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Fluctuation effects in the theory of weak supercrystallization in block copolymer systems of complicated chemical structure

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Abstract. — To investigate the influence of fluctuation effects on conditions of microphase separation in two-component incompressible molten block copolymers of complicated chemical structure an alternative and more general formulation of the weak crystallization theory is developed using a new variational principle for the calculation of the free energy. Unlike the Fredrickson-Helfand theory, ours accounts for a given angular dependence of vertex functions more rigorously and enables us to evaluate correlation functions in both disordered and supercrystal states. A comparison of phase diagrams constructed by means of both our and the FH theories is made for the case of star copolymers $(A_n)_k (B_m)_k$. The numerical minimization of free energies corresponding to supercrystal and homogeneous states was carried out with account of exact expressions for higher correlators of these systems calculated by us early. It is shown that both theories are in good agreement within the limit of strong fluctuation effects whereas the FH theory underestimates moderate fluctuation effects in crossover region.

1. Introduction.

The theoretical investigation of microphase separation (formation of domain structure, supercrystallization) in two-component incompressible melts of block copolymers on the basis of detail microscopic consideration within the framework of the so-called weak crystallization theory [1-4] was first done by Leibler [5] in the mean field approximation. Some other results concerning the problem were obtained in this approximation in references [6-12]. Meanwhile the importance of the question about conditions of applicability of the Leibler mean field approximation in block copolymer systems seems very important in view of Brazovskii paper [3] (see also [4]). It was shown that due to interaction of fluctuations the system, instead of undergoing phase transition from the liquid state to a supercrystal one, can stay in metastable state with short-range ordering having anomalously large radius of correlation. One should note that the state cannot be described in the framework of the mean field approximation. It is not clear, however, whether the situation takes place in polymers where the problem is complicated owing to interference of configurational set (set of conformational states most probable under given conditions) of macromolecules and correlation of fluctuations [9]. Apart from this physical difference one encounters two other difficulties in accounting for

fluctuation effects at microphase separation in blockcopolymers. The case is that unlike the situation investigated in reference [3] in polymer systems so-called higher vertex functions (see below) have some angular dependence as well as dependence on order parameter value which may be different in different coexisting phases. Thus, here one cannot use the results of [3, 4] literally.

The first attempt to construct a phase diagram of molten diblock copolymer taking fluctuation effects into account was done by Fredrickson and Helfand in reference [13] (see also Ref. [14]). By means of some witty trick (see below) the problem of describing a real diblock polymer system was reduced in references [13, 14] to the problem of describing a model system similar to both original polymer system and a system studied by Brazovskii. It was shown, as consistent with references [3, 4], that the fluctuation effects can change the phase diagram qualitatively. The result is very important and we justify it in this paper. However, as will be shown below, some basic approximation used in references [13, 14] to implement the aforementioned trick is not applicable in the crossover region of moderate fluctuation effects. In this region the phase diagrams obtained using the approximation may differ considerably from the actual ones. Besides, there are some quantities (say, correlation functions, energy of screened interaction and so on) which cannot be calculated exactly using the method of Brazovskii-Fredrickson-Helfand.

So, to calculate the thermodynamic and correlational characteristics of block copolymer systems of complicated chemical structure we present in this paper a general method allowing for fluctuation effects in both homogeneous and supercrystal states and apply it to consider the influence of these effects on conditions of phase transitions in the systems. In section 2 we present a general consideration of fluctuation effects in polymer systems and derive a new diagram technique which enables us to calculate corresponding corrections to quantities obtained within the framework of mean field approximation. Using the diagram technique we give in section 3 an alternative and more general formulation of Brazovskii's theory on the base of a field-theoretical variational principle, which can be used for a quantitative description of systems with an arbitrary number of components. In section 4 we apply this principle to the most simple case of two-component incompressible molten copolymers. The numerical comparison of phase diagrams obtained in the framework of both the FH theory and ours is presented in section 5 for star copolymers of kind $(A_n B_m)_k$ (the case of $k = 1$ corresponds to ordinary diblock copolymers).

2. Coarse-grained Hamiltonian (density functional) description and diagram technique for calculation of fluctuation effects in polymer systems.

It seems, by analogy with the well known case of the scaling theory of polymer solutions, that the most straightforward way to understand a relation between mean field and fluctuation approximations of weak crystallization theory is to describe free energy of block copolymer systems as a coarse-grained Hamiltonian and then to use well-known field-theoretical method of functional integration followed by applying diagram methods of resumming corresponding perturbative terms. The first version of this approach was given in reference [15] (see also Refs. [16, 17]); ideas, which are similar to ours in many respects, were advanced by many other authors (see Refs. [5, 8, 10, 13, 14, 18]) too. However, it seems useful to give in this section another way to implement the idea which is a development of the approach of reference [15].

So, let us consider a polymer system which is confined in the volume V and has the number N_s of (macro)molecules defined by a certain structural chemical formula s in a volume unit. As was discussed in references [5-14], to describe the system state as a whole one should know, apart from its molecular-structural distribution (MSD) $\{N_s\}$, also a smoothed spatial

distribution of local densities $\{\rho_i(\mathbf{r})\}$, ρ_i being the number of particles of type i in a unit volume. (As particles we shall refer to both links of macromolecules and small molecules of solvent if any, two particles are said to be of the same sort when they are indistinguishable by character of their short-range interaction.) Let the free energy of the system with a given distribution $\{\rho_i(\mathbf{r})\}$ be some functional $F(\{\rho_i(\mathbf{r})\}, \{N_s\}, T)$ which will be further referred to as virtual free energy. Then, as consistent with general principles of statistical physics [19] (see also Refs. [17, 20]), the system will be in a state with given distribution $\{\rho_i(\mathbf{r})\}$ with a probability

$$w(\{\rho_i(\mathbf{r})\}) = \exp(-F(\{\rho_i(\mathbf{r})\}, \{N_s\}, T)/T) / Z(\{N_s\}, T) \quad (1)$$

the normalization constant $Z(\{N_s\}, T)$ being the partition function which can be written as the following functional integral over all distributions $\{\rho_i(\mathbf{r})\}$:

$$Z(\{N_s\}, T) = \int \delta\rho_i(\mathbf{r}) \exp(-F(\{\rho_i(\mathbf{r})\}, \{N_s\}, T)/T). \quad (2)$$

Thus, the total free energy $F(\{N_s\}, T)$ of the system under consideration and any observable quantity a which, evidently, is an average taken with probabilistic measure (1) can be written as follows:

$$F(\{N_s\}, T) = -T \ln Z(\{N_s\}, T) - T \ln \int \delta\rho_i(\mathbf{r}) \exp(-F(\{\rho_i(\mathbf{r})\}, \{N_s\}, T)/T) \quad (3)$$

$$\bar{a} = \frac{\int \delta\rho_i(\mathbf{r}) a(\{\rho_i(\mathbf{r})\}, T) \exp(-F(\{\rho_i(\mathbf{r})\}, \{N_s\}, T)/T)}{\int \delta\rho_i(\mathbf{r}) \exp(-F(\{\rho_i(\mathbf{r})\}, \{N_s\}, T)/T)} \quad (4)$$

Calculating the free energy F by means of deepest descent method within so-called pre-exponential accuracy we arrive at the following well known expression:

$$F(\{N_s\}, T) = \min F(\{\tilde{\rho}_i(\mathbf{r})\}, \{N_s\}, T) \quad (5)$$

which corresponds to conventional mean field approximation, an average (4) acquires the form

$$\bar{a} = a(\{\tilde{\rho}_i(\mathbf{r})\}, T). \quad (6)$$

The designation $\tilde{\rho}_i(\mathbf{r})$ is used for the density distribution at which the virtual free energy $F(\{\rho_i(\mathbf{r})\}, \{N_s\}, T)$ reaches its minimum.

To obtain an explicit expression for quantity F beyond this approximation one should, strictly, define the notion of functional integral (2) more clearly, say, by means of the collective variable method. The problem does not arise, however, in calculating average quantities of type (4). Indeed, let us consider the expansion of the virtual free energy

$$F(\{\rho_i(\mathbf{r})\}, \{N_s\}, T) = F_0(\{\tilde{\rho}_i\}, T) + \sum_{n=2}^{n=4} (\Gamma^{(n)} \Phi^n) / n! \quad (7)$$

near its minimum on powers of fluctuations

$$\Phi_\alpha(\mathbf{r}) = \rho_\alpha(\mathbf{r}) - \tilde{\rho}_\alpha(\mathbf{r}). \tag{8}$$

(Like in Landau theory of second kind phase transitions we keep in (7) only members up to 4th order and use the following notation :

$$(\Gamma^{(n)} \Phi^n) = \sum_{\{\alpha_1, \dots, \alpha_n\}} \int \Gamma_{\alpha_1, \dots, \alpha_n}^{(n)}(\mathbf{x}_1, \dots, \mathbf{x}_n) \prod_{i=1}^n \Phi_{\alpha_i}(\mathbf{x}_i) d\mathbf{x}_i. \tag{9}$$

Here the integration over each of the coordinates \mathbf{x}_i is carried out over all the system volume and the summation is implied over all rearrangements $\{\alpha_1, \dots, \alpha_n\}$ of indices α_i, α_j . The indices encounter values from 1 to m , m being the total number of different types of particles pertaining to the polymer system considered. (For melts of two-component copolymers that will be considered in the paper $m = 2$.) Further we will use the Einstein rule of summation over all repeated indices $\sum_{i=1}^m u_i v_i = u_i v_i$.

Let us substitute the expansion (7) in definition (4) and divide numerator and denominator of the latter by the same quantity

$$Z_0 = \int \delta \Phi_i(\mathbf{r}) \exp(-H_0/T)$$

Here

$$\begin{aligned} H_0 &= \Phi_i(\mathbf{x}_1) (\Gamma_0^{(2)}(|\mathbf{x}_1 - \mathbf{x}_2|))_{ij} \Phi_j(\mathbf{x}_2)/2 \\ &= \int \frac{d\mathbf{q}}{(2\pi)^3} \Phi_i(\mathbf{q}) \Phi_j^*(\mathbf{q}) \Gamma_{ij}^0(q)/2 = (\Gamma_0^{(2)} \Phi^2)/2 \end{aligned}$$

where $\phi_i(\mathbf{q}) = \int d\mathbf{x} \Phi_i(\mathbf{x}) \exp(i\mathbf{q}\mathbf{x})$ and $\Gamma_{ij}^0(q) = \int d\mathbf{x} (\Gamma_0^{(2)}(|\mathbf{x}|))_{ij} \exp(i\mathbf{q}\mathbf{x})$ are corresponding Fourier components and $\Gamma_{ij}^0(q)$ is a symmetric matrix, all eigenvalues of each are positive, choice of the matrix will be made further. (Here and below we introduce a rule of integration over repeated coordinates : $\int d\mathbf{x} A(\mathbf{x}) B(\mathbf{x}) = A(\mathbf{x}) B(\mathbf{x})$, the integral being taken over the whole system volume, which is analogous to the beforementioned Einstein rule of summation over all repeated indices.) Then we obtain

$$\bar{a} = \frac{\int a(\{\Phi_i(\mathbf{r})\}, T) \exp\left(-\sum_{n=2}^{n=4} (\Gamma^{(n)} \Phi^n)/Tn!\right) \prod \delta \Phi_i(\mathbf{r})}{\int \exp\left(-(\Gamma_0^{(2)} \Phi^2)/2 T\right) \prod \delta \Phi_i(\mathbf{r})} \tag{10}$$

$$\frac{\int \exp\left(-\sum_{n=2}^{n=4} (\Gamma^{(n)} \Phi^n)/Tn!\right) \prod \delta \Phi_i(\mathbf{r})}{\int \exp\left(-(\Gamma_0^{(2)} \Phi^2)/2 T\right) \prod \delta \Phi_i(\mathbf{r})}$$

Because of dividing by normalization multiplier Z_0 both the numerator and the denominator of the ratio (10) are quite definite quantities very familiar to the theory of phase transitions

(see Refs. [17, 20]; the denominator, in particular, is just the partition function of a system described by conventional Landau Hamiltonian

$$H = \sum_{n=2}^{n=4} (\Gamma^{(n)} \Phi^n)/n! \quad (11)$$

with a bare matrix propagator (Green function) $g(\mathbf{x}_1, \mathbf{x}_2)$, its components $g_{ij}(\mathbf{x}_1, \mathbf{x}_2) = (g(\mathbf{x}_1, \mathbf{x}_2))_{ij}$ being related to matrix vertex $\Gamma^{(2)}(\mathbf{x}_1, \mathbf{x}_2)$ by means of the following integral equation :

$$g_{ij}(\mathbf{x}_1, \mathbf{x}')(\Gamma_0^{(2)}(\mathbf{x}' - \mathbf{x}_2))_{jk} = \delta_{ik} \delta(\mathbf{x}_1 - \mathbf{x}_2). \quad (12)$$

Note, however, that in the case of ordinary second kind phase transitions higher vertices $\Gamma_{\alpha_1, \dots, \alpha_n}^{(n)}(\mathbf{x}_1, \dots, \mathbf{x}_n)$ ($n = 3, 4$) are local, otherwise they have the form

$$\Gamma_{\alpha_1, \dots, \alpha_n}^{(n)}(\mathbf{x}_1, \dots, \mathbf{x}_n) = \int \prod_{i=1}^{i=n} \delta(\mathbf{x}_i - \mathbf{x}) d\mathbf{x}, \quad (n = 3, 4)$$

whereas in our case they are non-local functions related to the chemical structure of the copolymer systems under investigation by means of some explicit expressions (see Refs. [5-11]).

Let the fluctuations Φ_i be small. Then we can neglect in the Hamiltonian H all terms but first nonvanishing term in powers of Φ_i :

$$H = H_{\text{RPA}} = \Phi_i(\mathbf{x}_1) \Gamma_{ij}^{(2)}(\mathbf{x}_1, \mathbf{x}_2) \Phi_j(\mathbf{x}_2)/2. \quad (13)$$

In the approximation (13), which is just the random phase one, all integrals of type (10) are Gaussian and can be calculated exactly.

The following step is to consider higher terms in Landau Hamiltonian as a perturbation :

$$H = H_{\text{RPA}} + H_{\text{int}}; \quad H_{\text{int}} = (\Gamma^{(3)} \Phi^3)/3! + (\Gamma^{(4)} \Phi^4)/4! \quad (14)$$

Substituting representation (14) into definition (10), expanding on powers of H_{int} integrands of both the numerator and the denominator of the latter and calculating each term of the expansions as a Gaussian integral we obtain an expression for any observable quantity as a sum of an infinite series of corresponding Feynman diagrams. In particular, the denominator of ratio (10) can be represented as follows :

$$Z = \frac{\int \delta \Phi_i(\mathbf{r}) \exp \left(- \sum_{n=2}^{n=4} (\Gamma^{(n)} \Phi^n)/n! \right)}{\int \delta \Phi_i(\mathbf{r}) \exp \left(- (\Gamma_0^{(2)} \Phi^2)/2 T \right)} = \exp VW. \quad (15)$$

To calculate the so-called generating function VW of all connected diagrams S consisting of unlabelled vertices of second, third and fourth orders one should use the following well-known rules (see, for example, Refs. [21-24]) :

1. Let us choose a set of $N_{\alpha_1 \alpha_2}^{(2)}$ vertices of second order, $N_{\alpha_1, \dots, \alpha_3}^{(3)}$ vertices of third order and $N_{\alpha_1, \dots, \alpha_4}^{(4)}$ vertices of fourth order, each vertex of n -th order being represented as a little circle having n shoots, to each of the shoots a coordinate \mathbf{x}_i and a colour α_i being assigned ($i = 1, \dots, n, \alpha_i = 1, \dots, m$), and connect all their shoots in one way or another by solid lines to build a connected graph (diagram).

2. Let us assign a) the function $\Delta \Gamma_{\alpha_1 \alpha_2}(\mathbf{x}_1, \mathbf{x}_2) = (\Gamma_0^{(2)}(|\mathbf{x}_1 - \mathbf{x}_2|))_{\alpha_1 \alpha_2} - \Gamma_{\alpha_1 \alpha_2}^{(2)}(\mathbf{x}_1, \mathbf{x}_2)$ to each vertex of second order (a little circle having 2 shoots with coordinates \mathbf{x}_1 ,

\mathbf{x}_2 and colours α_1, α_2), b) the vertex function $(-\Gamma_{\alpha_1, \dots, \alpha_n}^{(n)}(\mathbf{x}_1, \dots, \mathbf{x}_n))$ to each vertex of n -th order with $n > 2$ and c) the bare Green function $g_{\alpha_i, \alpha_j}(\mathbf{x}_i, \mathbf{y}_j)$ defined by equation (12) to solid line connecting shoots of α_i and α_j colours with coordinates \mathbf{x}_i and \mathbf{y}_j .

3. Now the contribution W of a diagram is an integral, its integrand being the product of all multipliers assigned to vertices and lines of the diagram as stated above, the integral being taken over all coordinates of vertices shoots over all the volume of the system.

4. Having defined in this way rules of diagram technique we can calculate the function VW as the sum of all these contributions divided by symmetry index $r(S)$ of corresponding diagram S :

$$VW = \sum W(\{ \Gamma_{\alpha_1, \dots, \alpha_n}^{(n)}(\mathbf{x}_1, \dots, \mathbf{x}_n) \}, \{ \Delta \Gamma_{\alpha_1 \alpha_2}^{(2)}(\mathbf{x}_1, \mathbf{x}_2) \}, S) / r(S). \quad (16)$$

The sum (16) is to be taken at first over all ways of combination of vertex shoots at a certain set $\{ N_{\alpha_1, \dots, \alpha_n}^{(n)} \}$ and then over all the sets and is, evidently, the sum of an infinite series. So, in order to calculate it explicitly we have, first, to know explicit expressions for all vertex functions $\Gamma_{\alpha_1, \dots, \alpha_n}^{(n)}(\mathbf{x}_1, \dots, \mathbf{x}_n)$ and, second, to decide which diagrams are to be taken into account and which ones can be neglected. Note that it is just the choice of relevant diagrams which distinguishes various approximations.

The first problem is resolved easily for those systems in which distribution of smoothed densities $\{ \tilde{\rho}_i(\mathbf{r}) \}$ differs from spatially homogeneous one only slightly. In considering the systems one should expand the virtual free energy in a power series on deviations of density distribution from the homogeneous state of the system:

$$\Phi_\alpha(\mathbf{r}) = \rho_\alpha(\mathbf{r}) - \bar{\rho}_\alpha(\mathbf{r}), \quad (8a)$$

$\bar{\rho}_\alpha = \int \rho_\alpha(\mathbf{r}) dV$ being a value of corresponding average density. In this case the vertex functions are known to be related to some structural correlators of macromolecules calculated from the assumption that their conformational behaviour is Gaussian (ideal) (for a thorough discussion of the relation and explicit expressions of vertex functions for various block copolymer systems see Refs. [5-11]). The second problem will be addressed to in the next section.

3. Variational principle: a general consideration.

To make another step in accounting for the fluctuation effects let us recalc the definitions of two most important observables: an average order parameter

$$\bar{\Phi}_j(\mathbf{r}) = \langle \Phi_j(\mathbf{r}) \rangle \quad (17)$$

and the correlation function (renormalized Green function)

$$G(\mathbf{r}_1, \mathbf{r}_2) = \| G_{ij}(\mathbf{r}_1, \mathbf{r}_2) \| = \| \langle \Phi_k(\mathbf{r}_1) \Phi_l(\mathbf{r}_2) \rangle - \langle \Phi_k(\mathbf{r}_1) \rangle \langle \Phi_l(\mathbf{r}_2) \rangle \| . \quad (18)$$

Brackets $\langle \rangle$ denote averaging over all possible distributions of $\Phi(\mathbf{x})$:

$$\langle a(\{ \Phi_l(\mathbf{r}) \}) \rangle = \frac{\int a(\{ \Phi_l(\mathbf{r}) \}) \exp \left(- \sum_{n=2}^{n=4} (\Gamma^{(n)} \Phi^n) / Tn! \right) \prod \delta \Phi_i(\mathbf{r})}{\int \exp \left(- \sum_{n=2}^{n=4} (\Gamma^{(n)} \Phi^n) / Tn! \right) \prod \delta \Phi_i(\mathbf{r})} \quad (19)$$

Now, to calculate these observables let us consider the auxiliary quantity $\Delta F(\{\Gamma^{(n)}\}, \{h(\mathbf{r})\})$ defined as follows :

$$\exp - \{ \Delta F(\{\Gamma^{(n)}\}, \{h(\mathbf{r})\})/T \} = \frac{\int \exp - \left\{ \left(h, \Phi \right) + \sum_{n=2}^{n=4} (\Gamma^{(n)} \Phi^n)/n! \right\} / T \prod \delta \Phi_i(\mathbf{r})}{\int \exp(-(\Gamma_0^{(2)} \Phi^2)/2 T) \prod \delta \Phi_i(\mathbf{r})} \quad (20)$$

Taking corresponding variational (functional) derivatives of the quantity having an obvious meaning of free energy of the investigated system as affected of some external field $h(\mathbf{r})$ one can easily make sure that the following equalities are valid :

$$(\delta/\delta h(\mathbf{r})) \Delta F = \bar{\Phi}_i(\mathbf{r}); \quad (21)$$

$$(\delta/\delta (\Gamma^{(2)}(\mathbf{r}_1, \mathbf{r}_2))_{kl}) \Delta F = - \langle \bar{\Phi}_k(\mathbf{r}_1) \bar{\Phi}_l(\mathbf{r}_2) \rangle / 2 = - \{ \bar{\Phi}_k(\mathbf{r}_1) \bar{\Phi}_l(\mathbf{r}_2) + G_{kl}(\mathbf{r}_1, \mathbf{r}_2) \} / 2; \quad (22)$$

On the other hand the quantity $W = -\Delta F/T$ has the meaning of a generating function of all connected diagrams calculated using rules similar to those defined above when introducing the functional (16). The only difference is that now diagrams having some free shoots (otherwise, first order vertices) are allowed, the multiplier $(-h_\alpha(\mathbf{r})/T)$ being assigned to a free shoot having a coordinate \mathbf{r} and a colour α . Considering corresponding diagrams one can obtain the following equalities :

$$\bar{\Phi}_i(\mathbf{r}) = (G^{\text{RPA}}(\mathbf{r}, \mathbf{r}'))_{ij} \{ (\delta/\delta \bar{\Phi}_i(\mathbf{r}')) \sigma - h(\mathbf{r}')/T \}; \quad (23)$$

$$(G^{-1}(\mathbf{r}_1, \mathbf{r}_2))_{ij} = (\Gamma^{(2)}(\mathbf{r}_1, \mathbf{r}_2))_{ij} - 2(\delta/\delta G_{ij}(\mathbf{r}_1, \mathbf{r}_2)) \sigma. \quad (24)$$

Here $G^{\text{RPA}}(\mathbf{r}, \mathbf{r}')$ is calculated in the framework of random phase approximation matrix Green function which is related to second order vertex function as follows (see Refs. [20-22]) :

$$(G^{\text{RPA}}(\mathbf{x}_1, \mathbf{x}'))_{ij} (\Gamma^{(2)}(\mathbf{x}' - \mathbf{x}_2))_{jk} = \delta_{ik} \delta(\mathbf{x}_1 - \mathbf{x}_2). \quad (25)$$

The functional

$$\sigma(\{ \Phi_\ell(\mathbf{r}) \}, \{ G(\mathbf{x}_1, \mathbf{x}_2) \}) = \sum W(\{ \Phi_\ell(\mathbf{r}) \}, \{ \Gamma_{\alpha, \dots}^{(n)}(\mathbf{x}_1, \dots, \mathbf{x}_n) \}, \{ G(\mathbf{x}_1, \mathbf{x}_2) \}, S)/r(S) \quad (26)$$

is calculated using rules similar to those defined above when introducing the functional (16) but with the following differences :

1. The sum appearing in the definition (26) is to be taken over all the so-called 2-irreducible diagrams (see Fig. 1). (Remember that a diagram is referred to as n -irreducible provided that it contains no those parts that can be separated from the rest of the diagram by means of removing no more than n solid lines.) Vertices having free shoots (i.e. unconnected with any other ones) are allowed.

2. To the solid line connecting shoots of α_i and α_j colours with coordinates \mathbf{x}_i and \mathbf{y}_j one should assign the full (renormalized) Green function $G_{\alpha_i, \alpha_j}(\mathbf{x}_i, \mathbf{y}_j)$ defined by equation

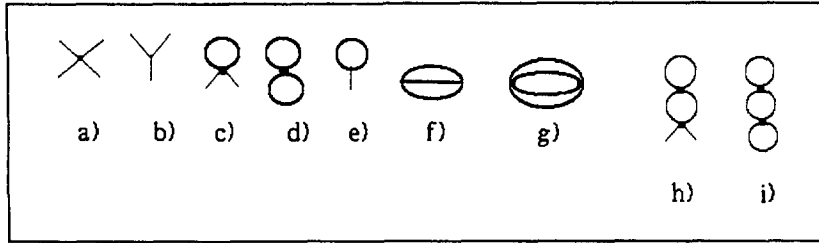


Fig. 1. — Typical diagrams appearing in perturbative approach : a) and b) vertices of fourth and third order, c)-e) the only diagrams to be accounted for in Brazovskii's approximation, f) and g) first order diagrams to be accounted for in the regime of very strong fluctuations beyond Brazovskii's approximation. Diagrams a)-g) are 2-irreducible ones, 2-reducible diagrams h) and i) are typical addenda contributing to c) and d) respectively, bold lines corresponding to full (renormalized) propagator G and solid lines corresponding to the bare propagator g .

(18) instead of bare Green function $g_{\alpha, \alpha}(\mathbf{x}_i, \mathbf{y}_j)$ defined by equation (12); the function $\bar{\Phi}_j(\mathbf{x})$ is assigned to a free shoot of j -th colour with coordinate \mathbf{x} .

Note that equation (24) is obtained from the well known Dyson equation

$$(G(\mathbf{x}_1, \mathbf{x}'))_{ij} \{ (\Gamma^{(2)}(\mathbf{x}' - \mathbf{x}_2))_{jk} - \Sigma_{jk}(\mathbf{x}', \mathbf{x}_2) \} = \delta_{ik} \delta(\mathbf{x}_1 - \mathbf{x}_2) \tag{27}$$

using the following relation between the functional (26) and the so-called mass operator $\Sigma_{jk}(\mathbf{x}, \mathbf{y})$ which is the sum of contributions of all 2-irreducible diagrams having exactly two free shoots and calculated as consistent with rules of calculation of the functional (16) :

$$\Sigma_{ij}(\mathbf{r}_1, \mathbf{r}_2) = 2(\delta/\delta G_{ij}(\mathbf{r}_1, \mathbf{r}_2)) \sigma \tag{28}$$

equations (23, 28) being obtained using diagram methods similar to those derived in the theory of simple fluids (see Refs. [19, 23]). Its derivation is omitted here for the sake of brevity.

Now we can obtain an expression for the change of the free energy of the system under consideration (when its « bare » parameters h and $\Gamma^{(2)}$ are changed) by means of the following straightforward integration along a path in the corresponding Hilbert space from a point $(h_0, \Gamma_0^{(2)})$ to a point $(h_1, \Gamma_1^{(2)})$:

$$\begin{aligned} \Delta F(h_1, \Gamma_1^{(2)}) - \Delta F(h_0, \Gamma_0^{(2)}) = \\ = \int \{ \delta h_i(\mathbf{r}) \delta \Delta F / \delta h_i(\mathbf{r}) + \delta (\Gamma^{(2)}(\mathbf{r}_1, \mathbf{r}_2))_{kl} \delta \Delta F / \delta (\Gamma^{(2)}(\mathbf{r}_1, \mathbf{r}_2))_{kl} \} . \end{aligned} \tag{29}$$

Let us substitute in the r.h.s. of equation (29) for functional derivatives of ΔF their values obtained from equations (23, 24) and integrate the equation by parts. Then, assuming that in the initial state the external field is absent ($h_0 = 0$) we arrive at the following expression :

$$\begin{aligned} \Delta F / \dot{T} = \int \{ (\Gamma_{ij}^{(2)}(\mathbf{x}_1 - \mathbf{x}_2) - G_{ij}^{-1}(\mathbf{x}_1, \mathbf{x}_2)) G_{ji}(\mathbf{x}_1, \mathbf{x}_2) - \\ - Sp(\ln G(\mathbf{x}_1, \mathbf{x}_2) - \ln g(\mathbf{x}_1, \mathbf{x}_2)) \} d\mathbf{x}_1 d\mathbf{x}_2 / 2 - \sigma(\{ \bar{\Phi}_l(\mathbf{r}) \}, \{ G(\mathbf{x}_1, \mathbf{x}_2) \}) \\ + \int \bar{\Phi}_i(\mathbf{x}_1) \Gamma_{ij}^{(2)}(\mathbf{x}_1 - \mathbf{x}_2) \bar{\Phi}_j(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 / 2 - \int h_l(\mathbf{x}) \bar{\Phi}_l(\mathbf{x}) d\mathbf{x} \end{aligned} \tag{30}$$

where $\{\bar{\Phi}_\ell(\mathbf{r})\}$ and $G(\mathbf{x}_1, \mathbf{x}_2)$ must satisfy equations (23, 24). (The spur of matrix-function $\text{Ln } G(\mathbf{x}_1, \mathbf{x}_2)$ is calculated in the Appendix). On the other hand, equations (23, 24) are just extremal equations describing the conditions under which the functional 30 takes its minimal (generally speaking, extremal) value. Otherwise,

$$\Delta F = -T \max W(\{\bar{\Phi}_\ell(\mathbf{r})\}, \{G(\mathbf{x}_1, \mathbf{x}_2)\}, \{h_\ell(\mathbf{r})\}, \{\Gamma^{(2)}(\mathbf{x}_1, \mathbf{x}_2)\}) \quad (31)$$

where $-W$ is the functional written at the r.h.s. of equality (30) and the minimum is to be sought with respect to functions $G_{ij}(\mathbf{x}_1, \mathbf{x}_2)$ and $\bar{\Phi}_\ell(\mathbf{r})$ considered as independent variables at fixed h and $\Gamma^{(2)}$. So, to evaluate free energy one can choose a certain set of relevant diagrams in (30) and calculate the corresponding contributions using for $\bar{\Phi}_\ell(\mathbf{r})$ and $G_{ij}(\mathbf{x}_1, \mathbf{x}_2)$ some trial functions $\Phi_{ij}^t(\mathbf{r})$ and $G_{ij}^t(\mathbf{x}_1, \mathbf{x}_2)$ which depend on some parameters a_i . In minimizing obtained in this way function $\Delta F(\{a_i\})$ with respect to parameters a_i , we arrive at the best (on this class of trial functions) estimate of the free energy.

Note that the idea of presented derivation of the variational principle (31) is essentially the same as the original one of reference [3] with exception that we included additional peculiar order parameter $G_{ij}(\mathbf{x}_1, \mathbf{x}_2)$ (apart from the usual one $\bar{\Phi}_\ell(\mathbf{r})$). However, as will be shown in the next section, our variational principle (31) is much more convenient than the original one of references [3, 4] in order to treat systems with strong angular dependence of higher vertex functions (otherwise, the systems in which Fourier components

$$\Gamma_{a_1, \dots, a_n}^{(n)}(\mathbf{q}_1, \dots, \mathbf{q}_n) = \int \Gamma_{a_1, \dots, a_n}^{(n)}(\mathbf{x}_1, \dots, \mathbf{x}_n) \prod_{i=1}^{i=n} \exp(i\mathbf{q}_i \cdot \mathbf{x}_i) d\mathbf{x}_i$$

are dependent essentially on angles between momenta \mathbf{q}_i). Besides, minimization of the functional (30) gives the absolute value of fluctuation contribution to free energy of a considered phase, whereas variational principle of reference [3] (see also Refs. [4, 13, 14]) enables us to obtain only the difference of free energies of coexisting phases provided that the vertex functions in the phases are the same. The property of the functional (30) will be of great advantage in calculating phase diagrams of three and more component block copolymer and polyelectrolyte systems (see Ref. [25]).

4. Variational principle and modified Brazovskii approximation for two-component molten blockcopolymers.

Now, for the sake of simplicity we will show in this paper how the variational principle (31) works for the case of molten block copolymers consisting of two sorts monomers in the incompressibility limit

$$v(\rho_1(\mathbf{r}) + \rho_2(\mathbf{r})) = 1, \quad (32)$$

v being an excluded volume which is assumed to be the same for monomers of both sorts. The advantage of this case is that now all arguments of the functional σ are scalar functions instead of vector and tensor ones. For example,

$$\begin{aligned} \Phi_1(\mathbf{x}) &= v(\rho_1(\mathbf{r}) - \bar{\rho}_1) = \phi(\mathbf{x}); \\ \Phi_2(\mathbf{x}) &= v(\rho_2(\mathbf{r}) - \bar{\rho}_2) = -\phi(\mathbf{x}). \end{aligned} \quad (33)$$

Besides, it is convenient to take as the bare propagator the correlation function

$G_0(q)$ of athermal molten block copolymer system having the same chemical structure as the one considered :

$$G_0(q) = \int d\mathbf{x} g(|\mathbf{x} - \mathbf{x}'|) \exp(i\mathbf{q}\mathbf{x}) = (\Gamma_0^{(2)}(q))^{-1} \quad (34)$$

$$\Gamma_0^{(2)}(q) = \int d\mathbf{x} \Gamma_0^{(2)}(\mathbf{x}' - \mathbf{x}) \exp(i\mathbf{q}\mathbf{x}) = \frac{g_{11}(q) + g_{22}(q) + 2g_{12}(q)}{g_{11}(q)g_{22}(q) - g_{12}^2(q)}$$

Explicit expressions for structural correlators $g_{ij}(q)$ for various systems were derived early by many authors (see Refs. [5-11]). For the sake of brevity we shall not write them here as well as explicit expressions for higher vertex functions of these systems given in references [1, 7]. Note only that consistently with references [5, 6, 26, 27]

$$\Gamma^{(2)}(q) = \Gamma_0^{(2)}(q) - 2\chi \quad (35)$$

χ being the conventional Flory parameter (see Refs. [26, 27]).

Now the partition function and the free energy of the system considered can be written as follows :

$$Z = Z_0 \frac{\int \delta\phi(\mathbf{r}) \exp\left(-\sum_{n=2}^{n=4} (\Gamma^{(n)} \phi^n)/Tn!\right)}{\int \delta\phi(\mathbf{r}) \exp(-(\Gamma_0^{(2)} \phi^2)/2T)} = \exp\left(-\frac{F_0 + \Delta F}{T}\right) \quad (15a)$$

$$\begin{aligned} \Delta F/T = \min \left\{ \int (\{\Gamma^{(2)}(\mathbf{x}_1 - \mathbf{x}_2) - G^{-1}(\mathbf{x}_1, \mathbf{x}_2)\} G(\mathbf{x}_1, \mathbf{x}_2) - \right. \\ \left. - \{\ln G(\mathbf{x}_1, \mathbf{x}_2) - \ln g(\mathbf{x}_1, \mathbf{x}_2)\}) d\mathbf{x}_1 d\mathbf{x}_2/2 - \sigma(\{\phi(\mathbf{r})\}, \{G(\mathbf{x}_1, \mathbf{x}_2)\}) \right. \\ \left. + \int \phi(\mathbf{x}_1) \Gamma^{(2)}(\mathbf{x}_1 - \mathbf{x}_2) \phi(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2/2 \right\} \quad (36) \end{aligned}$$

where

$$\begin{aligned} \sigma(\{\phi(\mathbf{x})\}, \{G(\mathbf{x}_1, \mathbf{x}_2)\}) = - \int \Gamma^{(4)}(\mathbf{x}_1, \dots, \mathbf{x}_4) \left(\prod_{i=1}^{i=4} \phi(\mathbf{x}_i) d\mathbf{x}_i \right) /4! - \\ - \int \Gamma^{(3)}(\mathbf{x}_1, \dots, \mathbf{x}_3) \left(\prod_{i=1}^{i=3} \phi(\mathbf{x}_i) d\mathbf{x}_i \right) /3! \\ - \int \Gamma^{(4)}(\mathbf{x}_1, \dots, \mathbf{x}_4) G(\mathbf{x}_1 - \mathbf{x}_2) \phi(\mathbf{x}_3) \phi(\mathbf{x}_4) \left(\prod_{i=1}^{i=4} d\mathbf{x}_i \right) /4 \\ - \int \Gamma^{(4)}(\mathbf{x}_1, \dots, \mathbf{x}_4) G(\mathbf{x}_1 - \mathbf{x}_2) G(\mathbf{x}_3 - \mathbf{x}_4) \left(\prod_{i=1}^{i=4} d\mathbf{x}_i \right) /8. \quad (37) \end{aligned}$$

Here the terms on the r.h.s. correspond to diagrams *a*, *b*, *c* and *d* of figure 1 respectively. The contribution of the diagram 1 *e* is proportional to $\int \phi(\mathbf{x}) d\mathbf{x}$ which is the change of the average concentration of the system under microphase separation (see the definition (33)). Because of the incompressibility condition the change is equal to zero for monodisperse block

copolymer considered further. (However, it is not the case for many component and/or polydisperse systems like those considered in Ref. [6] where micro- and macrophase separation can proceed simultaneously.) Other diagrams are neglected here consistently with approximation of references [3, 4]. In order to write out the conditions of validity of the latter let us use the following considerations.

For many two-component block copolymer systems $\Gamma_0^{(2)}(\mathbf{q})$ has a minimum at a certain value of modulus \mathbf{q} equal to q_0 , the region of stability of the system with respect to infinitesimal spatial fluctuations of the order parameter $\phi(\mathbf{x})$ being limited by a spinodal defined as follows (see Refs. [5, 6, 26, 27]):

$$\tau = \Gamma^{(2)}(q_0) = \Gamma_0^{(2)}(q_0) - 2\chi = 2(\chi_c - \chi) = 0; \quad (38)$$

(Following Eq. (38) the quantity τ can be considered as an effective temperature characterizing the proximity to phase transition point.) So, the fluctuations having wave vectors q_0 should be the largest near the spinodal. Therefore, minimizing (36) one can use the following trial function for $\phi(\mathbf{x})$:

$$\phi(\mathbf{x}) = \sum_{|\mathbf{q}_i| = q_0} A_i \exp i\mathbf{q}_i \cdot \mathbf{x}/n^{1/2} \quad (39)$$

where the sum is carried out over all those vectors \mathbf{q}_i of an inverse lattice conjugated to some Bravais lattice which have the same modulus $|\mathbf{q}| = q_0$, n being the number of different vectors \mathbf{q}_i .

Furthermore consistently with reference [3] we will suppose that fluctuation effects result in renormalizing the effective temperature value only and do not influence the value of critical wave vector q_0 . (Actually, one should take into account fluctuation renormalizing of q_0 beyond the scope of Brazovskii's approximation.) It follows that a suitable trial function for renormalized propagator can be written as follows:

$$G^{-1}(\mathbf{q}) = C(|\mathbf{q}| - q_0)^2 + r \quad (40)$$

the constant C being defined as follows:

$$C = \partial^2 \Gamma_0^{(2)}(q_0) / \partial q^2 |_{q=q_0} / 2.$$

(The approximation (40) is correct provided that the condition $r/q_0^2 C \ll 1$ is valid.) Now, substituting the trial function (40) for renormalized propagator in the functional (36) and using Fourier transformation in calculations of corresponding integrals one can easily notice that the moduli of all relevant vectors \mathbf{q} of Fourier space are close to q_0 . So, it is convenient to adopt Leibler's, notation for the Fourier transformation of higher vertex functions:

$$\begin{aligned} \Gamma^{(4)}(\mathbf{q}_1, \dots, \mathbf{q}_4) &= \int \Gamma^{(4)}(\mathbf{x}_1, \dots, \mathbf{x}_n) \prod_{n=1}^{n=4} \exp(iq_0 \mathbf{e}_n \cdot \mathbf{x}_n) d\mathbf{x}_n \\ &= \gamma^{(4)}(h_1, h_2) \delta(\mathbf{e}_1 + \mathbf{e}_2 + \mathbf{e}_3 + \mathbf{e}_4), \end{aligned}$$

$$\begin{aligned} \Gamma^{(3)}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) &= \int \Gamma^{(3)}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) \prod_{n=1}^{n=3} \exp(iq_0 \mathbf{e}_n \cdot \mathbf{x}_n) d\mathbf{x}_n \\ &= \gamma^{(3)}(1) \delta(\mathbf{e}_1 + \mathbf{e}_2 + \mathbf{e}_3) \end{aligned}$$

where $h_1 = (\mathbf{e}_1 + \mathbf{e}_2)^2$, $h_2 = (\mathbf{e}_1 + \mathbf{e}_4)^2$ and $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3, \mathbf{e}_4$ are some unit vectors.

Now we can evaluate perturbation parameters of the series (37) generated by the functional integral (15a). To this end one should compare with each other contributions of diagrams retained in the series and omitted ones. To facilitate this task let us reduce it first to proper dimensionless variables taking into account that vertex functions $\Gamma_{\alpha_1, \dots, \alpha_n}^{(n)}(\mathbf{q}_1, \dots, \mathbf{q}_n)$ occurring in expansion (7) have the following form in the case of monodisperse molten copolymers (see Refs. [5, 7]):

$$\Gamma_{\alpha_1, \dots, \alpha_n}^{(n)}(\mathbf{q}_1, \dots, \mathbf{q}_n) = \rho^{1-n} \tilde{\Gamma}_{\alpha_1, \dots, \alpha_n}^{(n)}(\mathbf{p}_1, \dots, \mathbf{p}_n)/N.$$

Here $\rho = \bar{\rho}_1 + \bar{\rho}_2 = v^{-1}$ is the total monomer density of incompressible molten copolymer having degree of polymerization N and $\mathbf{p} = \mathbf{q}/q_0$ is a dimensionless coordinate of Fourier space. The quantity q_0 defined above has a value of the order of the gyration radius $(\alpha^2 N/6)^{1/2}$ of corresponding one-chain copolymer macromolecule:

$$q_0^2 = x^2/N a^2$$

both values of x and $\tilde{\Gamma}_{\alpha_1, \dots, \alpha_n}^{(n)}(\mathbf{p}_1, \dots, \mathbf{p}_n)$ being of order of unity and depending on the actual copolymer structure. Reducing to desired dimensionless variables is executed by means of the following substitution:

$$\begin{aligned} \mathbf{q} &= \mathbf{p} q_0, \quad \Phi^2(\mathbf{p}) = (v q_0^3/N) \phi^2(\mathbf{q}), \quad \tilde{\tau} = N(\chi_c - \chi), \quad z = v/a^3 N^{1/2}, \\ \tilde{\gamma} &= \tilde{\Gamma}_{\alpha_1, \dots, \alpha_3}^{(3)}(\mathbf{p}_1, \dots, \mathbf{p}_3)(x^3 z)^{1/2}, \quad \tilde{\lambda} = \tilde{\Gamma}_{\alpha_1, \dots, \alpha_4}^{(4)}(\mathbf{p}_1, \dots, \mathbf{p}_4)(x^3 z). \end{aligned}$$

One can write the following expressions for whole (including symmetry multipliers) contributions of some of diagrams which are generated by reduced in this way functional integral (15a) and shown in figure 1:

$$\begin{aligned} W_c &= \xi x^3 z / 8 (4 \pi)^2 r C; \quad W_g = (\lambda x^3 z)^2 / 48 (4 \pi)^3 (r C)^2, \\ \lambda^2 &= \int_0^4 \int_0^4 \int_0^4 (\Gamma^{(4)}(h_1, h_2))^2 \delta(h_1 + h_2 + h_3 - 4) dh_1 dh_2 dh_3 / (h_1 h_2 h_3)^{1/2}, \\ W_f &= (\gamma^{(3)}(1))^2 x^3 z / 12 \pi (64 r C)^{3/2} \end{aligned}$$

Thus, the conditions of validity of the approximation chosen here are the following:

$$\begin{aligned} W_f/W_c &= (\gamma^{(3)}(1))^2 \pi / 48 \xi (r C)^{1/2} \ll 1, \\ W_g/W_c &= \lambda^2 (x^3 z) / 24 \pi \xi (r C) \ll 1. \end{aligned}$$

At last, taking into account that fluctuation corrections are essential provided that the following condition holds:

$$\xi (x^3 z) / 2 \pi (r C)^{3/2} \geq 1$$

we finally get the conditions defining the region of applicability of the Brazovskii approximation in our case:

$$\max \{ \lambda^2 (x^3 z) / 24 \pi \xi, (\gamma^{(3)}(1))^4 (\pi / 48 \xi)^2 \} \ll r C \leq (\xi (x^3 z) / 2 \pi)^{2/3} \quad (41)$$

which hold when

$$((v/a^3) N^{-1/2})^{1/3} \ll 12 (2 \pi \xi^5)^{1/3} / x \lambda^2 \quad (42)$$

One can show from direct calculations that $\gamma^{(3)}(1)$ is equal to zero in incompressible star blockcopolymers $(A_n)_k (B_m)_k$ investigated below when $n/N = m/N = 0.5$. In particular in the vicinity of this point $|n/N - 0.5| \leq 0.3$ the parameter $(\gamma^{(3)}(1))^2 (\pi/48 \xi)$ is small and we can neglect the contribution from diagram in figure 1f to the free energy.

Now let us return to the calculation of the free energy (36) assuming that conditions (41), (42) are fulfilled. Calculating the integrals involved in the definition (37) and minimizing free energy (36) with respect to parameters A_i at given value of r one can make sure (see Refs. [4, 5]) that all these quantities have the same modulus $|A_i| = A$. The quantity A as well as parameter r are determined as the roots of the following system of equations :

$$\partial \Delta F_n(A, r)/\partial A = \partial \Delta F_n(A, r)/\partial r = 0 \quad (43)$$

$$\begin{aligned} \Delta F_n(A, r)/V = & 1/2 sr^{1/2} + 1/2 s\tau/r^{1/2} + \beta_n A^4 - \alpha_n A^3 + \\ & + 1/2 s\xi A^2/r^{1/2} + 1/8 s^2 \xi/r + \tau A^2 \end{aligned} \quad (44)$$

Otherwise, equations (43) define the point of an extremum (for stable equilibrium states the extremum is a minimum) of free energy (44) as a function of parameters A and r . The following designations were introduced : $\xi = \int_0^4 \gamma^{(4)}(h, 0) dh/4$, $s = q_0^2/(2 \pi C^{1/2})$, where functions α_n and β_n depend on the sort of supercrystal lattice and are related to vertex function as follows (see Ref. [5]) :

$$\left. \begin{aligned} & \text{for lamellar structure } \alpha_1 = 0, \beta_1 = \gamma^{(4)}(0, 0)/4; \\ & \text{for triangular structure} \\ & \alpha_3 = 2/3^{3/2} \gamma^{(3)}(1), \quad 12 \beta_3 = \gamma^{(4)}(0, 0) + 4 \gamma^{(4)}(0, 1); \\ & \text{for body cubic center structure} \\ & \alpha_6 = (2/3)^{3/2} \gamma^{(3)}(1), \\ & 24 \beta_6 = \gamma^{(4)}(0, 0) + 8 \gamma^{(4)}(0, 1) + 2 \gamma^{(4)}(0, 2) + 4 \gamma^{(4)}(1, 2). \end{aligned} \right\} \quad (45)$$

The terms in expression (44) correspond to those of expression (36) in the same succession except for the first two terms corresponding to the first three terms of expression (36).

In order to determine the equilibrium values r and A as functions of both τ and sort of supercrystals lattice, one should minimize ΔF_n with respect to A and r . Extremal equations (43) can be written in the chosen approximation as follows :

$$r - \tau - s\xi/2 r^{1/2} - \xi A^2 = 0; \quad (43a)$$

$$A(s\xi/r^{1/2} + 2\tau - 3\alpha_n A + 4\beta_n A^2) = 0; \quad (43b)$$

The root $A = 0$ of equation (43b) corresponds, evidently, to homogeneous (« liquid ») state. Substituting it in equation (43a) one can determine r as an implicit function of τ :

$$r - s\xi/2 r^{1/2} = \tau. \quad (46)$$

Equation (46) has exactly one root for any value of τ ($-\infty < \tau < \infty$), the value of r tends to 0 when the value of τ tends to $-\infty$. It means that within the framework of the approximation adopted the homogeneous state stays stable as to infinitesimal fluctuations of the order parameter $\Phi(r)$ at any limited value of effective temperature τ .

Considering the inhomogeneous (supercrystalline) states one should solve the following system :

$$\begin{aligned} r - \tau - s\xi/2 r^{1/2} - \xi A^2 &= 0 \\ s\xi/r^{1/2} + 2\tau - 3\alpha_n A + 4\beta_n A^2 &= 0. \end{aligned} \quad (47)$$

Thus, substituting into (44) the solution of equation (46) or system (47) for different sorts of supercrystal lattice, we can determine the fluctuation correction to free energy ΔF_n as function of τ and sort of supercrystal lattice. Note, by the way, that using the substitution for the case of local higher vertices one can show that our expression (44) gives the differences between free energies of different (both disordered and ordered) phases which are just corresponding expressions of reference (3). The diagram shown in figure 1d determines the fluctuation correction to the free energy of the disordered state at given τ . Besides, the value of r obtained in this way enables us to find the best approximation of kind (40) for the correlation function. (It is useful to make this point clear. The Dyson equation allowing for higher vertices' angle dependence was presented early in reference [4]. One can arrive at the equation minimizing the free energy (36) with respect to trial functions $G^{-1}(\mathbf{q}) = (q - q_0)^2 + r(\mathbf{h})$, $\mathbf{h} = \mathbf{q}/q$.) However, this equation can hardly be solved. On the contrary, our choice of trial functions in the form (40) is more crude but more effective for arbitrary higher vertices' angle dependence.) So, we get a quantitative description of scattering phenomena in supercrystal phases.

It is worth noting that another advantage of our approach is the ability to evaluate the correlation functions of supercrystal states in the random phase approximation. Indeed, the latter corresponds to the limit $s\xi/r^{3/2} \Rightarrow 0$ in which fluctuation corrections are negligible. So, one can get a system to be solved to find value of r in the approximation omitting in (47) members with $s\xi/r^{1/2}$.

$$2\tau - 3\alpha_n A + 4\beta_n A^2 = 0 \quad (48a)$$

$$r - \tau - \xi A^2 = 0. \quad (48b)$$

The first of these simultaneous equations enables us to obtain the value of an order parameter in the RPA and was presented earlier in references [2, 5]. Equation (48b) defines correlation radius in supercrystal phases in the RPA and seems to be new. (Note, that it is impossible to obtain any approximate expression for RPA supercrystal states correlation functions within the framework of this approximation because of the fact that the last term in equation (48b) arises from the diagram 1c.) Solving equations (48) we get

$$A = \{3\alpha_n + (9\alpha_n^2 - 32\tau\beta_n)^{1/2}\} / 8\beta_n; \quad (49)$$

$$r = \tau(1 - C_n) + 3\alpha_n C_n A/2$$

$C_n = \xi/2\beta_n$ being parameter independent of τ characterizing the structure of the system under investigation.

Because of the incompressibility condition the mean density of a molten two-component heteropolymer remains the same both in homogeneous state (1) and in all supercrystal states (m). Therefore condition

$$\Delta F_1 = \Delta F_m \quad (50)$$

defines the line (surface) of coexistence of these phases and condition

$$\Delta F_{m_1} = \Delta F_{m_2} \quad (51)$$

defines the line (surface) of two supercrystal phases (m_1 and m_2) coexistence. Using this procedure, phase diagrams for different copolymer systems were constructed in references [5, 11, 12].

5. Comparison with Fredrickson-Helfand theory.

To compare our results with corresponding ones of reference [13] we carry out the numerical solution of equations (50) and (51) for incompressible molten star copolymers of kind $(A_n)_k (B_m)_k$. Macromolecules of this kind can be obtained (at least viewed) by means of crosslinking k joints of diblock copolymer chains $A_n B_m$ consisting of $N = n + m$ monomers. So, numbers k and N as well as volume fraction $\phi = n/N$ can be taken as parameters characterizing the chemical structure of these systems. Besides, there exists a parameter $z = (v/a^3) N^{-1/2}$ which describes a level of fluctuation effects (see Ref. [13]). For real polymer systems the value of the parameter z does not exceed 0.1 and decreases when N increases.

We choose these systems for the following reasons. In the case of $k = 1$ the system is just molten diblock copolymer which was well studied both in random phase approximation in reference [5] and in approximation of reference [3] by Fredrickson and Helfand (FH) in reference [13]. Remember that the trick of reference [13] mentioned in Introduction is the following. Noting that for molten diblock copolymers higher vertices depend both on angles between vectors \mathbf{q}_i and on concentration ϕ , Fredrickson and Helfand (FH) assumed that to construct phase diagram of the system on a plane $(\tau - \phi)$ it is sufficient to let

$$\gamma^{(4)}(h_1, h_2) \equiv \gamma^{(4)}(0, 0) \quad (52)$$

taking into account the ϕ -dependence of $\gamma^{(4)}(0, 0)$ and $\gamma^{(3)}(1)$ exactly as is consistent with the calculations of reference [1]. Otherwise, in the approximation 52 values of coefficients (43) and ξ can be written as follows:

$$\left. \begin{aligned} \xi &= \gamma^{(4)}(0, 0); \\ \text{for lamellar structure } \alpha_1 &= 0, \beta_1 = \gamma^{(4)}(0, 0)/4; \\ \text{for triangular structure} \\ \alpha_3 &= 2/3^{3/2} \gamma^{(3)}(1), \quad 12 \beta_3 = 5 \gamma^{(4)}(0, 0); \\ \text{for body cubic center structure} \\ \alpha_6 &= (2/3)^{3/2} \gamma^{(3)}(1), \quad 24 \beta_6 = 15 \gamma^{(4)}(0, 0). \end{aligned} \right\} \quad (53)$$

(Note, by the way, that in the case of approximation 52 the coefficient C_n , which determines phase stability in random phase approximation as consistent with equation (49), takes the values of 2, 6/5 and 4/5 in the cases of lamellar, triangular and b.c.c. lattices, respectively. Only the last of them is less than unity. It follows that in the region of $-\tau \gg 1$ (or provided $\alpha_n \Rightarrow 0$) the values of both r_1 and r_3 are positive unlike negative here value of r_6 . It seems that it is this fact that explains the well known instability of b.c.c. phase in these circumstances.)

On the other hand, it is these systems that were shown in reference [12c] to reveal a strong angular dependence of high vertices which results in tricritical-like behaviour of lamellar phase in the case of $k > 5$. (More exactly, in this case the approximation (52) becomes nonvalid and the value of the coefficient β_1 occurring in expression (44) for the free energy ΔF_n becomes negative whereas β_3 and β_6 stay positive.)

The phase diagrams for incompressible molten star copolymers of kind $(A_n)_k (B_m)_k$ with different values of k are represented for the case of fluctuation parameter $z = 0.1$ in figure 2 and for the case of $z = 0.01$ in figure 3. The calculations carried out by means of our variational principle show that for any value of k in the first case there are only transitions

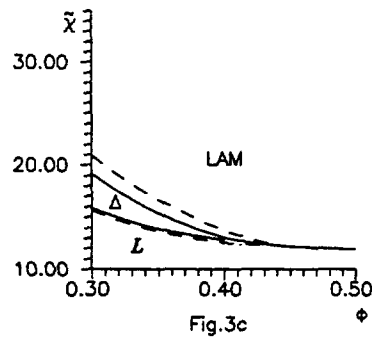
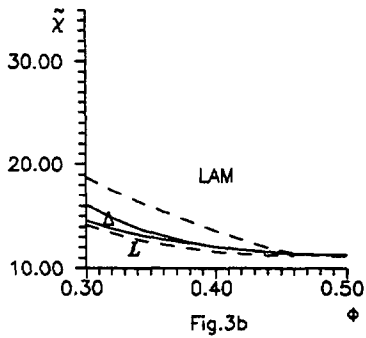
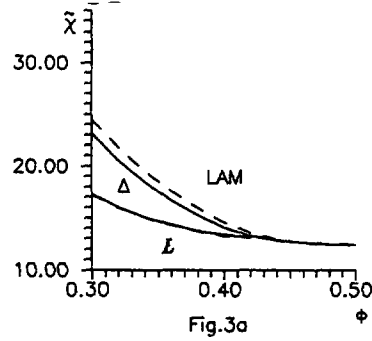
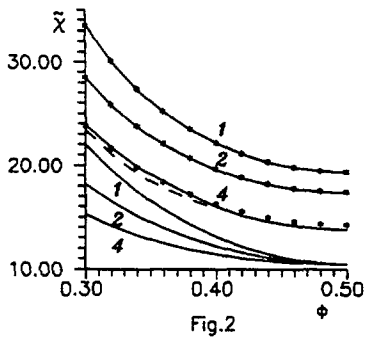


Fig. 2. — Phase diagrams of $(A_n)_k (B_m)_k$ -stars with $z = 0.1$ on plane $(\tilde{\chi}, \phi)$, $\tilde{\chi} = \chi^N$. The numbers assigned to lines denote the corresponding values of k . Solid lines pertaining to upper group are ones of transition to lamellar (LAM) phase from disordered (L) (for $k = 1$ or 2) or triangular (Δ) (for $k = 4$) phase calculated using FH-like approximation 50; the dashed line is that of transition L- Δ obtained in the approximation. The lines of phase coexistence calculated by means of our variational principle 36 using exact expressions for angular dependence of higher vertices calculated in references [1, 7] are shown by asterisks. The lines of the lower group are those of corresponding transition Δ -LAM calculated in the mean field (Leibler) approximation ($z = 0$).

Fig. 3. — Phase diagrams of $(A_n)_k (B_m)_k$ -stars with $z = 0.01$ and values of $k = 1, 2, 4$ (Figs. a, c and b respectively). The solid lines correspond to our theory and the dashed lines to FH-like calculations. L, Δ and LAM are used to denote regions of liquid (disordered) phase and lamellar and triangular (supercrystal) ones respectively.

from disordered or liquid (L) phase to lamellar (LAM) one. In the case of $k = 4$, $z = 0.1$, FH-like calculations using approximation 50 predict both the L-LAM transition in the region $0.4 < \phi < 0.6$ and a sequence of transitions L- Δ -LAM with very narrow area of triangular (Δ) phase in the regions $\phi < 0.4$ and $\phi > 0.6$. We see that the larger the value of k , the more visible the difference between phase diagrams obtained in the framework of our theory and of the less rigorous FH theory respectively. In a somewhat different manner the same tendency is revealed in figure 3 where the region of the existence of Δ -phase appears because the fluctuational parameter z decreases. Namely, this region calculated by using our variational principle is more narrow than that obtained using FH-like calculations. Otherwise, the destruction of more ordered phases caused by fluctuations is more pronounced when corresponding free energies are calculated more precisely. Summarizing, the tendency can be expressed as follows: FH-approximation underestimates to some extent caused by fluctu-

ations change of phase diagrams. However, the influence of angular dependence of higher vertex function on the character of phase diagrams becomes less pronounced with increasing fluctuation effects.

6. Conclusion.

We have presented a general approach to account for fluctuation effects in copolymer systems of complicated chemical structure under microphase separation in the weak segregation limit. It has advantages over the FH theory in calculating correlation functions in supercrystal phases (see formulas (40), (47-49) above) and in describing the crossover from mean field (Leibler) regime to fluctuative (Brazovskii) one. However, in the latter regime the results of our and of the FH theories and especially the qualitative picture (general topology) of phase diagrams are generally the same.

Appendix.

Evaluation of $Sp \ln G$.

As consistent with standard definitions of matrix theory the following chain of equalities holds :

$$Sp \ln G = Sp \sum_i \psi_i(x_1) \psi_i^*(x_2) \ln \lambda_i = \sum_i \ln \lambda_i \int |\psi_i(x)|^2 dx = \sum_i \ln \lambda_i, \quad (A1.1)$$

λ_i and $\psi_i(x)$ being eigenvalues and fundamental functions of the following integral operator :

$$(\hat{G}f)(\mathbf{r}) = \int G_{ij}(\mathbf{r}, \mathbf{r}') f_j(\mathbf{r}') d\mathbf{r}'. \quad (A1.2)$$

Going over to Fourier representation of equalities (A1.1) and (A1.2) and substituting for $G(q)$ expression (40) we obtain

$$Sp \ln G = -V \int \ln \{C((|\mathbf{q}| - q_0)^2) + r\} d\mathbf{q}/(2\pi)^3. \quad (A1.3)$$

The integral (A1.3) diverges in the large values of q region. The ultraviolet divergency, however, is of no significance because it contributes only to a constant in free energy (see Refs. [15, 28]). Therefore it is the r -dependence of integral (A1.3) which is the only one of interest in the situation. To find it let us differentiate (A1.3) as to r :

$$(\partial/\partial r) Sp \ln G = -V \int \{C((|\mathbf{q}| - q_0)^2) + r\}^{-1} d\mathbf{q}/(2\pi)^3 = -V (q_0^2/2\pi)(Cr)^{-1/2} \quad (A1.4)$$

Finally, it follows from (A4)

$$Sp \ln G = -V (q_0^2/\pi)(r/C)^{1/2} \quad (A1.5)$$

an unimportant constant being omitted.

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