Microphase separation transition of random copolymers in a random media

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We study the microphase separation transition of symmetric AB random copolymers in a gel with preferential adsorption of A monomers on the gel strands. It is shown that random copolymers in a gel are an example of the random field model. In the framework of the second Legendre transformation we have calculated the free energy and the phase diagram of the system. There are three different regimes on the phase diagram: the disordered-liquidlike phase, the replica symmetry breaking regime with broken replica symmetry for the two-replica correlation function where monomer composition fluctuations are pinned to the region with higher concentration of the cross links, and the ordered phase with short-range translational order. [S1063-651X(97)08507-3]

I. INTRODUCTION

Numerous theoretical studies in recent years have been devoted to the phase transition phenomena in copolymer systems. Copolymers are macro-molecules consisting of two or more different monomer units or monomer blocks randomly or regularly distributed along the polymer chains. The distribution of the monomers both along the chains and between different chains was fixed during the polymerization process [1]. The simplest example of copolymers is diblock copolymers that consist of two different blocks A_n and B_m with n and m monomers, respectively. With decreasing temperature the diblock copolymers with repulsive interaction between A and B monomers undergo a microphase separation transition. This transition is caused by the instability of the homogeneous state of the system with respect to composition fluctuations with the finite wave number q_*. This instability is due to a competition of the two effects: a short-range monomer-monomer interaction that tends to reduced the number of unfavorable contacts between different sorts of monomers and long-range entropic forces caused by the presence of the chemical bonds linking two blocks together. Depending on the temperature, composition (fraction of the monomers of different sorts on the chains), and chemical structure of copolymers (the way different blocks connect together into a polymer chain) one can observe one-, two-, or three-dimensional domain structures [2–7]. The first stage of the domain pattern formation, when the amplitude of composition fluctuations between different domains is still small in comparison to its average value, can be described in terms of the *Landau-Brazovskii* effective Hamiltonian [8]. The order parameter for this Hamiltonian is the deviation of the local concentrations of monomers from their average concentrations.

If we start to introduce defects (frustrations) into a chemical structure of the block copolymers, for example, randomly choosing the monomers in A and B blocks and switching them, after repeating this procedure many times we will arrive at an uncorrelated distribution of the monomers along the polymer chains. These copolymers are called *random copolymers* [9–16]. The presence of a small amount of defects slightly decreases the temperature of the phase transi-

tion. In fact, this temperature changes linearly with the number of defects. The behavior of the system changes dramatically when the number of defects becomes so high that we can no longer find long-range correlations between monomers along a chain. This change is manifested in the shift of the critical wave number q_* to the region of small q. This peak will remain at $q=0$ for strongly frustrated systems [9–16]. The instability of the homogeneous state at zeroth wave numbers suggests that the system undergoes a macrophase separation into pure A and B phases. The above statement is the result of the mean-field arguments. The fluctuation analysis of phase transitions in random copolymers show that the fluctuation corrections to the mean field are very important [12,14,16]. These corrections lead to the microphase separation transition instead of a macrophase one. The characteristic length scale of critical fluctuations above the phase transition and the period of the domain structure below it are extremely sensitive to the variation of the temperature [10–16]. One should note that these length scales could be as small as the bond size if there is no correlation between different types of monomers along polymer chains. The symmetry of the domain structure appearing under cooling is determined by the composition of the random copolymers. For example, below the microphase separation transition the symmetric random copolymers with an equal number of A and B monomers will self-organize into lamellar domains.

One can think about another type of frustration of a block copolymer system: putting block copolymers into a gel with preferential adsorption of one sort of monomer on the gel strands. This random distribution of the attractive centers destroys the translational invariance of the system. It was pointed out by de Gennes [17] that the interaction between mixtures and a gel can be modeled by the effective random fields with statistical characteristics dependent on the distribution of cross links of a gel and fixed during the polymerization of the gel. The behavior of the diblock copolymers in a gel was considered by Stepanow *et al.* [18]. They have shown that the presence of the gel leads to the decrease of the temperature of the microphase separation transition at very weak adsorption energy. Below the microphase separation transition the random fields acting on the domains pre-

vent the formation of the long-range modulated order and result in the formation of highly anisotropic translational incoherent microstructures. At some intermediate concentrations of cross links the fluctuations of copolymer composition are pinned to the regions with higher concentration of the cross links. In this regime the properties of the system become dependent on the preparation conditions of the gel matrix.

The interesting emerging question is how different would the behavior of the system be with two types of quenched disorder (i.e., with a random distribution of monomers along polymer chains and with a random spatial distribution of attractive centers)? To answer this question we have analyzed the phase behavior of random copolymers in a gel.

The paper is organized in the following way. In Sec. II we formulate the problem in terms of the effective Hamiltonian and demonstrate that the interaction between gel and random copolymers can be reduced to the effective external random field acting on the monomers. Using the technique of the second Legendre transformation [18–22], the free energy of the system is calculated. In Sec. III we consider the stability of the replica symmetric solution with respect to replica symmetry breaking. Section IV presents the study of the stability of the lamellar phase exposed to the external random field. In Sec. V we discuss the results and the phase diagram of random copolymers in a gel.

II. MODEL AND EFFECTIVE HAMILTONIAN

The order parameter $\psi(r)$ for the symmetric AB random copolymer melt containing the same amount of A and B monomers is the local composition fluctuations of A monomers with respect to the composition of B monomers $\psi(r) = \rho_a(r) - \rho_b(r)$, where $\rho_a(r)$ and $\rho_b(r)$ are the local concentrations of A and B monomers at the point r, respectively. Near the phase transition point, the behavior of the AB melt can be described in terms of the Landau expansion of the free energy in powers of the Fourier component of the normalized order parameter $\psi(q) = [\rho_a(q) - \rho_b(q)]/(\rho l R_g^3)^{1/2}$,

$$H_0(\psi(q)) = \frac{1}{2} \int_q (q^2 + \tau)\psi(q)\psi(-q)$$

$$+ \frac{\lambda}{24} \int_{q_1}\int_{q_2}\int_{q_3}\int_{q_4} \delta\left(\sum_{i=1}^{4} q_i\right)\prod_{i=1}^{4}\psi(q_i)$$

$$+ \frac{\kappa}{8V} \int_{q_1}\int_{q_2} \frac{\psi(q_1)\psi(-q_1)\psi(q_2)\psi(-q_2)}{q_1^2 + q_2^2},$$

$$(1)$$

where we introduced the notation $\int_q \rightarrow \int d^3q/(2\pi)^3$; λ and κ are the fourth-order vertex functions that can be calculated from the microscopic characteristics of the system [10–15]. $\tau = \rho v l(\chi_{tr} - \chi)$ is the effective temperature (χ is the Flory-Huggins parameter and χ_{tr} is its value at the phase transition point and v is the excluded volume assumed to be the same for all types of interactions in the system) and ρ is the average monomer density of the order of v^{-1} for the melt. In Eq. (1) the wave numbers q were normalized by the gyration

radius $R_g = al^{1/2}/6^{1/2}$ of the blocks of length l containing only one sort of monomers. The parameter a is equal to the bond size. The parameters κ, λ in this normalization are proportional to $l/\rho R_g^3 \sim l^{-1/2}$. One should note that the cubic term is absent in the effective Hamiltonian only for the symmetric random copolymer systems with an equal number of A and B monomers.

If the random copolymers are immersed into the gel matrix, we have to modify the effective Hamiltonian (1) by introducing the term linear in the gel monomer density $\rho_g(q)$. This term describes the interaction between the gel and random copolymers

$$H_{int}(\psi(q),\rho_g(q)) = \frac{\sqrt{\rho l}}{R_g^{3/2}} v(e_a - e_b)\int_q \psi(q)\rho_g(-q), \quad (2)$$

where the parameters e_i are the strength of the gel-A and gel-B monomers interactions measured in units kT and the parameter $\sqrt{\rho l}/R_g^{3/2}$ appears to be due to the normalization of the order parameter $\psi(q)$. One of the characteristics of the polymer network is the presence of quenched inhomogeneities of the density $\rho_g^{qn}(q)$ [23]. This quenched disorder is due to the statistical nature of the cross-linking process. For this reason the Fourier component of the density fluctuation $\rho_g(q)$ can be represented as a sum of two terms

$$\rho_g(q) = \rho_g^{qn}(q) + \rho_g^{an}(q), \quad (3)$$

where $\rho_g^{an}(q)$ is the annealed density fluctuations. The correlation function of the annealed density fluctuations has the well-known form

$$\langle \rho_g^{an}(q)\rho_g^{an}(q)\rangle = [G^{-1}(q) - v\chi_g]^{-1}, \quad (4)$$

where $G^{-1}(q)$ is the structural (entropic) contribution and $v\chi_g$ is the energetic one. The correlator of the quenched density fluctuations is more complicated,

$$C(q) = \langle \rho_g^{qn}(q)\rho_g^{qn}(q)\rangle = \frac{\nu(q)}{[1 + v\chi_g G(q)]^2}, \quad (5)$$

where the function $\nu(q)$ depends on the preparation conditions of the gel [23]. The structural factor of the gel is the sum of quenched and annealed parts

$$S(q) = [G^{-1}(q) - v\chi_g]^{-1} + \frac{\nu(q)}{[1 + v\chi_g G(q)]^2}. \quad (6)$$

We can estimate the correlation function $\langle \rho_g(-q)\rho_g(q)\rangle$ as $N_{gel}^2/R_{gel}^3 h(q_*)$ [17] if the characteristic length scale $L = 2\pi/q_*$ of the composition fluctuations $\psi(q)$ is of the order of the gel mesh size R_{gel}, where N_{gel} is the number of gel monomers between cross links and $h(q_*)$ is a number of the order of unity. In the general case R_{gel} is proportional to $N_{gel}^{d_f}$, where d_f is the fractal dimension of the gel strand. For rigid rods $d_f = 1$ and for Gaussian chains $d_f = 2$.

In order to average the free energy of the system

$$F = -\ln\left(\int D\psi(q)\exp[-H_0(\psi(q)) - H_{int}(\psi(q),\rho_g(q))]\right)$$

$$(7)$$

over all distributions of the quenched density fluctuations of the gel $\rho_g^{qn}(q)$ we will use the replica approach [24]. One considers n copies of the same system, averages over the whole distribution of the quenched disorder, and then takes the limit $n \to 0$,

$$\langle F \rangle_{av} = -\lim_{n \to 0} \frac{\exp(-F_n) - 1}{n}, \qquad (8)$$

where F_n is the n-replica free energy

$$F_n = -\ln\left[\int \prod_\alpha D\psi_\alpha(q) \exp\left(-\sum_\alpha H_0(\psi_\alpha(q)) \right) \right.$$
$$\left. \times \left\langle \exp\left(-\sum_\alpha H_{int}(\psi_\alpha(q), \rho_g(q)) \right) \right\rangle_{av} \right]$$
$$= -\ln\left(\int \prod_\alpha D\psi_\alpha(q) \exp[-H_n(\psi_\alpha(q))] \right), \qquad (9)$$

with $H_n(\psi_\alpha(q))$ being the n-replica effective Hamiltonian

$$H_n(\psi_\alpha(q)) = \sum_\alpha H_0(\psi_\alpha(q)) - \frac{\Delta}{2} \sum_{\alpha,\beta} \int_q \psi_\alpha(q) \psi_\beta(-q), \qquad (10)$$

where the parameter $\Delta \approx \rho v^2 l (e_a - e_b)^2 (N_{gel}^2/R_{gel}^3) h(q_*)$ was introduced. In order to calculate the n-replica free energy of the system under consideration

$$\exp(-F_n) = \int \prod_\alpha D\psi_\alpha(q) \exp[-H_n(\psi_\alpha(q))] \qquad (11)$$

we will use the technique of the second Legendre transformation [18–22]. The n-replica free energy in the framework of this approach can be written as the functional of the bare vertices λ and κ, the average value of the composition fluctuations $\langle \psi_\alpha(q) \rangle$ in the αth replica, and the renormalized two-replica correlation function $G_{\alpha\beta}(q)$,

$$F_n = -\tfrac{1}{2} \, \text{Tr}[\ln G_{\alpha\beta}(q)] + \tfrac{1}{2} \sum_\alpha \int_q G_{\alpha\alpha}(q) g_0^{-1}(q)$$
$$- \frac{\Delta}{2} \sum_{\alpha,\beta} \int_q G_{\alpha\beta}(q) H_n(\langle \psi_\alpha \rangle) + S_n(G_{\alpha\beta}, \langle \psi_\alpha \rangle), \qquad (12)$$

where g_0^{-1} is the bare propagator $q^2 + \tau$, $H_n(\langle \psi_\alpha \rangle)$ is the value of the effective Hamiltonian (10) at the function $\psi_\alpha(q)$ being equal to $\langle \psi_\alpha(q) \rangle$, and $S_n(G_{\alpha\beta}, \langle \psi_\alpha \rangle)$ is the sum of two irreducible diagrams that cannot be separated into two independent parts by removing any two lines. One should note that only the diagrams with the numbers of loops larger than the number of vertices contribute to the free energy of the system in the thermodynamic limit $V \to \infty$ due to the additional factor $1/V$ in front of the term in the effective Hamiltonian with vertex κ. There is only one diagram in the sum $S_n(G_{\alpha\beta}, \langle \psi_\alpha \rangle)$ that has the vertex κ to the first power [12,14,16].

The average value of the order parameter $\langle \psi_\alpha(q) \rangle$ is equal to zero above the microphase separation transition. A replica symmetric solution for the renormalized two-replica correlation function $G_{\alpha\beta}(q)$ can be written as a sum of two terms

$$G_{\alpha\beta}(q) = g(q)\delta_{\alpha\beta} + f(q)(1 - \delta_{\alpha\beta}), \qquad (13)$$

where $g(q)$ and $f(q)$ are functions to be defined below. Substituting the function $G_{\alpha\beta}(q)$ given by Eq. (13) into the right-hand side (rhs) of the Eq. (12) and taking the variational derivative of the n-replica free energy with respect to functions $g(q)$ and $f(q)$, one can write the system of equations

$$\frac{\delta F_n}{\delta g(q)} = -[g(q) - f(q)]^{-1} + \frac{f(q)}{[g(q) - f(q)]^2} - \Delta + g_0^{-1}(q)$$
$$+ \Sigma_{\alpha\alpha} = 0, \qquad (14)$$
$$\frac{\delta F_n}{\delta f(q)} = \frac{f(q)}{[g(q) - f(q)]^2} - \Delta + \Sigma_{\alpha\beta} = 0,$$

where $\Sigma_{\alpha\alpha} = 2[\delta S_n(G_{\alpha\beta}, \langle \psi_\alpha \rangle)/\delta g(q)]$ and $\Sigma_{\alpha\beta} = 2[\delta S_n(G_{\alpha\beta}, \langle \psi_\alpha \rangle)/\delta f(q)]$. In the one-loop (Hartree) approximation the system (14) reduces to the form

$$[g(q) - f(q)]^{-1} = g_0^{-1}(q) + \frac{\lambda}{2} \int_{q_1} g(q_1) + \frac{\kappa}{2} \int_{q_1} \frac{g(q_1)}{q^2 + q_1^2}, \qquad (15)$$

$$f(q) = \Delta[g(q) - f(q)]^2.$$

To solve Eq. (15) we will use a trial function method and choose the function $[g(q) - f(q)]^{-1}$ in the form $g_B^{-1}(q) = C(|q| - q_*)^2 + r$ [12,14,16], where the parameters C, r, q_* have to be found self-consistently. Substitution of this trial function into the rhs of Eq. (15) results in the equation

$$C(|q| - q_*)^2 + r = q^2 + \tau + \left[\frac{\lambda q_*^2}{4\pi\sqrt{Cr}} + \frac{\kappa q_*^2}{4\pi\sqrt{Cr}} \frac{1}{q^2 + q_*^2} \right]$$
$$\times \left[1 + \frac{\Delta}{2r} \right]. \qquad (16)$$

Expanding the rhs of this equation in the Taylor series in the powers of $|q| - q_*$, we can self-consistently define the parameters C, r, q_* as

$$C = 2, \qquad (17a)$$

$$q_*^2 = \frac{s\kappa}{\sqrt{r}} \left[1 + \frac{\Delta}{2r} \right], \qquad (17b)$$

$$r = \tau + 4 \frac{\lambda s}{\sqrt{r}} \frac{\kappa s}{\sqrt{r}} \left[1 + \frac{\Delta}{2r} \right]^2 + 3 \frac{\kappa s}{\sqrt{r}} \left[1 + \frac{\Delta}{2r} \right], \qquad (17c)$$

where the numerical constant $s = 1/16\pi\sqrt{2}$ was introduced. The analysis of the system (17) shows that the value of the critical wave number q_* in the case of the strong random

field ($\Delta/r > 1$) is proportional to $\Delta/r^{3/2}$. In order to find the temperature dependence we have to substitute $r^3 \sim \lambda \kappa s^2 \Delta^2/|\tau|$ into Eq. (17b), which gives the value of the critical wave number $q_*^2 \sim \sqrt{(\kappa/\lambda)|\tau|}$. In the other limit $|\tau| \sim \kappa s/r$ the characteristic length scale of the critical fluctuations $L \sim q_*^{-1}$ is inversely proportional to the square root of the effective temperature $1/\sqrt{|\tau|}$.

To simplify the analysis of the system (17) it is useful to introduce the reduced variables such as $z = r/s\sqrt{\kappa\lambda}$, $\delta = \Delta/s\sqrt{\kappa\lambda}$, and $t = \tau/s\sqrt{\kappa\lambda}$. In these variables we can write

$$t = z - \frac{4}{z}\left[1 + \frac{\delta}{2z}\right]^2 - 3\frac{\kappa^{1/4}}{s^{1/2}\lambda^{3/4}\sqrt{z}}\left[1 + \frac{\delta}{2z}\right]. \quad (18)$$

The parameter $\kappa^{1/4}/s^{1/2}\lambda^{3/4}$ is proportional to $l^{1/4}$, and depending on the length of the blocks l either the second or the third term gives the main contribution at small z on the rhs of Eq. (18). The fluctuations stabilize the disordered state for all effective temperatures as can be seen from Eq. (18). However, the absence of the instability does not preclude the existence of a first-order phase transition into a domain structure with a period of the order of length scale L. In order to decide whether such a transition may occur we have to calculate the free energy of the ordered state.

The ordered phase is characterized by a nonzero average value of the order parameter $\langle \psi_\alpha(q) \rangle$ that describes average composition fluctuations in the domains. In the weak segregation limit, for a lamellar domain structure with amplitude A and period $L = 2\pi/q_*$ oriented along the z axis the average value of the order parameter has the form

$$\langle \psi_\alpha(q) \rangle = A[\delta(q_z - q_*) + \delta(q_z + q_*)]. \quad (19)$$

Repeating the above calculations for the ordered phase, one can derive the system of equations

$$C = 2,$$

$$q_*^4 - q_*^2 \frac{s\kappa}{\sqrt{r}}\left[1 + \frac{\Delta}{2r}\right] - \frac{\kappa}{2\lambda}r = 0,$$

$$A^2 = \frac{2r}{\lambda},$$

$$\quad (20)$$

$$-t = z + \frac{2}{z}\left[1 + \frac{\delta}{2z}\right]\left[\left[1 + \frac{\delta}{2z}\right] + \sqrt{\left[1 + \frac{\delta}{2z}\right]^2 + 2z^2}\right]$$

$$+ 3\frac{\kappa^{1/4}}{s^{1/2}\lambda^{3/4}}\left[\frac{\left[1 + \frac{\delta}{2z}\right]}{\sqrt{z}}\right.$$

$$\left. + \frac{z^{3/2}}{\left[1 + \frac{\delta}{2z}\right] + \sqrt{\left[1 + \frac{\delta}{2z}\right]^2 + 2z^2}}\right].$$

In the case of the strong random field $\delta/z > 1$ the last Eq. (20) of the system (20) can be simplified

$$-t = z + \frac{\delta^2}{z^3} + \frac{3}{2}\frac{\kappa^{1/4}}{s^{1/2}\lambda^{3/4}}\frac{\delta}{z^{3/2}}. \quad (21)$$

The solution of Eq. (21) appears at $z_c \approx 3^{1/4}\delta^{1/2}$ for $\kappa^{1/4}/s^{1/2}\lambda^{3/4}\delta^{1/4} < 1$ and at $z_c \approx [(\frac{9}{4}(\kappa^{1/4}/s^{1/2}\lambda^{3/4})\delta]^{2/5}$ if the opposite inequality holds. Here we will be interested only in the first case. Substituting the solution $z_c \approx 3^{1/4}\delta^{1/2}$ into Eq. (21), one can obtain the critical temperature or spinodal of the ordered phase

$$t_c \approx -\frac{4}{3^{3/4}}\delta^{1/2}. \quad (22)$$

Note that the precise analysis of the phase transition between the ordered and the disordered phases shows that the temperature of the first-order phase transition has the same power dependence on the parameter δ as the critical temperature t_c. To conclude our analysis of the phase transition in the random copolymer systems in a gel we have to check the stability of the replica symmetric solution.

III. STABILITY OF THE REPLICA SYMMETRIC SOLUTION

To consider the stability of the replica symmetric solution we have to expand the free energy of the system in powers of $\delta Q_{\alpha\beta}(q)$, which is a small perturbation over the replica symmetric part of the two-replica correlation function $G_{\alpha\beta}(q)$ [see Eq. (13)] and check the sign of the quadratic in the perturbation term. In this approximation the two-replica correlation function can be written in the form

$$G_{\alpha\beta}(q) = g_B(q)\delta_{\alpha\beta} + \Delta g_B(q)^2 e_\alpha^T e_\beta + \delta Q_{\alpha\beta}(q), \quad (23)$$

where e is the unit vector $(1,1,...,1)$ of dimension n. Substituting this function $G_{\alpha\beta}(q)$ into rhs of Eq. (12) and expanding it in powers of the matrix $\delta Q_{\alpha\beta}(q)$ one can find

$$\Delta F_n = \frac{V}{4}\left[\int_q \left(\frac{\delta_{\gamma\nu}}{g_B(q)^2} - 2\frac{\Delta}{g_B(q)}e_\gamma^T e_\nu\right)\delta Q_{\alpha\gamma}(q)\delta Q_{\alpha\nu}(q)\right.$$

$$\left. - \frac{\lambda^2}{2}\int_q \int_k \int_p \delta Q_{\alpha\beta}(p)\delta Q_{\alpha\beta}(k)f(q)f(q-k-p)\right],$$

$$\quad (24)$$

where on the rhs we have assumed the summation over all repeated indices and have neglected terms of the order of n^2. The form of the perturbation $\delta Q_{\alpha\beta}(q)$ can be found by analyzing the Dyson equation for the off-diagonal part of the two-replica correlation function. One can easily see that the fluctuations with $|q| = q_*$ give the main contribution to this function, so at the zeroth-order approximation the function $\delta Q_{\alpha\beta}(q)$ can be chosen in the form

$$\delta Q_{\alpha\beta}(q) = Q_{\alpha\beta}g_B(q)^2, \quad (25)$$

where $Q_{\alpha\beta}$ is the $n \times n$ matrix with elements satisfying the symmetry relation $\Sigma_\alpha Q_{\alpha\beta} = \Sigma_\gamma Q_{\gamma\delta}$. After introducing the Parisi function [25] $q(x)$ defined in the interval [0,1],

$$\int_0^1 q^k(x)dx = \lim_{n \to 0} \frac{1}{n(n-1)} \sum_{a,b} Q_{ab}^k \quad \forall \ k, \qquad (26)$$

the quadratic part of the free energy in the powers of the matrix Q_{ab} can be rewritten as

$$\Delta F = -\frac{V}{4} \left\{ \int_0^1 \int_0^1 [(I_1 - I_3)\delta(x-y) + I_2]q(x)q(y)dx \ dy \right\}, \qquad (27)$$

where we have defined

$$I_1 = \int_q g_B^2(q) = \frac{q_*^2}{4\pi\sqrt{C}} r^{-3/2}, \qquad (28)$$

$$I_3 = \frac{1}{512\pi^2 C^2} \lambda^2 \Delta^2 q_*^5 r^{-6}, \qquad (29)$$

$$I_2 = 2\Delta \int_q g_B^3(q) = \frac{3}{8\pi\sqrt{C}} q_*^2 \Delta r^{-5/2}. \qquad (30)$$

The replica symmetric solution (13) is unstable in the region of the parameters where the matrix $(I_1 - I_3)\delta(x-y) + I_2$ has a negative eigenvalue

$$\lambda_- = I_1 + I_2 - I_3 < 0. \qquad (31)$$

In terms of the variables Δ and r expression (31) becomes

$$\lambda_- \propto \left(1 + \frac{3}{2}\frac{\Delta}{r} - \frac{\lambda^2 q_*^3}{64\pi C^{3/2}}\frac{\Delta^2}{r^{9/2}} \right) \leq 0. \qquad (32)$$

Equation (32) determines the spinodal line of the replica symmetric solution with respect to replica symmetry breaking. In the dimensionless variables this equation can be rewritten as

$$\lambda_- \propto 1 + \frac{3}{2}\frac{\delta}{z} - \frac{\lambda^{3/8}}{8s^{3/4}\kappa^{1/8}}\frac{\delta^2}{z^{21/4}}\left(1 + \frac{d}{2z} \right)^{3/2} \leq 0. \qquad (33)$$

In the case of the weak random field $\delta/z \lesssim 1$ the second term on the rhs of Eq. (32) can be neglected, leading to

$$z_{sp} \approx \left(\frac{\lambda^{3/8}}{8s^{3/4}\kappa^{1/8}} \right)^{4/21} \delta^{8/21}, \quad \delta \lesssim \left(\frac{\lambda^{3/8}}{8s^{3/4}\kappa^{1/8}} \right)^{4/13}. \qquad (34)$$

Extrapolating Eq. (32) to large δ, $\delta/z \gtrsim 1$, or $\delta > (\lambda^{3/8}/8s^{3/4}\kappa^{1/8})^{4/13}$, one can obtain

$$z_{sp} \approx \left(\frac{\lambda^{3/8}}{24\sqrt{2}s^{3/4}\kappa^{1/8}} \right)^{4/23} \delta^{10/23}, \quad \delta > \left(\frac{\lambda^{3/8}}{8s^{3/4}\kappa^{1/8}} \right)^{4/13}. \qquad (35)$$

In order to find the effective temperature of the phase transition these values of the renormalized effective temperature z_{sp} have to be substituted into expression for $t(z)$ given by Eq. (21). An analysis of this equation shows that the instability of the replica symmetric solution can only occur at the intermediate values of the external random field δ. This is due to the fact that for strong random fields δ

$> (\lambda^{3/8}/8s^{3/4}\kappa^{1/8})^{4/13}$ the spinodal temperature t_{sp} decreases faster ($t_{sp} \sim -\delta^{16/23}$) than the temperature of the first-order phase transition $t_{tr} \sim -\delta^{1/2}$.

IV. RANDOM COPOLYMERS BELOW THE MICROPHASE SEPARATION TRANSITION

In this section we consider the stability of the domain structure below the microphase separation transition. Let the layers at the point r in the domain structure undergo a fluctuation displacement $u(r)$ in the z direction. If the fluctuations $u(r)$ vary only slightly over distances of the order of a layer spacing $L \approx 1/q_*$, the changes in composition at each point in space may be regarded as the result of a shift of the layers by an amount equal to the local fluctuation of the displacement $u(r)$. The fluctuating composition is then written

$$\psi(r) = 2A \ \cos\{q_*[z + u(r)]\}. \qquad (36)$$

Substituting this formula for the order parameter into the effective Hamiltonian (10), one can derive the coarse-grained effective Hamiltonian for the fields $u_\alpha(r)$,

$$H(\{u_\alpha(r)\}) = \frac{\kappa A^4}{8q_*^4}\left(\sum_\alpha \int_r \{[\Delta_{x,y}u_\alpha(r)]^2 \right.$$
$$\left. + 4q_*^2[\nabla_z u_\alpha(r)]^2\} \right)$$
$$- \sum_{\alpha,\beta} \Delta \int_r \cos\{q_*[u_\alpha(r) - u_\beta(r)]\}, \qquad (37)$$

where the first term on the rhs describes the deformation of the lamellar layers and the second one couples this deformation in different replicas. It is interesting to note that the cosinelike coupling term between fluctuations of the order parameter in two different replicas appears in disordered physical systems such as an array of flux line in type-II superconducting film in magnetic field [26], a crystalline surface with a disordered substrate [27], random field XY model [28], and copolymers in a gel [18]. In all these systems the cosine term results in a break of the long-range order and in the spontaneous replica symmetry breaking [29,30].

In the framework of the Gaussian variational principle [31,30] the contribution to the free energy of the system due to fluctuations of the displacement $u_a(r)$ in different replicas is

$$F_{var} = -\frac{1}{2}\text{Tr}\int_q \ln[G_{ab}(q)] + \langle H(\{u_a(q)\}) - H_0 \rangle_0, \qquad (38)$$

where we defined

$$H_0 = \frac{1}{2}\sum_{a,b} \int_q G_{ab}^{-1}(q)u_a(q)u_b(-q) \qquad (39)$$

and $G_{ab}^{-1}(q)$ is the two replica trial function whose form has to be found self-consistently. The $\langle \ \rangle_0$ denotes the thermal averaging with the weight $\exp(-H_0)$. After thermal averaging the variational free energy reads

$$\frac{F_{\text{var}}}{V} = -\tfrac{1}{2}\text{Tr}\int_q \ln[G_{ab}(q)] + \tfrac{1}{2}\text{Sp}\int_q [G_0^{-1}(q)\delta_{ab}$$

$$-G_{ab}^{-1}(q)]G_{ab}(q) - \sum_{b\neq a} \Delta A_a A_b \exp\left(-\frac{q_*^2}{2}B_{ab}\right),$$
(40)

where

$$B_{ab} = \int_q [G_{aa}(q) + G_{bb}(q) - G_{ab}(q) - G_{ba}(q)] \quad (41)$$

and the inverse bare propagator $G_0^{-1}(q)$ is $(A^2/2)[(q_y^2 + q_x^2)^2 + 4q_*^2 q_z^2]$, where we substitute $A^2 = \kappa A^4/2q_*^4$. The trial function $G_{ab}(q)$ can be found from the equations

$$G_{aa}^{-1}(q) = G_0^{-1}(q) + 2\sum_{a\neq b} \Delta q_*^2 A_a A_b \exp\left(-\frac{q_*^2}{2}B_{ab}\right),$$
(42)

$$G_{ab}^{-1}(q) = -2\Delta q_*^2 A_a A_b \exp\left(-\frac{q_*^2}{2}B_{ab}\right). \quad (43)$$

Analyzing Eq. (43) one can conclude that the function $G_{ab}^{-1}(q)$ does not depend on wave number q for $a\neq b$. So we can define $G_{ab}^{-1}(q) = -\sigma_{ab}$ $(a\neq b)$. In the case of the one-step replica symmetry breaking for which the elements of the matrix σ_{ab} are assumed to have two different values σ_0 and σ_1 depending on whether or not the two indices a and b belong to the same blocks of length m, one can rewrite the equations (see for details [30])

$$\sigma_1 = Y \exp(\eta \ln t), \quad (44)$$

$$\sigma_0 = Y \exp\left(\eta \ln t - \frac{1}{m}(2\eta \ln Lq_* + \eta \ln t)\right), \quad (45)$$

where L is the linear size of the system and we introduced the following parameters assuming A_a to be the same in the all replicas and equal A:

$$\eta = \frac{q_*}{16\pi A^2}, \quad t = 2\frac{m(\sigma_1 - \sigma_0)}{A^2 q_*^4}, \quad Y = 2\Delta q_*^2 A^2. \quad (46)$$

In the limit $Lq_* \gg 1$ Eq. (45) gives $\sigma_0 = 0$. Therefore, the trial function $G_{ab}(q)$ is

$$G_{aa}(q) = \frac{1}{G_0^{-1}(q) + m\sigma_1} + \frac{\sigma_1}{G_0^{-1}(q)[G_0^{-1}(q) + m\sigma_1]},$$
(47)

$$G_{ab}(q) = \frac{\sigma_1}{G_0^{-1}(q)[G_0^{-1}(q) + m\sigma_1]} \quad (48)$$

for $a,b \in$ diagonal blocks $m\times m$, and

$$G_{ab}(q) = 0 \quad (49)$$

for $a,b \in$ off-diagonal blocks $m\times m$. Substitution of the solution (47)–(49) for the trial function $G_{ab}(q)$ into variational free energy yields [30]

$$f_{\text{var}} = \lim_{n\to 0} \frac{1}{n}[F_{\text{var}}(t) - F_{\text{var}}(0)]$$

$$= \frac{VA^2 q_*^2}{4}\left[\left(1 - \frac{1}{m}\right)\eta t + Y'(1 - m)t^\eta\right], \quad (50)$$

where $Y' = 2Y/A^2 q_*^4 = 4\Delta/q_*^2$ is introduced. The equilibrium values of the parameters m and t can be found from the system of equations

$$\frac{1}{m^2}\eta t - Y't^\eta = 0, \quad (51)$$

$$\left(1 - \frac{1}{m}\right) + Y'(1 - m)t^{\eta-1} = 0. \quad (52)$$

For $\eta > 1$ this system has only a trivial solution $m = 1$, $t = 0$ that corresponds to the replica symmetric solution with all off-diagonal elements of the matrix $G_{ab}(q)$ equal to zero. The nontrivial solution appears for $\eta \leqslant 1$, which reads

$$m = \eta, \quad (53)$$

$$t = (Y'\eta)^{1/(1-\eta)}. \quad (54)$$

In other words, at $\eta = 1$ the system undergoes a phase transition for which the correlation function $G_{ab}(q)$ change its form.

To complete the analysis we now calculate the correlation function $\langle \psi(r)\psi(r')\rangle$ in the ordered phase below the phase transition ($\eta < 1$). Due to fluctuations of the displacement $u(r)$ the correlation function is

$$\langle \psi(r)\psi(r')\rangle \propto A^2 \cos[q_*(z-z')]$$

$$\times \exp\left(-\frac{q_*^2}{2}\langle[u(r)-u(r')]^2\rangle\right), \quad (55)$$

with

$$\langle[u(r)-u(r')]^2\rangle = 2\int_q \{1 - \cos[q(r-r')]\}\langle u(q)u(-q)\rangle. \quad (56)$$

Substituting expression for the correlator $\langle u(q)u(-q)\rangle$, which is given by the diagonal part (47) of the two-replica correlation function, one can write

$$\langle[u(z)-u(z')]^2\rangle$$

$$= \frac{2}{q_*^2}\begin{cases} (1-\eta)\ln t + 2\ln|z-z'|q_* & \text{for } |z-z'|\xi_z^{-1} > 1 \\ 2\eta \ln|z-z'|q_* & \text{for } |z-z'|\xi_z^{-1} \leqslant 1 \end{cases}$$
(57)

for $|x_\perp - x_\perp'| = 0$ and
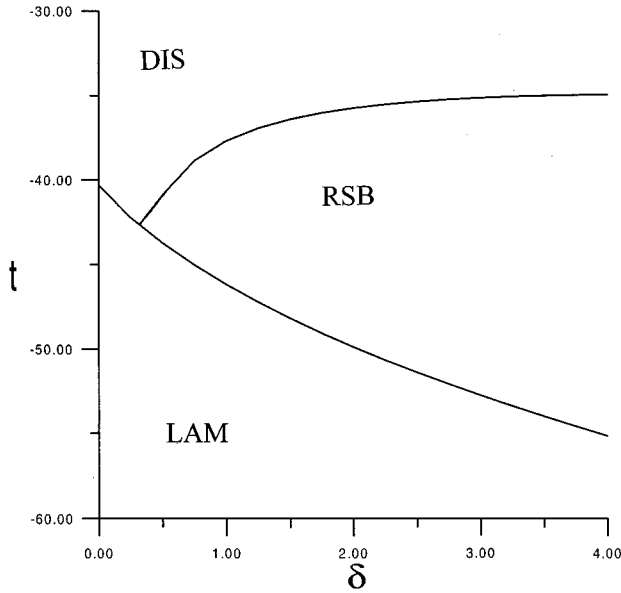
$$\langle[u(x_\perp) - u(x_\perp')]^2\rangle$$

FIG. 1. Phase diagram for the random copolymer melt in the gel in the variables (t, δ) at $\kappa = \lambda = 1$. The solid line between the homogeneous state (DIS) and replica symmetry breaking regime (RSB) is the spinodal line of the replica symmetric solution for the two-replica correlation function with respect to replica symmetry breaking. The solid line between the homogeneous state and the lamellar phase (LAM) as well as between the RSB phase and the lamellar phase is the line of the first-order phase transition.

$$= \frac{2}{q_*^2} \begin{cases} (1 - \eta)\ln t + 4 \ln|x_\perp - x_\perp'|q_* & \text{for } |x_\perp - x_\perp'|\xi_x^{-1} > 1 \\ 4\eta \ln|x_\perp - x_\perp'|q_* & \text{for } |x_\perp - x_\perp'|\xi_x^{-1} \leqslant 1 \end{cases}$$

$$(58)$$

for $|z - z'| = 0$, where $\xi_z q_* = t^{-1/2}$ and $\xi_x q_* = t^{-1/4}$ are the correlations lengths in the z and x and the y directions, respectively. The form of the correlation function shows that there are two different regions. Inside the domains of size $|x_\perp - x_\perp'| < \xi_x$ and $|z - z'| < \xi_z$ the system behaves like smectic A [32]. For the larger distances the fluctuations of the layer displacement $u(r)$ destroy the modulated order, which results in the formation of the highly anisotropic translational incoherent microstructures with $\xi_z/\xi_x \sim \Delta^{-1/4(1 - \eta)}$. Thus, in random copolymers in a gel there is only short-range translational order with correlation lengths ξ_z, ξ_x.

V. CONCLUSION

We have considered the behavior of the random copolymers in a gel and have shown that this problem can be reduced to the random field model with the correlation properties of the random field fixed during the process of a gel synthesis. To illustrate our predictions we calculate the phase diagram of the system (see Fig. 1). As one can see from Fig. 1 that the temperature of the first-order phase transition from the homogeneous state to the lamellar phase decreases with increasing strength of the random field δ. This result can be understood using simple Imry-Ma arguments [33]. The statistical fluctuations of the random field will produce the composition fluctuations in the regions with a higher concentration of cross links

$$\psi(q) = G(q)h(q). \tag{59}$$

In order for the domain structure to be distinguished from these background statistical fluctuations, the amplitude of the composition fluctuations between different domains $A \approx \sqrt{|\tau|/\lambda}$ has to be larger than the statistical fluctuations of the order parameter

$$\sqrt{\langle \psi^2 \rangle} \approx \sqrt{\int_q G^2(q)\langle h(q)h(-q)\rangle} \approx \sqrt{\frac{\Delta}{\kappa|\tau|}}. \tag{60}$$

This gives the estimate of the temperature of the first-order phase transition $|\tau| \approx \sqrt{\Delta}$ that reproduces the scaling dependence derived in Sec. II.

At some intermediate strength of the random field (or the adsorption energy) above the line of the first-order phase transition, there is a region of the phase diagram with replica symmetry breaking (RSB) for the two-replica correlation function. This means that in this region the pattern of copolymer composition fluctuations is pinned to the frozen inhomogeneity of the gel and the properties of the system become dependent on the preparation conditions of the gel. Below the microphase separation transition there is only short-range translational order with correlation lengths ξ_z, ξ_x. All our predictions can be tested by the x-ray scattering experiments. We hope that this work will stimulate such experiments. It is very interesting to note that qualitatively the phase diagram (Fig. 1) looks very similar to that calculated by Stepanow et al. [18] for symmetric diblock copolymers in a gel.

Let us comment on the case of asymmetric random copolymers containing an unequal numbers of A and B monomers. In this case there is a cubic term in the effective Hamiltonian. As a result, there will be a region on the phase diagram with three- and two-dimensional domain structures [34,35]. However, the general prediction of the paper is that the breaking of the replica symmetry of the two-replica correlation function will not be affected by the cubic term in the effective Hamiltonian.

Recently, Panyukov and Rubinstein [36] have considered the behavior of a network prepared by cross linking the mixture of A and B chains. This is another way of breaking the translational invariance of the system. They have shown that cross links prevent a microphase separation and chains can only form domains on the microscopic length scales of the order of network mesh size. The physical reason for such a phenomenon is the existence of the random stress in a network. These random forces acting on the microstructure destroy the long-range modulated order. The destruction of the long-range order in the network is different from that discussed in the present paper. The quenched random fields are external perturbations of the copolymer melts, while the random forces are intrinsic ingredient of the network.

Another possible application of our theory is to the problems of the freezing transition of proteins in random media [37] or the protein adsorption on the substrate with randomly distributed attractive centers [38]. We hope that this paper will stimulate work in this direction.

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