r)\} = S_{\text{mix}} \{n_i, \rho(r)\} + S_{\text{loc}} \{n_i, \rho(r)\}
\]

with given numbers \( \{n_i\} \) of macromolecules and distribution \( \{\rho(r)\} \) of the unit density

\[
n_i = \int dr \rho_i(r), \quad \rho(r) = \sum_i c_i(r) \ell_i,
\]

is found by maximisation of the entropy functional which depends on molecule concentrations \( \{c_i(r)\} \)

\[
S \{c_i(r)\} = -\sum_i \int dr \rho_i(r) \ln \left[ c_i(r)/e \right]
\]

with respect to the functions \( c_i(r) \). The conditions (1.2) can be taken into account by the introduction of corresponding Lagrange\(^\dagger\) multipliers, i.e. the chemical potentials \( \mu_i \), and the field \( v(r) \). For a low-molecular system \( \{\ell_i = 1\} \) we obtain \( \mu_i = \text{Const.} \) and

\[
S_{\text{loc}} \{\rho(r)\} = -\int dr \rho(r) \ln \left[ \rho(r)/e \right],
\]

whereas the mixing entropy \( S_{\text{mix}} = \text{Const.} \) is usual for ideal gas form. In the case of high-molecular system this term acquires the nonlocal dependence on the density \( \{\rho(r)\} \). The first term of its expansion in powers of deviation \( \varphi(r) = \rho(r) - \rho \) of density \( \rho(r) \) from its value \( \rho \) in the homogeneous state has the form

\[
S_{\text{mix}} \{n, \rho(r)\} = -(1/8 V) \int dr \int dr' K(r - r') \varphi^2(r) \varphi^2(r'),
\]

\[
K(r) = (m_4 m_2 - m_2^2)/m_2^2, \quad m_k = \sum_i c_i \ell_i^k, \quad c_i = n_i/V,
\]

where \( V \) is the volume of the system. The chemical potential \( \mu_i \) of the individual \( i \)-th type molecule depends now on the density distribution \( \{\rho(r)\} \) and in the same approximation as (1.5) it is equal to

\[
\mu_i \{\rho(r)\}/T = \ln c_i + (\kappa_i/2 V) \int dr \varphi^2(r), \quad \kappa_i = (m_3 \ell_i - m_2 \ell_i^2)/m_2^3,
\]

where \( T \) is the temperature. The functional \( S_{\text{loc}} (1.3) \) can be expanded into the usual local Landau series of the parameter \( \varphi(r) \).
The phase diagrams of actual polymer systems can be essentially modified when the mentioned nonlocal effects are taken into account. In this study we shall consider the influence of such nonlocality on the characteristics of inhomogeneous states in the polymer systems. Unfortunately the simplest approach based on the expression (1.3) for the entropy can not be applied for the description of comparable spatial scales or those less than the size of the macromolecules. Therefore to deal with such states in the polymers, with arbitrary chemical structure, there is a necessity to develop a more general approach to the description of thermodynamics of polymer systems.

2. General approach.

2.1 FREE ENERGY. — We begin with the calculation of the free energy of a d-dimensional polymer system in the presence of the external field \( H_\alpha (r) \), which acts at point \( r \) on the monomer units \( M_\alpha \) of the type \( \alpha \). It is convenient to introduce the generalised coordinate \( x = (r, \alpha) \) of the units, i.e. \( H(x) = H_\alpha (r) \). Within the framework of the model [11, 12] the interaction between units \( M_\alpha \) and \( M_\beta \), located at a given distance \( |r - r'| \) where one from another is characterized by the potential \( V(x, x') = V_{\alpha \beta} (r - r') \) and the conditional probability to find the units of the bond at this distance equals \( \lambda_d (x, x') = \lambda_d (r - r') \). Hereinafter analogous designations will be applied for all field variables and their Fourier transformations.

The partition function of the ensemble of macromolecules with the distribution \( \{n(C)\} \) may be represented [12] as the average

\[
Z \{n(C)\} = \left\langle \prod_c Q_d^{(C)}(C, \{v(x) + H(x)\}) n(C)! \right\rangle_v
\]

of the partition function for the noninteracting (ideal) macromolecules, the units of which are in the random Gaussian field \( v(x) \) characterized by the correlators

\[
\left\langle v(x) \right\rangle_v = 0, \quad \left\langle v(x)v(x') \right\rangle_v = V(x, x').
\]

The partition function \( Q_d (C, \{H(x)\}) \) of ideal macromolecule \( C \), units of which are in the external field \( H(x) \), according to its definition is

\[
Q_d (C, \{H(x)\}) = \prod_n \int dr_n \exp \left[ - \frac{H(x_n)}{T} \right] \prod_{\langle n, k \rangle} \lambda_d (r_n - r_k)
\]

where the first product is taken over all monomer units of this molecule while the second one is over its bonds.

It is worth noting, that the fluctuations of the field \( v(x) \) on the scales are small in comparison with \( a \) are anomalously large. To eliminate the corresponding «ultraviolet divergencies», which have no polymer specificity, let us make a preliminary summary of the contribution of these fluctuations to the partition function (2.1). The result of this summary, as seen in the Appendix looks as follows

\[
F \{n(C), H(x)\} = - T \ln \int Dv(x) \exp \left[ - \tilde{\Omega} \{v(x), H(x)\}/T \right] + T \sum_C \ln n(C)!,
\]

\[
\tilde{\Omega} \{v(x), H(x)\} = - TG \{v(x) + H(x)\} + \Omega^* \{v(x)\}
\]

where \( G \{H(x)\} \) is the generating functional for irreducible correlators of the density
fluctuations of ideal macromolecules

\[ G \{H(x)\} = \sum_C n(C) \ln [Q_d(C, \{H(x)\})] \]  \hspace{1cm} (2.5)

As it is shown in the Appendix, the functional \( \Omega^* \) can be expressed in terms of the equation of state \( P(\rho) \) and the chemical potentials \( \mu_a(\rho) \) of the system of «separate units» [5, 6], which are the equilibrium ensemble of monomer units with density \( \rho = \{\rho_1, \ldots, \rho_a, \ldots\} \), interacting with potential \( V(x, x') \) and forming no chemical bonds

\[ \Omega^* \{v(x)\} = -\int \text{d}r P^*(\rho(x)) \]  \hspace{1cm} (2.6)

\[ v_a(r) = \mu_a^*(\rho(x)) = \mu_a(\rho(x)) - T \ln \rho_a(r), \hspace{1cm} \rho(r) = \sum_a \rho_a(r). \]  \hspace{1cm} (2.7)

Within the framework of the «lattice model» the excluded volume effects are described by the parameter \( u \) while the pairwise interaction of the monomer units \( M_a \) and \( M_\beta \) is defined by the dimensionless parameter \( \gamma_{\alpha\beta}/T \)

\[ P^*(\rho)/T = -\frac{1}{V} \ln (1 - \nu \rho) - \rho + \frac{\nu}{2T} \sum_{\alpha\beta} \gamma_{\alpha\beta} \rho_\alpha \rho_\beta, \]  \hspace{1cm} (2.8)

\[ \mu_a^*/T = -\ln (1 - \nu \rho) + \frac{\nu}{T} \sum_\beta \gamma_{\alpha\beta} \rho_\alpha. \]

2.2 REPLICA METHOD. — We face now the problem of the calculation of the sum (2.5) for the generating functional \( G \). Let us use for this purpose the replica method [13]:

\[ G \{V(x)\} = \text{d}\Psi_{dm} \{s(X)\}/\text{d}m \big|_{m=0}, \hspace{1cm} s(X) = \exp[-H(X)/T]. \]  \hspace{1cm} (2.9)

Here the functional \( \Psi_{dm} \) is defined by the expression

\[ \Psi_{dm} \{s(X)\} = \sum_C n(C) Q_{dm}(C, \{H(X)\}). \]  \hspace{1cm} (2.10)

where \( X = (R, \alpha) \), \( R \) is the vector in the replica space with components \((r^{(1)}, \ldots, r^{(m)})\) and \( Q_{dm}(C, \{H(X)\}) \) is the partition function of the molecule \( C \) in \( dm \)-dimensional space. This functional is determined by the expression analogous to (2.3) in which integration is carried out over the coordinates \( R_n \) of all units and relationships

\[ H(X) = \sum_k v(x^{(k)}), \hspace{1cm} \lambda_{dm}(R - R') = \prod_k \lambda_{d}(r^{(k)} - r'^{(k)}). \]  \hspace{1cm} (2.11)

are hold. For many important practice polymer systems the explicit form for the generating functional \( \Psi_{dm} \) (2.10) can be found. One of these systems containing the Markovian copolymers will be considered in section 5. To take the limit \( m \to 0 \) in the expression (2.9) let us expand the functional \( \Psi_{dm} \) in the functional series into powers of the function \( H(X) \)

\[ \Psi_{dm} \{s(X)\} = \Psi_{dm} \{1\} + \sum_n \left( -\frac{1/T}{n!} \right) \sum_{x_1 \ldots x_n} G^{(n)}(X_1 \ldots X_n) H(X_1) \ldots H(X_n) \]  \hspace{1cm} (2.12)
where the functions $G^{(n)}$ are determined by the expressions

$$G^{(n)}(X_1, X_n) = \delta^n \psi_{dm} \left\{ \exp \left[ t(X) \right] \right\} / \delta t(X_1) \ldots \delta t(X_n) \bigg|_{t=0} \quad (2.13)$$

and the sum over $X$ designates both the integration over coordinates $R$ and summation over types $\alpha$ of the units. Below we shall often use this convenient designation as well as that for $\delta$-function

$$\delta(X - X') = \prod_k \delta(r^{(k)} - r'^{(k)}) \delta_{\alpha\alpha}. \quad (2.14)$$

Substituting expression (2.11) for $H(X)$ in (2.10) and taking the limit $m \to 0$ in expression (2.9) we find

$$G \{ \psi(x) \} = G \{ 0 \} + \sum_{n=1}^{\infty} \frac{(-1)^{nT}}{n!} \sum_{x_1 \cdot x_n} G^{(n)}(x_1 \cdot x_n) \psi(x_1) \ldots \psi(x_n) \quad (2.15)$$

where the function $G^{(n)}$ has the form

$$G^{(n)}(x_1 \ldots x_n) = \sum_{\{x_{\ell}^{(k)}\}} (-1)^{n_{\ell} - 1} \sum_{n_{\ell}} G^{(n)}(x_1 \ldots x_{n_{\ell}}). \quad (2.16)$$

To determine the function $G^{(n)}(x_1 \ldots x_n)$ let us divide all of $n$ its arguments into groups

$$\{x_i^{(k)}\}, \quad i = 1, \ldots, \ell, \quad k_{\ell} = 1, \ldots, n_{\ell}, \quad (2.17)$$

the total number $n_g$ of which is defined by the first expression

$$n_g = \sum n_{\ell}, \quad n = \sum n_{\ell} \ell. \quad (2.18)$$

The function $G^{(n)}(x_1 \ldots x_n)$ is found by integration of the function $G^{(n)}(X_1 \ldots X_n)$ (2.13) over coordinates $r^{(k)}$ of all replicas except the coordinates $\{r_i^{(k)}\}$ (2.16) of $n_g$ selected replicas. The internal and the external sums in the expression (2.16) are, respectively, over positive numbers $\{n_{\ell}\}$ obeying the second condition (2.18) and over all different transpositions of $n$ arguments $x_i^{(k)}$ of replicas $\{k_{\ell}\}$. The transpositions inside each replica should not be carried out because of the symmetry conditions. So, the total number of admitted transpositions equals

$$n! \left( \sum_{\ell} n_{\ell} - 1 \right)! / \prod_{\ell} n_{\ell} ! (\ell !)^n \ell. \quad (2.19)$$

For $n > 1$ the functions $G^{(n)}$ are symmetrical with respect to the transpositions of all their arguments and they happen to equal zero after the integration over any of a variable $r_i^{(k)}$. The Fourier-components

$$\tilde{G}^{(n)}(p_1 \ldots p_n) = V^{-1} \prod_{i=1}^{n} \int dr_i \ G^{(n)}(x_1 \ldots x_n) \exp \left( i \sum_{i=1}^{n} q_i r_i \right) \quad (2.20)$$
of these functions in the absence of external field have the form
\[ G_{\text{tot}}^{(1)}(p_1) = \rho \alpha, \quad G_{\text{tot}}^{(2)}(p_1, p_2) = G^{(2)}(\alpha_1, \alpha_2; q_1, q_2), \]
\[ G_{\text{tot}}^{(3)}(p_1, p_2, p_3) = G^{(3)}(\alpha_1, \alpha_2, \alpha_3; q_1, q_2, q_3), \]
\[ G_{\text{tot}}^{(4)}(p_1, p_2, p_3, p_4) = G^{(4)}(\alpha_1, \alpha_2, \alpha_3, \alpha_4; q_1, q_2, q_3, q_4) - \]
\[ - G^{(4)}(\alpha_1, \alpha_2, \alpha_3, \alpha_4; q_1, q_2, q_3, q_4) - (2 \leftrightarrow 4) - (2 \leftrightarrow 3). \] (2.21)

Where for the sake of designation simplicity we have introduced the generalized moment \( p = (q, \alpha) \). The value \( G_{\text{tot}}^{(n)} \) is identically zero if even one of the moments \( q_i, (i = 1, \ldots, n) \) equals zero. We have also taken into consideration the conditions of moment conservation in every replica
\[ G^{(n)}(p_1^{(1)} \mid p_1^{(2)}; p_2^{(1)} \mid p_2^{(2)}; \ldots) = \]
\[ = G^{(n)}(\alpha_1, \alpha_2, \alpha_3; q_1^{(1)}, q_2^{(1)}, q_3^{(1)}, \ldots; \alpha_1, \alpha_2, \alpha_3; q_1^{(2)}, q_2^{(2)}, q_3^{(2)}, \ldots). \] (2.22)

As it will be shown in the next section the functions \( G^{(n)} \) can be expressed through the «chemical correlation functions» which characterize the chemical structure of a polymer.

Essentially, the functions \( G_{\text{tot}}^{(n)} \) contain both local and nonlocal contributions. The first ones arise from one-replica terms \( G^{(n)}(...) \), whereas multi-replica terms \( G^{(n)}(...) \) describe the effect of nonlocality. These terms, having not been taken into account so far, appear in (2.16), (2.21) due to the dependence of chemical potentials \( \mu(C) \) on the density distribution \( \{\rho(x)\} \) (see (1.6)).

3. Chemical correlation functions.

The general theoretical description developed above can be especially efficient if we throw a bridge to the general fund of knowledge about the chemical structure of polymers. This structure of linear polymers may be characterized by chemical correlation functions [14]
\[ \langle \alpha_1 \mid k_1 \mid \alpha_2 \mid \ldots \mid \alpha_n \rangle \] (3.1)
which are equal to a joint probability to find respectively units \( M_{\alpha_1} \) and \( M_{\alpha_2} \) of these molecules at the distance \( k_1 \) and bonds between them along the chosen direction of the chain, \( M_{\alpha_2} \) and \( M_{\alpha_3} \) at the distance \( k_2 \) and bonds and so on. In order to express the correlation function \( G^{(n)} \) through the chemical correlators (3.1) let us introduce their generating function
\[ w^{(n)}(\alpha_1, \alpha_n \mid s_1, \ldots, s_{n-1}) = \sum_{k_1 > 0} \langle \alpha_1 \mid k_1 \mid \alpha_2 \mid \ldots \mid \alpha_n \rangle s_{k_1}^{k_1} \ldots s_{k_{n-1}}^{k_{n-1}}. \] (3.2)

It is very important for many polymer systems of practical interest [14] that these generating functions have been obtained earlier by the methods of chemical physics.

In order to solve the problem of correlation functions \( G^{(n)} \) calculation it is necessary to find their connection with generating functions (3.2). For this aim it is convenient to rewrite one-replica functions \( G^{(n)}(...) \) in the form
\[ G^{(1)}(1) = \chi^{(1)}(1), \quad G^{(2)}(1, 2) = \chi^{(1)}(1) \delta(1 - 2) + \chi^{(2)}(1, 2), \]
\[ G^{(3)}(1, 2, 3) = \chi^{(1)}(1) \delta(1 - 2) \delta(2 - 3) + [\chi^{(2)}(1, 2) \delta(2 - 3) + \cdots] + \chi^{(3)}(1, 2, 3), \]

\[ G^{(4)}(1, 2, 3, 4) = \chi^{(1)}(1) \delta(1 - 2) \delta(2 - 3) \delta(3 - 4) + [\chi^{(2)}(1, 2) \delta(2 - 3) \delta(3 - 4) + \cdots] + \chi^{(3)}(1, 2, 3) \delta(1 - 2) + \cdots + \chi^{(4)}(1, 2, 3, 4) \] (3.3)

where for brevity sake we wrote out only indications of arguments, for example

\[ \delta(1 - 2) = \delta(r_1 - r_2) \delta \alpha_1 \alpha_2. \]

The Fourier components of the functions \( \chi^{(n)} \) can be immediately expressed in terms of generating functions \( w^{(n)} \) (3.2)

\[ \tilde{\chi}^{(2)}(p_1 p_2) = \rho \left[ w^{(2)} \alpha_1 \alpha_2 (\lambda q_1 + \lambda q_2) \right] \delta(q_1 + q_2), \]

\[ \tilde{\chi}^{(3)}(p_1 p_2 p_3) = \rho \left[ w^{(3)} \alpha_1 \alpha_2 \alpha_3 (\lambda q_1, \lambda q_3 + \lambda q_3) + \delta(q_1 + q_2 + q_3) \right] \delta(q_1 + q_2 + q_3), \]

\[ \tilde{\chi}^{(4)}(p_1 p_2 p_3 p_4) = \rho \left[ w^{(4)} \alpha_1 \alpha_2 \alpha_3 \alpha_4 (\lambda q_1, \lambda q_1 + q_2, \lambda q_3) + \delta(q_1 + q_2 + q_3 + q_4) \right] \delta(q_1 + q_2 + q_3 + q_4) \] (3.4)

where \( \lambda q \) is the Fourier component of the function \( \lambda q(r) \), corresponding to a bond (see (2.3)).

The multi-replica functions \( G^{(n)}(\ldots | \ldots) \) can also be expressed in terms of generating functions \( w^{(n)} \). It is convenient to define analogously to (3.3) the corresponding functions \( \chi^{(n)}(\ldots | \ldots) \)

\[ G^{(2)}(1 | 2) = \chi^{(2)}(1 | 2), \quad G^{(3)}(1 | 2, 3) = \chi^{(2)}(1 | 2) \delta(2 - 3) + \chi^{(3)}(1 | 2, 3), \]

\[ G^{(4)}(1, 2 | 3, 4) = \chi^{(2)}(1 | 3) \delta(1 - 2) \delta(3 - 4) + \chi^{(3)}(1 | 3, 4) \delta(1 - 2) + \chi^{(4)}(1, 2 | 3, 4) \] (3.5)

whose Fourier components are expressed through the generating functions \( w^{(n)} \) (3.2)

\[ \tilde{\chi}^{(3)}(p_1 | p_2 p_3) = \rho \left[ w^{(3)} \alpha_1 \alpha_2 \alpha_3 (1, \lambda q_3) + \delta(3) \delta(q_1 + q_2) \right] \delta(q_1 + q_2 + q_3), \]

\[ \tilde{\chi}^{(4)}(p_1 p_2 | p_3 p_4) = \rho \left[ w^{(4)} \alpha_1 \alpha_2 \alpha_3 \alpha_4 (\lambda q_1, 1, \lambda q_4) + \delta(4) \delta(q_1 + q_2) \right] \delta(q_1 + q_2 + q_3 + q_4) \] (3.6)

In a general case the expressions for \( \tilde{\chi}^{(n)}(\ldots | \ldots) \) can be obtained from corresponding expressions for \( \tilde{\chi}^{(n)}(\ldots) \) by the substitutions

\[ \lambda \Sigma q^{(k)} \rightarrow \prod \lambda q^{(k)}, \quad \delta(\Sigma q^{(k)}) \rightarrow \prod \delta(q^{(k)}), \] (3.7)

which should be fulfilled in the case when the moments \( q^{(k)} \) belong to the different replicas \( k \). The second equality (3.7) corresponds to the conservation of the moment separately in every replica.

4.1 Landau's Expansion. — According to expression (2.4) the functional $\tilde{\mathcal{F}} \{ v(x) \}$ depending on the field $v(x)$ conjugated to the «order parameter» $\rho(x)$ can be considered as the Landau functional of the free energy [15]. The introduction of this field is a usual trick of theoretical physics, which simplifies calculations to a great extent. Therefore we shall use below just this approach, whereas a more widespread density functional method will be developed in section 6.

Fulfilling the Landau expansion of the functional $\tilde{\mathcal{F}} \{ v(x) \}$ in the absence of an external field we find

$$\tilde{\mathcal{F}} \{ v(x) \} - \tilde{\mathcal{F}} \{ v(x) \} = -VT \sum_{n=2}^{\infty} \prod_{p_1, \ldots, p_n} \tilde{G}_{\text{tot}}^{(n)}(p_1 \ldots p_n) \tilde{v}(p_1) \ldots \tilde{v}(p_n),$$

where the correlation functions are introduced

$$\tilde{G}_{\text{tot}}^{(n)}(p_1 \ldots p_n) = \tilde{G}_{\text{tot}}^{(n)}(p_1 \ldots p_n) - \tilde{D}^{(n)} \alpha_1 \alpha_1 \delta(q_1 + \ldots + q_n).$$

The matrix $\tilde{D}^{(2)} = \tilde{D} = \tilde{C}^{-1}$ is inverse to the matrix $\tilde{C}$ with the elements

$$\tilde{C}_{\alpha \beta} = \tilde{C}^{(2)}_{\alpha \beta} = - T^{-1} \frac{\partial \mu^*_{\alpha}(\rho_\gamma)}{\partial \rho_{\beta}}$$

and the highest correlation functions $\tilde{D}^{(n)} (n > 2)$ of the separate units system are given by the expression

$$\tilde{D}^{(n)} \alpha_1 \alpha_2 = \prod_{i=3}^{n} \left[ \sum_{\beta} \tilde{D} \alpha_1 \beta \frac{\delta}{\delta \rho_{\beta}} \right] \tilde{D} \alpha_1 \alpha_2.$$ (4.4)

Within the framework of the mean field approximation the functional integral (2.4) over $v(x)$ can be calculated by the steepest descent method

$$F \{ n(C), H(x) \} = \tilde{\mathcal{F}} \{ v(x), H(x) \} + T \sum_C \ln n(C)!$$

According to the saddle point condition

$$\rho(x) = - T \delta \mathcal{F} \{ v(x) \}/\delta v(x)$$

the density of monomer units is defined by the functional $\mathcal{G}$ for the noninteracting macromolecules.

The spatially-homogeneous solution of equation (4.6) is stable only under the condition of positive definiteness of the quadratic form of the expansion (4.1). Both eigenvalues $\lambda(q)$ and eigenfunctions $\psi_\alpha(q)$ of this form are obtained from the nontrivial solution of the equations

$$\sum_{\beta} [\tilde{D}_{\alpha \beta} - \tilde{G}^{(2)}_{\alpha \beta}(q)] \psi_{\beta}(q) = \lambda(q) \psi_{\alpha}(q), \quad \sum_{\alpha} \psi_\alpha(q) \psi_\alpha(-q) = 1.$$ (4.7)
The condition \( A(Q) = 0 \) can be rewritten in such a way

\[
D(q^2) = 0, \quad D(q^2) = \det \left\{ [\tilde{G}^{(2)}(q)]^{-1} - \tilde{C} \right\}. \tag{4.8}
\]

The value \( q_0 \) of the modulus of wave vector \( q \), where the spatially-homogeneous state of the system becomes absolutely unstable, should be found from the solution of equation

\[
\frac{\partial D(q_0^2)}{\partial q_0^2} = 0. \tag{4.9}
\]

4.2 Binodal Transition and Polycritical Points. — At the point of the binodal transition the new phase appears as the droplet of a small volume \( V' \ll V \). In the case of the transition from the spatially-homogeneous « old » phase with the density \( \bar{\rho} \), the generating functional \( G \) (2.5) in the first order in \( V' \) has the form

\[
G \{ v(x) \} = G \{ \mu_a^* (\bar{\rho}) \} + \Psi_d \{ s(x) \} - \Psi_d \{ 1 \},
\]

\[
s(x) = \exp \left\{ (\mu_a^* (\bar{\rho}) - v(x))T \right\}. \tag{4.10}
\]

Here the generating functional \( \Psi_d \) is defined by the expression

\[
\Psi_d \{ s(x) \} = \sum_C n(C) Q_d(C, \{ v(x) - \mu_a^* (\bar{\rho}) \}) \langle Q_d(C, \{ 0 \} \rangle. \tag{4.11}
\]

The integration in expression (2.3) for the partition function \( Q_d \) (4.11) is performed only over the volume \( V' \) of the « new » phase. Substituting (4.10) into (2.4) we find in the mean field approximation the difference in the free energy between the new and old phases

\[
\Delta F \{ v(x) \} = T \Psi_d \{ s(x) \} - \int dr P^* (\rho(x)) + PV', \tag{4.12}
\]

where the integration is over the volume \( V' \) of the new phase only and the pressure \( P \) equals

\[
P = V^{-1} \sum_C n(C) + P^* (\bar{\rho}). \tag{4.13}
\]

The position of the binodal and the field \( v(x) = \mu_a^* (\rho(x)) \) in the new phase are determined from equations

\[
\Delta F \{ v(x) \} = 0, \quad \delta \Delta F \{ v(x) \}/\delta v(x) = 0, \tag{4.14}
\]

the second of which can be rewritten as follows

\[
\rho(x) = s(x) \delta \Psi_d \{ s(x) \}/\delta s(x). \tag{4.15}
\]

In order to find the condition for the polycritical points it is convenient to expand the function \( v(x) \) in the series of eigenfunctions which are the solution of the equations (4.7). Picking out the contribution of the mode with a minimal eigenvalue \( A(q_0) \) in the Fourier representation of the function \( v(x) \) we find

\[
v(p) = c_0 \sum_{|q| < q_0} \psi_0(p) + \sum_{|q| > q_0} c_k(p) \psi_k(p), \tag{4.16}
\]

where the first sum is over the different eigenfunctions corresponding to the same eigenvalue
\( \Lambda(q_0) \). In the case \( q_0 \neq 0 \) this sum is over the minimal wave vectors of the reciprocal lattice of the superstructure under consideration. The condition \( |q| = q_0 \) restricts essentially the number of possible \( d \)-dimensional superstructures, a complete set of which comprises the lamellar structures \( (d = 1) \), the squared and triangular structures \( (d = 2) \), the body-centered-cubic structures \( (d = 3) \).

The fact that the value \( \Lambda(q_0) \) in the vicinity of spinodal is very small leads to the extremely large fluctuations of the variable \( c_0 \) (4.16). Let us find the free energy functional depending only on this variable. Substituting (4.16) into (4.12) and minimizing \( \Delta F \) with respect to all coefficients \( c_k(p) \) except \( c_0 \) we find

\[
\Delta F \left( c_0 \right) / T = \Lambda(q_0) c_0^2/2 + \gamma^{(3)} c_0^3/3! + \gamma^{(4)} c_0^4/4! + \ldots, \tag{4.17}
\]

where coefficients \( \gamma^{(k)} \) are defined by the expressions

\[
\gamma^{(3)} = \sum_{\alpha, \beta, \gamma} \left[ \tilde{D}^{(3)} \right]_{\alpha \beta \gamma} D^{(3)}(p_1 p_2 p_3) \psi_0(p_1) \psi_0(p_2) \psi_0(p_3),
\]

\[
\gamma^{(4)} = \sum_{\alpha, \beta, \gamma, \delta} \left[ \tilde{D}^{(4)} \right]_{\alpha \beta \gamma \delta} D^{(4)}(p_1 p_2 p_3 p_4) + \sum_{p, p'} \tilde{G}^{(3)}(p_1 p_2 p_3) \tilde{r}^{(2)} + (pp') \tilde{G}^{(3)}(p_5 p_6 p') \psi_0(p_1) \psi_0(p_2). \tag{4.18}
\]

The matrix \( \tilde{r}^{(2)} \) has the form

\[
\tilde{r}^{(2)}(pp') = (pp') \delta(q + q') \psi_0(q) \psi_0(q')/\Lambda(q_0), \tag{4.19}
\]

The expressions (4.17)-(4.19) are very important since they reduce the consideration of a many-component polymer system to the simple Landau expansion of the free energy for the system with a one-component order parameter. We shall not discuss here in detail this well elaborated problem, noting only that the tricritical point is defined by the conditions \( \Lambda(q_0) = \gamma^{(3)} = 0 \), while to find other polycritical points it is necessary to equate with zero corresponding coefficients \( \gamma^{(k)} \).

The functional (4.17) is also convenient to apply for a consideration of a phase diagram of a complex polymer system, since it takes into account not only \( |q| = q_0 \) but all harmonics \( q \) of the superstructure.

5. Markovian heteropolymers.

5.1 Chemical structure. — The alternation of monomer units along linear macromolecules can be often described by means of the Markov chain theory [14]. For such Markovian heteropolymers the average number of the macromolecules with a given configuration \( C \) is determined by the expression

\[
n(C) = 1/2 [\tilde{n}(C) + \tilde{n}^{-1}(C)] \tag{5.1}
\]

where the arrow denotes the direction along the chain while the value \( \tilde{n}(C) \) coincides with \( \tilde{n}(\tilde{C}) \) for the configuration \( \tilde{C} \), obtained by changing the direction along the chain with the
configuration C. For any of these directions
\[ n(C) = N \zeta \alpha \prod_{k=1}^{l-1} \nu \alpha_k \alpha_{k+1} \eta_{\alpha_k}, \quad \sum_{\beta} \nu_{\alpha\beta} + \eta_{\alpha} = 1, \quad (5.2) \]
where \( N \) is the overall number of monomer units in the system and the element \( \nu \alpha_k \alpha_{k+1} \) of the transition matrix \( \nu \) determines the conditional probability to find at \((k + 1)\)-th step the unit of the type \( \alpha_{k+1} \), if the previous unit at \( k \)-th step was of the type \( \alpha_k \). It can be easily shown that the parameters of the distribution \((5.2)\) for the different directions along the chain are mutually connected
\[ \tilde{\nu}_{\alpha\beta} = \pi_{\beta} \tilde{\nu}_{\beta\alpha} \pi_{\alpha}^{-1}, \quad \tilde{\xi}_{\alpha} = \pi_{\alpha} \tilde{\xi}_{\alpha}, \quad \tilde{\eta}_{\alpha} = \tilde{\eta}_{\alpha}/\pi_{\alpha}. \quad (5.3) \]
Here the fractions \( \pi_{\alpha} \) of monomer units \( M_{\alpha} \) are determined by the components of the corresponding matrix
\[ \pi_{\alpha} = [\tilde{\xi}(1 - \tilde{\nu})^{-1}]_{\alpha}. \quad (5.4) \]
The average length \( \bar{\ell} \) of the macromolecule can be expressed through the parameters of the distribution \( \{n(C)\} \)
\[ \bar{\ell}^{-1} = \sum_{\alpha} \pi_{\alpha} \tilde{\eta}_{\alpha} = \sum_{\alpha} \tilde{\eta}_{\alpha} = \sum_{\alpha} \tilde{\xi}_{\alpha} = \sum_{\alpha} \tilde{\xi}_{\alpha}/\pi_{\alpha}. \quad (5.5) \]
Calculating the generating function of chemical correlation functions \((3.2)\) we find the simple expression
\[ w^{(n)} \alpha_{1} \alpha_{n}(s_{1}, \ldots, s_{n-1}) = \pi_{\alpha} \kappa \alpha_{1} \alpha_{2}(s_{1}) \ldots \kappa \alpha_{n-1} \alpha_{n}(s_{n-1}) \quad (5.6) \]
where we have introduced the matrix
\[ \kappa = [\tilde{\nu}^{-1}(\lambda \mathbf{q})^{-1} - 1]^{-1}. \quad (5.7) \]
An important role among Markovian chains play symmetric ones \([14]\) with \( \tilde{n}(C) = \tilde{n}(C). \) For such chains following equalities are true
\[ \tilde{\nu}_{\alpha\beta} = \tilde{\nu}_{\beta\alpha} = \nu_{\alpha\beta}, \quad \tilde{\xi}_{\alpha} = \tilde{\xi}_{\alpha}, \quad \tilde{\eta}_{\alpha} = \tilde{\eta}_{\alpha} = \eta_{\alpha}, \quad \zeta_{\alpha} = \pi_{\alpha} \eta_{\alpha} \quad (5.8) \]
the last of which ensues from previous equalities \((5.8)\) with an account for formulas \((5.3)\).
In the case of two-component systems using expressions \((5.8)\) and normalisation condition \((5.2)\) it is easy to derive
\[ \zeta_{1} = \pi_{1} \eta_{1}/(\pi_{1} \eta_{1} + \pi_{2} \eta_{2}), \quad \zeta_{2} = \pi_{2} \eta_{2}/(\pi_{1} \eta_{1} + \pi_{2} \eta_{2}), \quad (5.9) \]
\[ \pi_{1} = \nu_{21}/(\nu_{12} + \nu_{21}), \quad \pi_{2} = \nu_{12}/(\nu_{12} + \nu_{21}). \quad (5.10) \]
Many important classes of polymers can be described by a Markov Chain with particular values of elements \( \nu_{\alpha\beta} \) of its transition probability matrix. The case \( \nu_{12} = \nu_{21} = 0 \) corresponds to the blend of polydisperse homopolymers, where parameters \( \bar{\ell}_{\alpha} \) are equal to the fractions of chains of the type \( \alpha \), whose average length \( \bar{\ell}_{\alpha} = \eta_{\alpha}^{-1} \) is determined by \( \eta_{\alpha}. \) The case \( \nu_{11} = \nu_{22} = 0 \) describes copolymers with regular alternation of the first and second types of units, whereas conditions \( \nu_{11} \nu_{22} - \nu_{12} \nu_{21} = 0 \) and \( \nu_{11} \nu_{22} \gg \nu_{12} \nu_{21} \) correspond to totally random (Bernoullian) and multiblock copolymers respectively.
5.2 Spinodal Transition. — In order to find limits of the region of absolute instability for the blends of binary symmetric copolymers let us substitute the expression (5.6) for \( n = 2 \) into the formulas (3.4) and the result obtained into (3.3). Further one can easily find the determinant (4.8)

\[
D(q^2) = \frac{A - B\lambda_q + C\lambda_q^2}{\rho_1\rho_2[1 + (\nu_{11} + \nu_{22})\lambda_q + (\nu_{11}\nu_{22} - \nu_{12}\nu_{21})\lambda_q^2]},
\]

\[
A = (1 - \rho_1\tilde{C}_{11})(1 - \rho_2\tilde{C}_{22}) - \rho_1\rho_2\tilde{C}_{12}^2,
\]

\[
B = \nu_{11}[(1 + \rho_1\tilde{C}_{11})(1 - \rho_2\tilde{C}_{22}) + \rho_1\rho_2\tilde{C}_{12}^2] + 
\]

\[
+ \nu_{22}[(1 - \rho_1\tilde{C}_{11})(1 + \rho_2\tilde{C}_{22}) + \rho_1\rho_2\tilde{C}_{12}^2] + 2(\rho_1\nu_{12} + \rho_2\nu_{21})\tilde{C}_{12},
\]

\[
C = (\nu_{11}\nu_{22} - \nu_{12}\nu_{21})[(1 + \rho_1\tilde{C}_{11})(1 + \rho_2\tilde{C}_{22}) - \rho_1\rho_2\tilde{C}_{12}^2].
\]

The sign of the determinant \( D(q^2) \) coincides with that of the numerator of expression (5.11), since its denominator is always positive. The condition of stability loss (4.7), (4.8) for fluctuations with the zeroth (a) and the nonzerotth (b) wave vector \( q_0 \) looking respectively as follows

\[
B = A + C \quad (a), \quad B^2 = 4AC \quad (b).
\]

These conditions, defining the range of the absolute instability area of heteropolymer blends under consideration are shown in the figure for the case \( A > 0 \). In the opposite case \( A < 0 \), corresponding to the absolute thermodynamic instability of the separate units system, the polymer system is always unstable. As it follows from the figure the positiveness of the coefficients, \( A, B, C, \) is a necessary condition for the loss of stability by the system in hand on the wave vector \( q_0 \rightarrow 0 \). Since \( \lambda q_0 = B/2C = 2A/B \) the study of such phase transition is of practical interest only in the vicinity of the point \( M \), where the condition \( q_0a \ll 1 \) holds.

Let us consider in detail the most interesting case \( q_0R \gg 1 \), where \( R = aR^{1/2} \) is the geometric size of the macromolecule. Solving the second equation (5.12) with respect to \( \nu_{12} + \nu_{21} \) and applying formulas (5.9), (5.10) we find

\[
\nu_{12} + \nu_{21} = 2\beta^2[(\beta^2 + \alpha^2)(\beta^2 + \gamma^2)]^{1/2} + \beta^2 + \alpha\gamma
\]

\[
\beta^2 = (\rho_1\tilde{C}_{11} - \rho_2\tilde{C}_{22})^2 + 4\rho_1\rho_2\tilde{C}_{12}^2, \quad \alpha = 1 - \rho_1\rho_2(\tilde{C}_{11}\tilde{C}_{22} - \tilde{C}_{12}^2),
\]

\[
\gamma = \rho\left[\sum \tilde{C}_{ij}\sigma_i\sigma_j + \sigma_i\sigma_j(2\tilde{C}_{12} - \tilde{C}_{11} - \tilde{C}_{22})\right].
\]

According to (5.13) on the spinodal inequalities \( 0 < \nu_{12} + \nu_{21} < 1 \) are true. So, the spinodal phase transition into the state with \( q_0 > 0 \) is impossible in two important limiting cases, i.e. the mixture of homopolymers \( (\nu_{12} + \nu_{21}) = 0 \) and Bernoullian heteropolymers \( (\nu_{12} + \nu_{21}) = 1 \).

5.3 Spatially-Periodic Superstructure. — In the case of Markovian heteropolymers the implicit form of the generating functional (2.9) can be easily found [16]

\[
\Psi_{dm}\{s(X)\} = (N/V^m)\left[\sum_{x,x'}(\tilde{v}^{-1})_{\alpha\alpha'}\lambda^{-1}(X - X') \tilde{\phi}(X) \phi(X') -
\right.

\[
- \sum_x s(X)(\tilde{\phi}(X) + \tilde{\xi}_\alpha)(\phi(X) + \tilde{\eta}_\alpha)\right]\quad (5.14)
\]
where the functions $\tilde{\phi}(X)$ and $\phi(X)$ are determined by the minimum condition of the right-hand side of the expression (5.14). The corresponding equations define these functions as some functionals of $s(X)$. Substituting them into (5.14) we can satisfy ourselves that the expansion of (5.14) into the powers of the functions $s(X)$ exactly reproduces the series (2.9). The compact representation (5.14) is very convenient for the investigation of spatial superstructures in the polymer system under consideration.

We shall consider here the heteropolymer melt, of which the compressibility can be neglected for calculations with good accuracy. Therefore we can use for the description of the volume interactions the simple model of the lattice gas (2.8). Let us suppose for simplicity's sake that the probability $\zeta_a$ to find the initial monomer unit of the given type $a$ equals their overall fraction $\pi_a$ when from expressions (5.8)-(5.10) it ensues that $\eta_1 = \eta_2 = \tilde{\eta}^{-1}$. According to the results of the previous section, the spatially-homogeneous state of incompressible system under consideration can lose its stability only due to the spinodal fluctuations with the wave vector $q_0 = 0$. The incompressibility condition corresponds to the limit $\rho \to \nu^{-1}$ in the expression (2.7) for the function $\mu_{\alpha}^{\beta}(\rho)$, determining parameters $\tilde{C}_{\alpha\beta}$ (4.3). As a result we find that the area of absolute instability is defined by the condition

$$\chi = (\gamma_{11} + \gamma_{22} - 2 \nu_{12})^2 T > \chi_c,$$  \hspace{1cm} (5.15)

where the critical value of the Flory parameter

$$\chi_c = \frac{\nu_{12} + \nu_{21}}{(1 + \nu_{11})(1 + \nu_{22}) - \nu_{21} \nu_{12}} \left[ 1 + \nu_{12} + \nu_{21} + \frac{(1 + \nu_{11})(1 + \nu_{22})}{\nu_{12}} + \frac{(1 + \nu_{11})(1 + \nu_{22})}{\nu_{21}} \right]$$  \hspace{1cm} (5.16)

has an especially simple form in the heteropolymer limit $\tilde{\eta}(\nu_{12} + \nu_{21}) \gg 1$

$$\chi_c = (\nu_{12} + \nu_{21}) \pi_{12} (2 - \nu_{12} - \nu_{21})$$  \hspace{1cm} (5.17)

It will be shown below that in the case $\chi > \chi_c$, regardless of the condition $q_0 = 0$, the period of the appearing superstructure is proportional to $(\chi - \chi_c)^{-1/2}$ and essentially exceeds the spatial

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![Phase diagram of the solution of the Markovian copolymers. The boundary of shaded region of thermodynamic instability consists of straight line $a$ and parabola $b$, which are defined in (5.12).](image-url)
size of one block. This incommensurable superstructure differs qualitatively from known structures [17, 18], for which both these scales are comparable.

To find the characteristics of such a superstructure in the vicinity of the transition point \( \chi = \chi_c \) let us expand the functional \( \Psi_{dm} \) (5.14) in powers of the functions

\[
\begin{align*}
  u_1(R) &= \pi_1 s_1(R) + \pi_2 s_2(R) - 1, \\
  u_2(R) &= \pi_2 s_1(R) + \pi_1 s_2(R) - 1, \\
  u_3(R) &= s_1(R) - s_2(R),
\end{align*}
\]

(5.18)

considering them as a small perturbation. In the case \( u_i = 0 \) the quadratic form (5.14) can be diagonalized by transforming the initial variables into the new ones

\[
\vec{\psi}(R) = \vec{\phi}(R) S, \quad \psi(R) = S^{-1} \phi(R), \quad S = \begin{pmatrix} \pi_2 & 1 \\ -\pi_1 & 1 \end{pmatrix}.
\]

(5.19)

In the Fourier representation, the eigenvalues of the quadratic form are proportional to the quantities

\[
\lambda_i^{-1} = \lambda_i^{-1} \lambda_Q^{-1} - 1, \quad i = 1, 2; \quad \lambda_Q = \exp(-a^2 Q^2)
\]

(5.20)

where \( \lambda_i \) are the eigenvalues of the transition matrix \( \nu \):

\[
\lambda_1 = 1 - \vec{\lambda}^{-1}, \quad \lambda_2 = 1 - \vec{\lambda}^{-1} - \nu_{12} - \nu_{21}.
\]

(5.21)

Taking into account expression (5.20) we find the expansion of the functional \( \Psi_{dm} \) (5.14) in powers of the Fourier components of functions (5.18)

\[
\Psi_{dm}/T = \text{Const.} - \rho V \left[ u_{00} + \sum_Q u_{0Q} g_{1Q} u_{Q0} + \cdots \right],
\]

(5.22)

\[
u_{Q-Q'} = u_{1Q} \delta(Q - Q') + \sum_P u_{3QP} g_{2P} u_{3-Q'-P} +
\]

\[
  + \sum_{P,T} u_{3QP} g_{2P} u_{2T-P} g_{2T} u_{3-Q'-T} + \cdots,
\]

(5.23)

where \( \delta(Q) \) is the Kronecker symbol and all wave vectors \( P, Q, T \) are defined in \( 3(1 + m) \)-dimensional space.

The functional \( \Omega^* \) (2.6), describing the interaction of monomer units in the incompressible system, has the simplest form

\[
\Omega^* \{v(x)\} = \rho \int dr [u(r) + v^2(r)/2 \chi]
\]

(5.24)

in terms of the variables \( u \) and \( v \), related to the parameters \( v_i \) (2.7) by relations

\[
\begin{align*}
  v_1(r) &= \pi_2 v(r) + u(r), \\
  v_2(r) &= -\pi_1 v(r) + u(r).
\end{align*}
\]

(5.25)

The expressions (5.24) and (5.25) are obtained by taking the limit \( \rho \to \rho^{-1} \) in the formulas (2.8). The function \( v(r) \) is proportional to the deviation \( \Delta \rho_1(r) \) of the density of the first type monomer units in the given point \( r \) from its average over volume value

\[
v(r) = \chi \Delta \rho_1(r)/\rho, \quad \Delta \rho_1(r) = \pi_2 \rho_1(r) - \pi_1 \rho_2(r).
\]

(5.26)
Thus, densities of the monomer units $M_a$ are equal to

$$\rho_1(r) = \pi_1 \rho + \Delta \rho_1(r), \quad \rho_2(r) = \pi_2 \rho - \Delta \rho_1(r). \tag{5.27}$$

Substituting the relations (5.24), (5.25) and (5.22), (5.23) into (2.4), we find within the framework of the mean field approximation

$$m \tilde{\Omega} \{ v(x), 0 \} / Tr V = \text{Const.} - \sum_{k=1}^m f(u^{(k)}, v^{(k)}) + \sum_{k \neq k'} f_{\text{int}}(v^{(k)}, v^{(k')}) + \cdots. \tag{5.28}$$

$f(u, v) = \sum_{q \neq 0} \left\{ \left[ \frac{1}{2} \chi - \pi_1 \pi_2 (g_{2q} + 1/2) \right] v_q v_{-q} - 1/2 u_q u_{-q} \right\} -

\left( \pi_2 - \pi_1 \right) \sum_{q, q' \neq 0} g_{2q} g_{2q'} v_q v_{q'} - \sum_{q \neq 0} g_{1q} \xi_q \xi_{-q},$

$$\xi_q = u_q - \pi_1 \pi_2 \sum_{q' \neq 0} (g_{2q'} + 1/2) v_{q'} + v_{-q'}, \quad f_{\text{int}}(v, v') = \pi_1^2 \pi_2^2 \sum_{q, q', q'' \neq 0} g_{1q, q'} (g_{2q} + 1/2) (g_{2q'} + 1/2) v_q v_{-q} v_{q'} v_{-q'},$$

$$g_{1q, q'} = g_{1q}, \quad Q = (q, q', 0, \ldots, 0). \tag{5.29}$$

Here all the wave vectors $q, q'$ are located in the 3-dimensional space. The minimisation of the functional (5.28) with respect to $u^{(k)}$ gives

$$u^{(k)}_q = g_{1q} (g_{1q} + 1/2)^{-1} \pi_1 \pi_2 \sum_{q'} (g_{2q'} + 1/2) v^{(k)}_{q'} v^{(k)}_{-q'}. \tag{5.30}$$

Substituting (5.30) into (5.29) we find the functional $\Psi_{\text{dm}}$ depending only on fields $v^{(k)}$. Let us consider now the most interesting region of the wave vectors $\bar{q}^{-1} \approx a^2 q^2 \ll \nu_{12} + \nu_{21}$, which correspond to the scales $q^{-1}$, small with respect to the mean size $R = a \bar{q}^{1/2}$ of a macromolecule but large with respect to the mean size $a(\nu_{12} + \nu_{21})^{-1/2}$ of a block. In this region we can expand the functions $g$, up to the linear with respect to $q^2$ terms. Introducing the dimensionless variables

$$v_q = \frac{\tau (\nu_{12} + \nu_{21}) c_q}{[\pi_1 \pi_2 (1 - \nu_{12} - \nu_{21})]^{1/2}}, \quad \tau = 1 - \frac{\chi c}{\chi},$$

$$\bar{q} = \frac{p}{a} \gamma^{1/2} \tau^{1/2}, \quad \gamma = \frac{(\nu_{12} + \nu_{21})(2 - \nu_{12} - \nu_{21})}{2(1 - \nu_{12} - \nu_{21})} \tag{5.31}$$

we find the expression for the functional $\tilde{\Omega} \{ v(x), 0 \}$ (5.28)

$$m \tilde{\Omega} \{ v(x), 0 \} / Tr V = \gamma \tau^3 \sum_{k=1}^m \left[ \sum_{p \neq 0} c_p^{(k)} c_{-p}^{(k)} (-1 + p^2) - \Delta \sum_{p, p' \neq 0, p + p' \neq 0} c_p^{(k)} c_{-p}^{(k)} c_{-p'}^{(k)} \right] -

- \sum_{k \neq k'} \sum_{p, p' \neq 0, p + p' \neq 0} c_p^{(k)} c_{-p}^{(k)} c_p^{(k')} c_{-p'}^{(k')}, \tag{5.32}$$

$$\Delta = \frac{2(\pi_2 - \pi_1)}{2 - \nu_{12} - \nu_{21}} \left( \frac{1 - \nu_{12} - \nu_{21}}{\pi_1 \pi_2} \right)^{3/2}.$$
Let us consider the replica-symmetric solution \( c_p^{(k)} = c_p \) of the equations corresponding to the minimum condition of the functional (5.32). The nontrivial solution, existing only in the case \( \tau > 0 \), has been obtained in particular case \( \Delta = 0 \) \cite{22}. Considering \( \Delta \) as a small parameter when \( |\Delta| \ll 1 \) it is possible to find the solution in the form of the series of parameter \(|\Delta|\) powers

\[
c_p = c \sum_{i=1}^{6} \left[ \delta (p - p_0 e_i) + \delta (p + p_0 e_i) \right],
\]

\[
c = \frac{\text{sgn} (\Delta)}{3^{3/2} 2^{1/2}} \left( 1 + (2/3)^{1/2} |\Delta| \right), \quad p_0 = 3^{-1/2} (1 + 6^{-1/2} |\Delta|),
\]

(5.33)

where \( e_i, i = 1, \ldots, 6 \), are unit vectors directed along the edges of a regular tetrahedron.

5.4 Discussion. — The solution (5.33) with bcc symmetry corresponds to an absolute minimum of the free energy functional at \( \Delta \neq 0 \). It can be easily shown that this solution is stable at least for small \(|\Delta| \ll 1\). The harmonics \( c_p \) with the wave vectors \( \Sigma n_i e_i (n_i > 1) \) of the reciprocal bcc lattice contribute to (5.33) only in higher-order terms with respect to the parameter \(|\Delta|\). The solution of such type exists only for \(|\Delta| < \Delta_c \simeq 1\). The quantity \( \Delta_c \) can be evaluated \( \Delta_c < (3/2)^{1/2} \) using the variation principle with the trial function (5.33).

The condition \( a^2 q^2 \ll v_{12} + v_{21} \) for the applicability of the expansion (5.32) holds only at \( \tau \ll 1 \). In the case \( \tau \sim 1 \) the amplitude \( \Delta \rho_1(\tau) \) of the superstructure (5.26) is about total density \( \rho \) and its period is comparable with the spatial size of a block. To describe such superstructure the higher-order terms in the functions \( u^{(k)}, v^{(k)} \) in the expansion (5.32) should be taken into account. This solution has the form of the strongly pronounced domain structure with a period equal to the size of a block. Similar spatial structures have been described theoretically [17-21] within the framework of models other than we use here. However, a description of such superstructures is out of the limits of the Ginzburg-Landau (GL) approach applied in this paper.

The difference in free energy of a state with the periodic superstructure and spatially-homogeneous state is equal to

\[
\Delta F/\rho V T = - (2 \gamma \tau^3/27)(1 + 2^{3/2}|\Delta|/3^{1/2}), \quad |\Delta| \ll 1,
\]

(5.34)

It is noteworthy, that the expression of the free energy includes odd powers of the parameter \(|\Delta|\) owing to the finite quantity of the cubic invariant of the order parameter for the solution (5.33).

Due to the factor \( \tau^3 \) in expressions (5.34) the phase transition under consideration is the third-order transition in the parameter \( \tau \) despite the presence of the cubic terms in the order parameter \( \nu \). This quite unusual situation for the traditional GL approach is related with the long-range character of the fourth-order term in expansion of the \( f_{int} \) which describes the interaction of the different replicas. It originates from the multi-replica function \( \tilde{G}_{a_1, a_2, a_3, a_4}^{(d)}(q_1, q_3) \) (2.20) which describes the nonlocal effects discussed above. To explain the character of the phase transition let us consider the GL functional depending only on the amplitude \( \Delta \rho_1 \) of the superstructure, which is obtained by the minimisation of (5.32) with respect to the value of wave vector \( q \). Substituting the result of this minimisation \( q^2 \sim |\Delta \rho_1| \) into (5.32) we find that the coefficient of the cubic term, \( |\Delta \rho_1|^3 \), is positive when \( |\Delta| < \Delta_c \). That is why a nontrivial solution \( \Delta \rho_1 \neq 0 \) minimising the GL functional exists only under the condition \( \tau > 0 \) of the loss of positive definiteness by the quadratic form of this functional and keeps being continuous at the transition point.
6. Theories of the spatial superstructures in di- and tri-block copolymer systems have been developed within the framework of the GL approach by Leibler [3] and by Erukhimovich [5, 6, 11, 23]. These approaches are correct, strictly speaking, for the description of blends and melts of regular block copolymers, whose macromolecules have fixed length blocks. In order to consider polydispersity of such blocks one has to extend the theory taking into account nonlocal effects. The ignorance of the latter brought the authors of papers [23, 24] to the incorrect results.

The configuration disorder in the model of statistical random heteropolymer has been studied [22] in the particular symmetric case \( \pi_1 = \pi_2 = 1/2 \). Essentially, that the conclusion of this work about the existence of the spatially-periodic structure in a heteropolymer system with the Bernoullian statistics of the distribution of monomer units in the macromolecule contradicts the results of the present paper, according to which long-range correlations in the sequence of the alternation of monomer units along the chains should exist for the appearance of the superstructure. These correlations are completely absent by definition for random heteropolymers. The mentioned discrepancy seems to be connected with the inadequacy of a continuous chain model, applied by authors of the work [22] for the description of the Bernoullian heteropolymers. In particular, the fact that conclusions of this work substantially depend on the characteristic scale of the volume interactions, which have no relation to polymer specificity of the problem under consideration testifies to the above inadequacy.

The mean field theory, which has been used in this section is applicable only in the case when the gain of the superstructure free energy on the scale of its period 2 \( \pi/q \) is large enough in comparison with the temperature \( T \). This condition imposes the restrictions on the value of the parameter \( \tau \)

\[
\tau \gg \tau_G = \gamma^{1/3}(v^{1/3}a)^2. \tag{5.35}
\]

For actual polymers inequality \( v^{1/3} < a \) is true, so in the case of block-copolymers the Ginzburg parameter (5.35) is always small \( \tau_G \ll 1 \). Thus, the mean field theory gives the correct description of the periodic superstructure except the very narrow region \( \tau < \tau_G \), where the account of fluctuations is indispensable.


6.1 General formalism. — Though the presentation (2.4) of the free energy in terms of the field \( v(x) = \mu_\alpha^*(\rho(x)) \) (2.7) is more convenient for calculations than the usually applied density functional, the majority of authors of theoretical works, nevertheless, prefer so far the latter. Therefore it is expedient to develop on the basis of the presentation (2.4) the general density functional approach for polymers with an arbitrary chemical structure, which takes into account both density fluctuations and nonlocal effects.

The partition function of the system with the given (fluctuating) density distribution \( \{\rho(x)\} \) is defined by expressions (2.1), (2.3) with the additional factor

\[
\delta \left[ \rho(x) - \sum_{\alpha} \delta(r - r_{\alpha}) \right] \tag{6.1}
\]

in integrand. Summing in (6.1) is over monomer units \( M_\alpha \) only. Taking into account the factor (6.1) it is possible to rewrite the partition function (2.4) in the form of the integral over fluctuating density

\[
F \{n(C)\} = -T \ln \int D\rho(x) \exp \left[ -\tilde{F} \{n(C), \rho(x)\}/T \right] + T \sum \ln n(C)! \tag{6.2}
\]
We shall use the exponential representation for the $\delta$-function (6.1) to calculate the partition function (2.1) with constraints (6.1)

$$\exp[-\tilde{F}\{n(C), \rho(x)\}/T] = \int DH(x) \exp \left\{ \sum_x H(x) \rho(x) - F\{n(C), H(x)\}/T \right\}$$

where the functional $F\{n(C), H(x)\}$ has been defined in (2.4). Substituting expression (2.4) into (6.3) and replacing the integration variable $H(x) \rightarrow h(x) = H(x) + v(x)$ we find

$$\tilde{F}\{n(C), \rho(x)\} = F^*\{\rho(x)\} - TS\{n(C), \rho(x)\}$$

where the Lifshitz entropy $S$ [25] of the polymer system equals

$$S\{n(C), \rho(x)\} = \ln \int Dh(x) \exp \left\{ \sum_x h(x) \rho(x)/T + G\{h(x)\} \right\}.$$  

The functional $F^*\{\rho(x)\}$ depends only on the characteristics of the separate units system. If the system is far from spinodal its density fluctuations are rather small, so the integral over the field $v(x)$ can be calculated by the steepest descent method

$$F^*\{\rho(x)\} = \int df^*(\rho(x)), \quad f^*(\rho_\alpha) = \sum_\beta \rho_\beta \mu_\beta^*(\rho_\alpha) - P^*(\rho_\alpha).$$

6.2 Mean field approximation. — Neglecting fluctuations of the density distribution $\{\rho(x)\}$ one can calculate the functional integral by the steepest descent method. The corresponding saddle-point equation

$$\rho(x) = -T\delta G\{h(x)\}/\delta h(x)$$

determines the functional dependence of the field $h(x)$ on the density $\rho(x)$. Solving equation (6.7) for $h(x)$ by the iteration method and substituting the obtained solution in the exponent of the integrand of the expression (6.5), which equals this exponent in the mean field approximation, we find

$$S\{n(C), \rho(x)\} = \ln n(C)!/Vn(C) - \gamma \sum_{n=2}^\infty \frac{1}{n!} \sum_{p_1 \ldots p_n} \tilde{f}^{(n)}_{\text{tot}}(p_1 \ldots p_n) \tilde{\rho}(p_1) \ldots \tilde{\rho}(p_n),$$

$$\tilde{\rho}(p_1) = \frac{1}{V} \int dr [\rho(r, \alpha) - \rho_\alpha]$$

where we have put

$$\tilde{f}^{(2)}_{\text{tot}}(p_1 p_2) = [\tilde{G}^{(2)}(q)]^{-1}_{q_1, q_2} \delta(q_1 + q_2)$$

and $[\tilde{G}^{(2)}(q)]^{-1}$ is the matrix inverse to the matrix $\tilde{G}^{(2)}(q)$ (2.22),

$$\tilde{f}^{(3)}_{\text{tot}}(p_1 p_2 p_3) = -\sum_{p_4} \tilde{G}^{(3)}_{\text{tot}}(p_1^i p_2^j p_3^k) \prod_{i=1}^3 \tilde{f}^{(2)}_{\text{tot}}(p_i, p_i^l),$$

$$\tilde{f}^{(4)}_{\text{tot}}(p_1 p_2 p_3 p_4) = \sum_{p_5} \tilde{G}^{(4)}_{\text{tot}}(p_1^i p_2^j p_3^k p_4^l) - \sum_{p^m} \tilde{f}^{(2)}_{\text{tot}}(p^m p^m) \times$$

$$\times [\tilde{G}^{(3)}_{\text{tot}}(p_1^i p_2^j p_3^k) \tilde{G}^{(3)}_{\text{tot}}(p_2^j p_3^k p_4^l) + (23) + (24)] \prod_{i=1}^4 \tilde{f}^{(2)}_{\text{tot}}(p_i, p_i^l).$$
Using expression (6.8) we write down the expansion of functional \( \bar{F} \) (6.4) in powers of the functions \( \rho_\alpha \)

\[
\bar{F} \{ n(C), \rho(x) \} - \bar{F} \{ n(C), \rho_\alpha \} = VT \sum_{n=0}^{\infty} \frac{1}{n!} \sum_{p_1 \ldots p_n} \bar{F}_{\text{tot}}^{(n)}(p_1 \ldots p_n) \bar{p}(p_1) \cdots \bar{p}(p_n)
\]

(6.11)

where we have introduced the vertices

\[
\bar{F}_{\text{tot}}^{(n)}(p_1 \ldots p_n) = \bar{F}_{\text{tot}}^{(n)}(p_1) \ldots \bar{p}(p_n) + \bar{C}_{\alpha_1 \ldots \alpha_n}^{(n)} \delta(q_1 + \ldots + q_n),
\]

(6.12)

\[
\bar{C}_{\alpha_1 \ldots \alpha_n}^{(n)} = T^{-1} \partial f^* (\rho_\alpha) / \partial \rho_{\alpha_1} \cdots \partial \rho_{\alpha_n}.
\]

(6.13)

The expressions (6.11)-(6.13) completely define the free energy of the polymer with a given density distribution \( \rho(x) \). It is worth emphasising, that they look just like analogous expressions for monodisperse polymer systems [3], differing only in nonlocal contributions to the functions \( G_{\text{tot}}^{(n)} \) (2.16).

7. Conclusion.

In this study we have proposed for the first time a general approach to the description of solutions, blends and melts of polymers with an arbitrary chemical structure. We have shown that the disorder of this structure leads to the appearance in the free energy functional of nonlocal terms, which can essentially change the phase diagram of polymer systems. The important case of Markovian heteropolymers has been studied in detail and the possibility of formation of spatially-periodic structures by these polymers has been considered. It is shown, that such structures can not be formed in principle in melts and blends of Bernoullian heteropolymers.

In the block-copolymers the spatial period of the structure essentially depends on monomer unit interaction and it can considerably exceed the size of a block. Appearance of such incommensurable superstructures, stipulated by the configuration disorder, is impossible in the case of chemically regular copolymers. Another important difference of actual multi-block heteropolymers from theoretically considered before chemically regular copolymers and block copolymers with the small number of blocks in a macromolecule is the type of their phase transition in the state with periodic structure. While systems, composed by copolymers of the last among mentioned classes undergo the first-order phase transition (altering to the second-order transition when \( \pi_1 = \pi_2 = 1/2 \) [3]), melts or blends of the Markovian copolymers, as we have shown above, undergo the third-order transition even in asymmetrical case \( \pi_1 \neq \pi_2 \).

We have obtained here the explicit expressions (4.2), (6.12) for expansion coefficients of the GL functional of the free energy for polymers with arbitrary chemical structure. In spite of its universal character the GL functional method can be applied for the description of first-order transitions if they are close to the second-order transitions only. The formalism developed in this paper allows us to remove these restrictions since it gives the explicit form of the generating functional (2.9) for many important for practice polymer systems, what seems to be especially prospective for the calculations of their thermodynamic characteristics. The general approach proposed permits us to describe not only heteropolymer systems of linear macromolecules, but branched heteropolymers too. The account of fluctuations of the functions \( v(x) \) (2.4) and \( \rho(x) \) (6.2) enables us in principle to refine the theory proposed by
means of taking into consideration the fluctuation effects in polymer systems with arbitrary molecular structure distribution \{n(C)\}.

Appendix.
Let us calculate the functional defined by the expression
\[
\exp \left[ - \Omega \ast \{ v'(x) \} / T \right] = \langle \delta (u(x) - \exp (-v(x)/T)) \rangle_v,
\]
\[ u(x) = \exp (-v'(x)/T). \quad (A.1) \]

Using the representation of the \( \delta \)-function in the form of the integral over complex field \( z(x) \)
\[
\delta (u(x)) = \int Dz(x) \exp \left[ - \sum_x u(x) z(x) \right] \quad (A.2)
\]

and changing the order of averaging over \( v(x) \) and integration over \( z(x) \), we can rewrite the expression (A.1) in the following way
\[
\int Dz(x) \exp \left[ - \sum_x u(x) z(x) - \Omega \{ z(x) \} / T \right] \quad (A.3)
\]

where we have used the representation of the partition function of the separate units system in the form of the average over random field \( v(x) \)
\[
\exp \left[ - \Omega \{ z(x) \} / T \right] = \left\langle \exp \left[ - \sum_x z(x) \exp (-v(x)/T) \right] \right\rangle_v \quad (A.4)
\]

Restricting ourselves to the case when the separate units system is far from its critical point, we can calculate functional integral (A.3) by the steepest descent method due to the small fluctuations of such system. The substitution of the variable of the integration \( u(x) \) for \( v'(x) \) (A.1) leads to the exclusion of the zeroth Fourier components of the field \( v'(x) \). As the result of these calculations we arrive at the expressions (2.6), (2.7).

References

Proof not corrected by the author.