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**Fluctuation Theory of Random Copolymers**

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**Abstract.** — We investigate the behavior of symmetric AB random copolymer melt near the point of microphase separation in the framework of a one-loop (Hartree-Fock) approximation, that exactly solves the problem. We have shown that composition fluctuations result to complete elimination of the microphase separation predicted in the framework a mean-field approximation [1-5]. Using variational techniques the temperature dependence of the density-density correlation function and its length scales are calculated. The diagonal in the replica space correlation function is stable with respect to the off-diagonal perturbation (glass-like order parameter). We discuss the general relation between microphase separation in random copolymers and spinodal decomposition in a mixture of A and B unconnected monomer units below their critical demixing point.

1. **Introduction: Order-Disorder Transition in Random Copolymers as a Stabilized Spinodal Decomposition**

There has recently been much interest in the phase transitions in the systems with a quenched disorder. In particular, the behavior of random copolymer melts (RCM) consisting of randomly [1, 5] or correlated [2-4] sequences of A and B monomers has been investigated. It was shown in meanfield approximation that below a critical temperature $T_c$ the system undergoes a third-order phase transition to a microphase structure. In our previous work [6] it has been proved that the presence of long-range spatial correlations in the AB random copolymer system results in an enhancement of composition fluctuations with decreasing of temperature $T$. These anomalously large fluctuations with finite wave number $q_0$ destroy the homogeneous state.

To understand the physical meaning of these results we will compare two different models: the molten RCM and a model two-component system of A and B unconnected monomers (SUM) [7]. It was shown in [8-10], using the random phase approximation, that the temperature $T_c$ below which the homogeneous state is getting unstable (the mean-field spinodal temperature) is the same for both these systems. We next outline analogies and different behavior of the fluctuation mode which destroyed the homogeneous state in these two systems.
According to [1-5], at $T < T_c$ a thermodynamically stable microphase structure is formed in the RCM whereas the SUM undergoes a spinodal decomposition into macrophases [11-13]. Both these processes occur in the region of absolute instability of the homogeneous state (within the framework of the mean-field approximation) and result in its destruction. With decreasing temperature $T < T_c$, both processes proceed by increasing the amplitude of certain critical composition fluctuations at finite wave number. But dynamic and thermodynamic properties of these systems are different.

In spinodal decomposition of mixtures of low-molecular compounds [11-13] and homopolymer blends [14-17], the homogeneous state is destroyed by the so-called Cahn-Hilliard (CH) waves which are inhomogeneities with a characteristic size

$$L_{CH} \approx \frac{r_0}{|\Delta T/T|^{1/2}}$$

controlled by the supercooling $\Delta T = T - T_c$ of the system ($r_0$ is a characteristic microscopic scale of the system). These inhomogeneities are formed at the initial stages of spinodal decomposition [11-17], and were proven to be unstable with respect to sequential doubling their period [18,19]. This process continues until the limiting state of two coexisting macroscopic phases is reached.

Using the mean-field approach developed in [1-5] for RCM one can show that the period $L_0$ of a microphase structure occurring in RCM at $\Delta T < 0$ has the same temperature dependence as wavelength $L_{CH}$ of Cahn-Hilliard waves formed in the corresponding SUM. (One should note that the scale appearing in [2-4] is $L_{CH}$ for the system of unconnected blocks which should be considered as a SUM in models of cooperative chemical linking presented in [2-4]). Unlike the Cahn-Hilliard dynamical structure occurring for SUM, the microphase structure emerging (as consistent with mean-field treatments of [1-5]) in the RCM is a thermodynamic equilibrium state. This may be due to the fact that deformation of random copolymer macromolecules as a whole, which accompanies redistribution of their monomer units in space during the formation of CH-structures with size $L_{CH} << R$ ($R$ is the characteristic Gaussian size of the random copolymer macromolecule assumed in [1-5] to be infinite) results in an additional entropy loss. This loss acts as a long-range stabilizing factor and transforms in the mean-field approximation the set of absolutely unstable CH-structures in the SUM into a thermodynamically equilibrium microphase structure in the RCM (see [20]).

The discrepancy between the results of [1-5] and the ones presented in [6] appears to be quite typical discrepancy between predictions of the mean-field approximation used in [1-5] and ones of Brazovskii-Fredrickson-Helfand approximation [21-23] used in [6]. The general fluctuation effect described for the RCM in [6] is the existence (at least as metastable) of homogeneous state at $T < T_c$. This state, as suggested by the expression for its correlation function [6,10]

$$G(x) \approx \frac{\sin (x/L_0)}{x} \exp \left(-\frac{x}{R_{cor}}\right)$$

is characterized by two scales: the scale $L_0 = 2\pi/q_0$, corresponding to the size of a typical fluctuation, which scale is of the order of the random inhomogeneity described by the CH-wavelength given by (1), and the correlation radius $R_{cor}$ describing the decay of correlation between the fluctuations. $R_{cor}$ was shown in [6] to be a quantity increasing with a decrease in temperature.

Summarizing, we see that the CH-waves formed in the unconnected monomer units system at $T < T_c$ is stable only kinetically (i.e. it is only long-living but eventually unstable structure) whereas in the RCM formed by linking these units by covalent bonds this structure may be stabilized in two ways: i) by forming microphase structure having a long-range order and ii)
by developing a short-range ordering characterized by the anomalously large fluctuations and an anomalously large correlation radius.

It turns out, however, that in fact only the second possibility takes place and no actual order-disorder transition occurs when decreasing the temperature in a random AB copolymer system with short-range correlation along the chain. There is only a smooth change in type of correlation function. The aim of the presented paper is to prove the assertion.

The paper is organized as follows: Section 2 discusses the model and derives a replica Hamiltonian for the random copolymer system with equal number of A and B monomers on the chain. Section 3 demonstrates that the one-loop (Hartree-Fock) approximation is exact because the higher order diagrams in the series expansion of the renormalized Green function with respect to the interaction constant have an additional multiplier $V^{-1}$ where $V$ is the system volume and are irrelevant in the thermodynamic limit. Based on this result, we present a variational principle and calculate the free energy of the random copolymer system. At the end of this section we prove that the diagonal in the replica space density-density correlation function is stable with respect to formation of Edwards-Anderson glass-like order parameter (off-diagonal perturbations). A discussion of the validity of the presented treatment is given in Conclusion.

2. The Model and Effective Hamiltonian

Consider a copolymer melt consisting of $M$ macromolecules formed by two types of monomer units randomly distributed along chains. For simplicity we suppose that all macromolecules have the same degree of polymerization $N$ and the same monomer excluded volumes $v$. To describe quenched disorder in the monomer distribution along the chains a set of variables $\{\sigma_i(s)\}$ is introduced, the indices $i$ label the chains ($i = 1..M$) and variable $s$ indicates the unit position along a chain ($s = 1...N$). We model the monomer units as spin variables $\sigma_i(s)$, which assume values of $+1$ and $-1$ for A and B monomer units respectively [1-5].

The configurational partition function of the system under consideration with a given set of variables $\{\sigma_i(s)\}$ is

$$Z(\{\sigma_i(s)\}) = \int d\Gamma \ g(\Gamma) \exp(-U(\Gamma))$$

Here $\Gamma = (x_1(1),..,x_1(N),..,x_M(N))$ is a point of configurational space of the system, $x_i(s)$ is a radius-vector of $s$-th unit situated on $i$-th chain, the function $g(\Gamma)$ describing the correlations due to the presence of chemical bonds between monomers is defined as

$$g(\Gamma) = \prod_{i,s} g(x_i(s) - x_i(s - 1))$$

(4a)

Note that for the case of the conventional Gaussian model of a chain [7],

$$g(x) = \left(a\sqrt{2\pi}\right)^{-3} \exp(-x^2/2a^2)$$

where the Kuhn segment $a$ is assumed to be the same for all chemical bonds.

We assume the monomer-monomer interaction $U(\Gamma)$ can be represented as a sum of pair interaction energies:

$$U(\Gamma) = \frac{1}{2} \sum_{i,j} \sum_{s,k} V(x_i(s) - x_j(k))$$

(4b)
(Here and below, all functions assumed to be measured in energetic units $kT$.) The pair interaction energy $V(x_i(s) - x_j(k))$ can be written in general form [24]:

$$V(x_i(s) - x_j(k)) = (B_0 + B_1(\sigma_i(s) + \sigma_j(k)) - \chi \sigma_i(s)\sigma_j(k)) f(x_i(s) - x_j(k))$$  \hspace{1cm} (5)

$B_0, B_1, \chi$ are some phenomenological constants describing the strength of the interaction between monomers, and the function $f(x_i(s) - x_j(k))$ describes the range of the potential (5). The last term in r.h.s. of (5) describes attraction between similar units and repulsion between different ones. It is convenient to define the following order parameters:

$$\rho(x) = \sum_{i,s} \delta(x - x_i(s)); \quad \psi(x) = \sum_{i,s} \sigma_i(s)\delta(x - x_i(s))$$  \hspace{1cm} (6)

$\rho(x)$ is the total monomer density, $\psi(x)$ is the local monomer composition fluctuation. Using these new order parameters the configurational partition function can be written as the following density functional integral:

$$Z(\{\sigma_i(s)\}) = \int \delta \rho(x) \delta \psi(x) \exp(-F^*(\rho, \psi) - F_s(\rho, \psi, \{\sigma_i(s)\}))$$  \hspace{1cm} (7)

The first term $F^*$ in r.h.s. of (7) does not depend on the copolymer structure $\{\sigma_i(s)\}$ and can be interpreted as an energetic contribution to the free energy that is common both random copolymer and the mixture of unconnected A and B monomers at a given distribution of order parameters (6). Using the lattice gas model for the unconnected monomers system $F^*$ can be written as a Landau expansion [1,3,11-13]:

$$F^*(\rho, \psi) = F_0^*(\rho(x)) + \frac{1}{2} \int \frac{d^3q}{(2\pi)^3} c(q)\psi(q)\psi(-q)$$

$$= F_0^*(\rho(x)) + \frac{v}{2} \int \frac{d^3q}{(2\pi)^3} (r_0 q^2 - \chi) \psi(q)\psi(-q)$$  \hspace{1cm} (8)

where $\psi(q)$ is a Fourier transformation of $\psi(x)$, $F_0^*(\rho(x))$ is a function of the total monomer density (a constant in the incompressibility limit), and $r_0$ is related to the second moment of the direct correlation function $c(q)$ [11-13], $v \approx r_0^2$ is excluded volume of monomer.

The second (structural or entropic) term $F_s$ is just the free energy of the corresponding ideal random copolymer, i.e. a system of noninteracting macromolecules with the same distribution of quenched disorder $\{\sigma_i(s)\}$:

$$F_s(\rho, \psi, \{\sigma_i(s)\}) = -\ln \left(\delta(\rho(x) - \sum_{i,s} \delta(x - x_i(s))) \delta(\psi(x) - \sum_{i,s} \sigma_i(s)\delta(x - x_i(s)))\right)$$  \hspace{1cm} (9)

The brackets $\langle \ldots \rangle_0$ denote averaging over all macromolecular conformations with measure $d\Gamma g(\Gamma)$. The representation (7) of the free energy of polymer systems was introduced by Lifshitz [7], and is valid for concentrated polymer solutions and melts.

To average the free energy over quenched disorder the replica approach is used [1,2,25,26]. One considers $n$ copies of the same system, averages over distribution $\{\sigma_i(s)\}$ first and then
takes the limit \( n \to 0 \):

\[
\langle F \rangle_{\text{av}} = - \lim_{n \to 0} \left( \frac{\langle Z^n (\{\sigma_i(s)\}) \rangle_{\text{av}} - 1}{n} \right)
\]

where

\[
\langle Z^n (\{\sigma_i(s)\}) \rangle_{\text{av}} = \int \prod_{\alpha=1}^{n} \delta \rho_{\alpha} (x^{\alpha}) \delta \psi_{\alpha} (x^{\alpha}) \exp \left( - \sum_{\alpha=1}^{n} F^{*} (\rho_{\alpha}, \psi_{\alpha}) - F_{\text{av}} (\rho_{\alpha}, \psi_{\alpha}) \right)
\]

the brackets \( \langle \ldots \rangle_{\text{av}} \) denote averaging over quenched disorder \( \{\sigma_i(s)\} \), \( \alpha \) is a replica index and the summation in r.h.s. of (11) is taken over \( n \) replicas. Here we introduce:

\[
\exp (-F_{\text{av}} (\rho_{\alpha}, \psi_{\alpha})) = \left\langle \exp \left( - \sum_{\alpha=1}^{n} F_{\alpha} (\rho_{\alpha}, \psi_{\alpha}, \{\sigma_i(s)\}) \right) \right\rangle_{\text{av}}
\]

In order to carry out the averaging prescribed in r.h.s. of (12), recall first that we consider now the case of a concentrated polymer solution or melt. In this case the order parameter \( \rho(x) \), the total density of all monomers (both of A- and B-type), is a weakly fluctuating variable (in the incompressibility limit it tends to a constant). Thus, in what follows we omit the \( \rho_{\alpha}\)-dependence of \( F_{\text{av}} (\rho_{\alpha}, \psi_{\alpha}) \) and take into account only the \( \psi_{\alpha}\)-dependence of the functional.

Using an integral representation of the delta function in r.h.s. of (9) the expression (12) can be rewritten:

\[
\exp (-F_{\text{av}} (\psi_{\alpha})) = \int \prod_{\alpha=1}^{n} \frac{\delta h_{\alpha} (x^{\alpha})}{(2\pi)^3} \exp \left\{ i \sum_{\alpha} \int dx^{\alpha} h_{\alpha} (x^{\alpha}) \psi_{\alpha} (x^{\alpha}) - S_{\text{av}} (\{h_{\alpha} (x^{\alpha})\}) \right\}
\]

where

\[
\exp (-S_{\text{av}} (\{h_{\alpha} (x^{\alpha})\})) = \left\langle \left\langle \exp \left\{ -i \sum_{j,s} \sigma_j (s) \sum_{\alpha} h_{\alpha} (x^{\alpha}_{j,s}) \right\} \right\rangle_0 \right\rangle_{\text{av}}
\]

In this paper we concentrate on systems of symmetric AB-copolymer chains consisting of uncorrelated monomer sequences. The simplest way to describe this type of quenched disorder is to suppose formally that the unit spin \( \sigma_i(s) \) can take any value rather than two discrete values +1 or -1 with probability equal to 1/2, the distribution \( p(\sigma_i(s)) \) being the following Gaussian distribution [5]:

\[
p(\sigma) = \frac{1}{\sqrt{2\pi \mu}} \exp \left( - \frac{\sigma^2}{2\mu^2} \right)
\]

where \( \mu \) is a parameter of the distribution.

For the distribution (15) the all terms in r.h.s. of (14) average independently, so it can be rewritten after its averaging over quenched disorder (i.e. over the distribution (15)) as follows:

\[
\exp (-S_{\text{av}} (\{h_{\alpha} (x^{\alpha})\})) = \exp \left\{ -\frac{\mu^2 \rho}{2} \sum_{\alpha} \int dx^{\alpha} h_{\alpha}^2 (x^{\alpha}) - I (\{h_{\alpha} (x^{\alpha})\}) \right\}
\]
\[ I (\{h_\alpha (x^\alpha)\}) = -\ln \left\langle \exp \left\{ -\frac{\mu^2}{2} \sum_{\alpha \neq \beta} \sum_{j, s} h_\alpha (x_j^\alpha (s)) h_\beta (x_j^\beta (s)) \right\} \right\rangle_0 \]

where \( \rho \) is the total monomer density.

As regards the functional \( I (\{h_\alpha (x^\alpha)\}) \), it is simply entropic contribution to \( n \)-replica free energy of an ideal copolymer melt in a weakly inhomogeneous external field \( \sum_{\alpha \neq \beta} \sum_{j, s} h_\alpha (x_j^\alpha (s)) h_\beta (x_j^\beta (s)) \). Evaluating (17) by the second moment approximation we get

\[ I (\{h_\alpha (x^\alpha)\}) = -\frac{\mu^4}{4} \sum_{\alpha \neq \beta} \int G^{(2)} (q_1^\alpha, q_2^\alpha ; q_1^\beta, q_2^\beta) \prod_{i=1}^2 \left( \frac{d^3 q_i^\alpha}{(2\pi)^3} \frac{d^3 q_i^\beta}{(2\pi)^3} h_\alpha (q_i^\alpha) h_\beta (q_i^\beta) \right) \]

where \( h_\alpha (q^\alpha) \) is Fourier transformation of the field \( h_\alpha (x^\alpha) \) and the function \( G^{(2)} (q_1^\alpha, q_2^\alpha ; q_1^\beta, q_2^\beta) \) is two-replica structural factor:

\[ G^{(2)} (q_1^\alpha, q_2^\alpha ; q_1^\beta, q_2^\beta) = \sum_{j=1}^M \sum_{s, t=1}^N \left\langle \exp \left( i \left[ q_1^\alpha x_j^\alpha (s) + q_2^\alpha x_j^\alpha (t) + q_1^\beta x_j^\beta (s) + q_2^\beta x_j^\beta (t) \right] \right) \right\rangle_0 \]

\[ = MV^{-2} \delta (q_1^\alpha + q_2^\alpha) \delta(q_1^\beta + q_2^\beta) FD \left( (q_1^\alpha)^2 + (q_1^\beta)^2 \right) \]

where \( V \) is the system volume and \( FD \) is two-replica Debye function for the discrete model [3,10]:

\[ FD \left( (q_1^\alpha)^2 + (q_1^\beta)^2 \right) = N + 2 \sum_{l=1}^{N-1} (N - l) (g_{\alpha \beta})^l = \frac{N - 2g_{\alpha \beta} - Ng_{\alpha \beta}^2 + 2g_{\alpha \beta}^{N+1}}{(1 - g_{\alpha \beta})^2} \]

and

\[ g_{\alpha \beta} = \exp \left( -\frac{(q_1^\alpha)^2 + (q_1^\beta)^2}{6} \right) \]

The function (20) has a simple form in the region \( 1/N << (q a)^2 << 1 \)

\[ FD \left( (q_1^\alpha)^2 + (q_1^\beta)^2 \right) = \frac{12N}{(q_1^\alpha)^2 + (q_1^\beta)^2} a^2 \]

There are two important points worth noting here. First, the origin of the factor \( V^{-2} \) in (19) is of the foremost significance and is connected with independent translational motion of the chain in both replicas. Second, the expression (18) for \( I (\{h_\alpha (x^\alpha)\}) \) is in fact only the first member of its exact expansion on powers of the \( n \)-replica external field. The following members of the expansion can be readily written by analogy with well-known 1-replica procedure [4,27].

Now in order to calculate the functional integral over all distributions of external fields in r.h.s. of (13) we use the saddle point method which enables us to represent \( F_{av} (\psi_\alpha) \) as a Landau expansion in the Fourier component of \( \psi_\alpha (q^\alpha) \). (Note that in this case coefficients of
the expansion (so-called higher vertices) are expressed in terms of the irreducible structural correlators in accordance with the conventional procedure [27]). Omitting the intermediate calculation we get the final expression for free energy in term of local composition fluctuations:

\[ F_{av}(\psi_\alpha) = \frac{\rho^{-1} \mu^{-2}}{2} \sum_{\alpha=1}^{n} \int \frac{d^3q_\alpha}{(2\pi)^3} \psi_\alpha(q^\alpha) \psi_\alpha(-q^\alpha) \]

\[ -\frac{1}{4V} \sum_{\alpha \neq \beta} \int \frac{d^3q_\alpha d^3q_\beta}{(2\pi)^3 (2\pi)^3} \lambda(q^\alpha, q^\beta) \psi_\alpha(q^\alpha) \psi_\alpha(-q^\alpha) \psi_\beta(q^\beta) \psi_\beta(-q^\beta) \]  

(22)

where

\[ \lambda(q^\alpha, q^\beta) = \frac{\kappa}{(q^\alpha)^2 + (q^\beta)^2} \]

is the vertex of inter-replica interaction and \( \kappa = 12/\mu^4 \rho^3 \). Substituting (22) and (8) in r.h.s. (11) and introducing a new dimensionless variables:

\[ q = qa; \quad \xi = \frac{r_0^2}{a^2}; \quad \psi^2(x^\alpha) = \frac{v}{a^3} \psi_\alpha(x^\alpha); \quad V = \frac{V}{a^3} \]

(23)

one can derive the final expression for the n-replica partition function and effective Hamiltonian describing the random copolymer system

\[ \langle Z^n([\sigma_i(s)]) \rangle_{av} = \prod_{\alpha=1}^{n} \delta \psi_\alpha(q^\alpha) \exp \{-H([\psi_\alpha(q^\alpha)])\} \]  

(24)

\[ H([\psi_\alpha(q^\alpha)]) = \frac{1}{2} \sum_{\alpha=1}^{n} \int \frac{d^3q_\alpha}{(2\pi)^3} \frac{1}{G_0^{-1}(q^\alpha)} \frac{1}{\psi_\alpha(q^\alpha) \psi_\alpha(-q^\alpha)} \]

\[ -\frac{1}{4} \sum_{\alpha \neq \beta} \int \frac{\lambda(q^\alpha, q^\beta)}{V} \delta(q_1^\alpha + q_2^\beta) \delta(q_1^\beta + q_2^\alpha) \prod_{i=1}^{2} \frac{d^3q_i^\alpha d^3q_i^\beta}{(2\pi)^3 (2\pi)^3} \psi_\alpha(q_i^\alpha) \psi_\beta(q_i^\beta) \]  

(25)

where

\[ G_0^{-1}(q^\alpha) = \xi (q^\alpha)^2 + \tau \]  

(26)

is a bare Green function; \( \tau = \mu^{-2} - \chi \) is reduced temperature, and \( \kappa = 12v/(a^3 \mu^4) \). At \( \mu = 1 \) we have a Hamiltonian describing symmetric random AB copolymers [1]. Here we assume the quantity \( \rho v \) to be equal to unity which corresponds to the incompressibility limit. One should note that the mean field spinodal of the homogeneous state is defined by the condition \( \tau = 0 \) which takes place at \( \chi = \mu^{-2} \)

3. The Variational Principle and Free Energy

3.1. Homogeneous State. — In the homogeneous state the Dyson equation for the renormalized Green function is

\[ G_{\alpha\alpha}^{-1}(q^\alpha) = \xi q^2 + \tau - \sum_{\alpha \neq \beta} \int \frac{d^3q_\beta}{(2\pi)^3} \lambda(q^\alpha, q^\beta) G_{\beta\beta}(q^\beta) \]  

(27)
where the diagrams having more than one factor \( \lambda \) are omitted. It is very important to note that the omitted diagrams vanish in the thermodynamic limit because of the presence of an additional factor \( V^{-1} \) in these diagrams. For example, a diagram of the second order in the expansion of the renormalized Green function in powers of inter replica interaction vertex \( \lambda \):

\[
I_2 \approx \frac{G_{\alpha\alpha}(q^\alpha)}{V^2} \sum_{\alpha \neq \beta} \int \frac{d^3q_1^\beta}{(2\pi)^3} \frac{d^3q_2^\beta}{(2\pi)^3} \lambda(q^\alpha, q_1^\beta) \lambda(q^\alpha, q_2^\beta) \delta(q_1^\beta + q_2^\beta) G^2_{\beta\beta}(q_1^\beta) \tag{28}
\]

After integrating over wave vectors \( q_2^\beta \) of the internal loop we get an additional multiplier \( V \) in the denominator and write finally

\[
I_2 \approx \frac{G_{\alpha\alpha}(q^\alpha)}{V} \sum_{\alpha \neq \beta} \int \frac{d^3q_1^\beta}{(2\pi)^3} \lambda^2(q^\alpha, q_1^\beta) G^2_{\beta\beta}(q_1^\beta) \Rightarrow 0 \tag{28a}
\]

In the general case a diagram has a zero order in power of volume \( V \) when the number of its vertices is equal to the number of its internal loops. So, there exists only one non-vanishing loop diagram in the expansion of the renormalized Green function in r.h.s. of (27).

Although the bare Green function is unstable at \( \tau < 0 \) in the region of sufficiently small values of wave number \( q \), in the limit \( n \to 0 \) the minimum of renormalized Green function \( G^{-1}_{\alpha\alpha}(q^\alpha) \) lies at finite value \( q_0 \) due to the long-range nature of the vertex \( \lambda \). It can be easily seen by substituting the bare function \( G^{-1}_{\alpha\alpha}(q^\alpha) \) in form (26) into the integrals of r.h.s. of (27). Thus, seek an approximate expression for the renormalized Green function in conventional for weak crystallization theory form [21–23]

\[
G^{-1}_{\alpha\alpha}(q^\alpha) = C (|q^\alpha| - q_0)^2 + \tau \tag{29}
\]

but now parameters \( C, q_0, \tau \) should be adjusted properly. The correlation function (2) is the inverse Fourier transformation of the correlation function \( G_{\alpha\alpha}(q^\alpha) \) (29). Substituting function (29) into (27) and setting \( n = 0 \) one can determine these parameters from the equations:

\[
\begin{align*}
\tau & = \tau + \frac{3\kappa}{8\pi\sqrt{C\tau}} \\
q_0^2 & = \frac{\kappa}{8\pi\xi\sqrt{C\tau}} \\
C & = 2\xi 
\end{align*} \tag{30}
\]

The first of equations (30) has exactly one root for any value of \((-\infty < \tau < \infty)\), and the value of the root \( \tau \) tends to zero when the value of \( \tau \) tends to minus infinity. (One should note that the correlation radius \( R_{\text{cor}} \) in (2) has an inverse power dependence on \( \tau \) \( R_{\text{cor}} \sim \tau^{-1/2} \) consequently it diverges as \( \tau \) tends to zero). It means that within the framework of the Hartree-Fock approximation (27) the homogeneous state stays stable with respect to fluctuations of the order parameter \( \psi_\alpha(q^\alpha) \) at any effective temperature \( \tau \). It is interesting to note that the value of \( q_0 \) tends to infinity when the effective temperature \( \tau \) tends to minus infinity \( (\tau \to -\infty) \). So the period of the fluctuations will be of the order of the bond size and the behavior of the system in this region will be defined by the short range monomer-monomer interactions.
3.2. ORDERED STATE. — Since one loop approximation is exact the Feynman variational method for Hamiltonian (25) may be applied to calculate free energy of the system under consideration in the ordered phase. Because in the ordered phase there is a nonzero average value of the order parameter \( \langle \psi_\alpha(q^\alpha) \rangle \), the order parameter \( \psi_\alpha(q^\alpha) \) has to be written as a sum of two terms \( \langle \psi_\alpha(q^\alpha) \rangle + \delta \psi_\alpha(q^\alpha) \), where \( \delta \psi_\alpha(q^\alpha) \) is the fluctuations of the order parameter with respect to its average value. The variational free energy is [26]:

\[
- \ln \langle Z^n(\sigma(s)) \rangle_{av} = \langle H(\{ \psi_\alpha(q^\alpha) \}) - H_0(\{ \delta \psi_\alpha(q^\alpha) \}) \rangle_{H_0} - \frac{1}{2} \text{Tr} (\ln G_{\alpha\beta}) \tag{31}
\]

where

\[
H_0(\{ \delta \psi_\alpha(q^\alpha) \}) = \frac{1}{2} \sum_{\alpha,\beta} \int \frac{d^3q^\alpha}{(2\pi)^3} \frac{d^3q^\beta}{(2\pi)^3} G_{\alpha\beta}^{-1}(q^\alpha, q^\beta) \delta \psi_\alpha(q^\alpha) \delta \psi_\beta(q^\beta)
\]

where the expectation value \( \langle \rangle_{H_0} \) is calculated with respect to a Gaussian measure \( \exp(-H_0(\{ \delta \psi_\alpha(q^\alpha) \})) \) and \( G_{\alpha\beta}^{-1}(q^\alpha, q^\beta) \) is inverse matrix to \( G_{\alpha\beta}(q^\alpha, q^\beta) \). The minimum of the functional (31) is sought on the class of trial functions of the following form:

\[
G_{\alpha\beta}(q^\alpha, q^\beta) = \left( C (|q^\alpha| - q_0)^2 + \tau \right) \delta(q^\alpha + q^\beta) \delta_{\alpha\beta}
\]

\[
\langle \psi_\alpha(x^\alpha) \rangle = \sum_{j=1}^{k} \frac{A_j}{\sqrt{k}} \left[ \exp(iq^\alpha_j x^\alpha) + \text{c.c.} \right] \tag{32}
\]

where sum in (33) is carried out over all \( k \) noncolinear vectors pertaining to the first coordination sphere of inverse lattice with \( |q^\alpha_0| = q_0 \). Substituting (32), (33) into (30) and setting \( n = 0 \), we derive the final expression for free energy

\[
\langle F \rangle_{av} = \min \left\{ \frac{1}{2} \frac{q_0^2 s}{\tau} + \frac{1}{2} \frac{q_0^2 s (\xi q_0^2 + \tau)}{\sqrt{\tau}} + \frac{1}{8} \frac{\kappa q_0^2 s^2}{\tau} + \frac{1}{2} \frac{\kappa s A}{\sqrt{\tau}} + (\xi q_0^2 + \tau) A + \frac{1}{2} \frac{\kappa A^2}{q_0^2} \right\} \tag{34}
\]

where \( s = 1/(2\pi\sqrt{C}) \) and \( A = \sum_{j=1}^{k} \frac{A_j^2}{k} \). The values of parameters \( q_0, C \) are determined from the Dyson equation:

\[
G_{\alpha\alpha}^{-1}(q^\alpha) = \xi q^2 + \tau - \sum_{\alpha \neq \beta} \left[ \int \frac{d^3q^\beta}{(2\pi)^3} \lambda(q^\alpha, q^\beta) G_{\beta\beta}(q^\beta) + 2\lambda(q^\alpha, q_0) A \right] \tag{35}
\]

The equilibrium values of \( r, A \) are determined from the extremal equations

\[
\partial \langle F \rangle_{av} / \partial r = \partial \langle F \rangle_{av} / \partial A = 0 \tag{36}
\]

which give

\[
r = \frac{q_0^2}{\xi} + \frac{\kappa s}{2\sqrt{\tau}} \tag{37a}
\]

\[
t + \frac{\kappa A}{q_0^2} + \frac{\kappa s}{2\sqrt{\tau}} = 0 \tag{37b}
\]
with $t = \tau + \xi q_0^2$. It is evident that (37a) and (37b) are not compatible for any finite value of $\tau$ for non-zero value $\lambda$. In other words, a state having a finite order parameter of form (33) is always unstable with respect to decrease of the quantity $\lambda$ and the stable state is the disordered one.

It is worth comparing our simultaneous equations (35) with the equations determining the values of the equilibrium order parameter $\lambda$ and $q_0$ in the mean field theory of Shakhnovich and Gutin [1] (see also [2, 4, 5]):

\begin{align*}
t + \frac{\kappa A}{q_0^2} &= 0 \quad (38a) \\
q_0^2 &= -\frac{t}{\xi} \quad (38b)
\end{align*}

One can see that (38a) follows from (37b) under assumption that the fluctuation correction can be neglected which is valid provided the following condition holds:

\begin{equation}
r^{3/2} \gg s\kappa \quad (39)
\end{equation}

But this assumption is self-contradictory: neglecting the fluctuation correction in (37a) and substituting the solution for $\lambda$ from (38a) we get the equation

\begin{equation}
r = 0 \quad (40)
\end{equation}

This conflict with the assumption that the inequality (39) holds. Thus, the mean field approximation is never correct in the region $\tau < 0$.

3.3. Stability of the Diagonal in the Replica Space Correlation Function. — In order to complete the analysis we investigate now the stability of the renormalized Green function (29) with respect to off-diagonal perturbations. To this end consider trial function $G_{\alpha\beta}(q^\alpha, q^\beta)$ as a sum of the diagonal (one-replica) trial function of the form (29) and off-diagonal members associated with the appearance of inter replica correlations (glass order parameter):

\begin{equation}
G_{\alpha\beta}(q^\alpha, q^\beta) = \delta(q^\alpha + q^\beta) \frac{\delta_{\alpha\beta}}{C(|q^\alpha| - q_0)^2 + r} + (1 - \delta_{\alpha\beta}) Q_{\alpha\beta}(q^\alpha, q^\beta) \quad (41)
\end{equation}

where

\begin{equation}
Q_{\alpha\beta}(q^\alpha, q^\beta) = Q_{\alpha\beta}f(q^\alpha)\delta(q^\alpha + q^\beta) \quad (42)
\end{equation}

$f(q)$ being an additional trial function, $Q_{\alpha\beta}$ is an $n \times n$ matrix. Substituting (41), (42) into the r.h.s. of (31) and expanding $\text{Tr} (\ln Q_{\alpha\beta})$ in the series in powers of $Q_{\alpha\beta}$ one can write the increment of the free energy associated with the appearance of non-zero two-replica correlations

\begin{equation}
\delta \langle F(Q_{\alpha\beta}) \rangle_{av} = \frac{V\Delta}{2} \text{Tr} Q_{\alpha\beta}^2 \quad (43)
\end{equation}

where

\begin{equation}
\Delta = \int \frac{d^3q}{(2\pi)^3} \left( \frac{f^2(q)}{G_{\alpha\alpha}(q)} - \frac{\lambda(q, q)}{V} f^2(q) \right) \quad (44)
\end{equation}
As evident from (43), the diagonal solution for Green function becomes unstable with respect to its off-diagonal perturbations provided the condition

\[ \Delta < 0 \]  

is valid [26, 27].

It is very important to stress that the second term in the expression (44) for \( \Delta \) contains a negative power of the system volume. Therefore, it vanishes in the thermodynamic limit, so that \( \Delta \) stays always positive and no instability of the diagonal correlation function takes place. However, the instability is not excluded for finite systems, such as protein macromolecules [5] or systems studied by computer simulation.

4. Conclusion

We have presented a fluctuation theory of microphase separation in random AB copolymer system. Within the framework of the one-loop (Hartree-Fock) approximation, which is exact for this system, we show, contrary to the predictions of references [1–6] that the homogeneous state with anomalously large fluctuations at wave number \( q_0 \sim |\tau|^{1/2} \) and anomalously large correlation radius \( R_{\text{cor}} \sim |\tau| \) stays stable with respect to a microphase separation. This stability of the homogeneous state of RCM is expected from two reasons. First, this stability is general for the replica Hamiltonian in which the interaction between fluctuations of the order parameter in different replicas is written in the form

\[
\begin{align*}
H_{\text{int}} \left( \{ \psi_\alpha (q^\alpha_i) \} \right) &= -\frac{1}{4} \sum_{\alpha \neq \beta} \int \frac{\lambda(q^\alpha_i, q^\beta_i)}{V} \delta(q^\alpha_i, q^\beta_i) \delta(q^\beta_1 + q^\beta_2) \prod_{i=1}^{2} \frac{d^3 q^\alpha_i}{(2\pi)^3} \frac{d^3 q^\beta_i}{(2\pi)^3} \psi_\alpha (q^\alpha_i) \psi_\beta (q^\beta_i) \\
&\text{In our previous papers [28, 29] we have proved this fact for a phenomenological multi-replica Landau-Brazovskii Hamiltonian [21–23], describing the instability of the homogeneous state with respect to the fluctuations with finite wave number \( q_0 \), included an inter-replica interaction term in form (46). We have shown that the effective temperature of the first order phase transition between the homogeneous state and microphase one tends to minus infinity when the value of an intra-replica interaction vertex tends to zero.}
\end{align*}
\]

The second reason is the close relationship between a cooled random copolymer melt and spinodal decomposition in the melt of unconnected monomers, that we presented in introduction. On this reason we do not expect an ordering in an inherently disordered system such as RCM in the region where CH-waves are stabilized only by a small decrease in macromolecular conformational entropy due to deformation of macromolecules as a whole.

The last issue to be discussed here is the region of the validity of our theory. Note first that the absence of the one-replica forth vertex is based on the continual approximation (21) that valid only at \( q_0 << 1 \). As following from equation (30) value of critical wave number \( q_0 \) is of the order of unity at temperature

\[ |\tau| \approx 9\xi \]  

At this temperature the correlation radius \( R_{\text{cor}} \) is of the order of

\[ R_{\text{cor}} \approx 4\pi \mu^4 a \sqrt{\xi} \]
Thus, there are two different scenario that depend on the value of the parameter $\xi$.

(a) $\sqrt{\xi} \leq (4\pi \mu^4)^{-1}$ In this case the main effect is the renormalization of the transition temperature due to the interaction of neighboring (along the chain) monomers. With decreasing temperature due to this renormalization the homogeneous state stays stable and weakly oscillating. Since, the value of correlation radius $R_{\text{cor}}$ has a microscopic value the behavior of the system is determined by specific behavior of monomer-monomer interaction and monomer distribution along the chain.

(b) $\sqrt{\xi} \geq (4\pi \mu^4)^{-1}$ In this case there is a region where both scales $R_{\text{cor}}$ and $L_0$ are large and our consideration is valid. Moreover, since the correlation radius $R_{\text{cor}}$ is increasing with decreasing temperature it is getting rather large in the point determined by (47) when $q_0$ is of the order of a microscopic scale. A very important question - if there still exists a large scale at lower temperature - stays open to discussion.

Our predictions can be tested by SANS or SAXS experiment on the random copolymer melts. The scattering intensity $S(q)$ in the homogeneous phase is proportional to the correlation function given by equation (29). So, the development of the fluctuations with the finite wave number $q_0$ will be manifested in these experiments as a broad correlation hole peak in the structure factor $S(q)$ whose position $q_0$ and intensity change with decreasing temperature.

In the very recent paper [30], Bouchaud and Cates considered a dynamics of random AB copolymers, and shown that there is a quasi-frozen glassy state which connected with frozen chain motion. It would be very interesting to investigate the dynamics of random AB copolymer chain in our homogeneous state with anomalously large correlation radius. We hope that our work stimulates these investigations.

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