8220 *Macromolecules* **1996,** *29,* 8220−8230

Stress-Induced Ordering in Microphase-Separated Multicomponent Networks

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Received May 20, 1996; Revised Manuscript Received August 21, 1996[⊗]

ABSTRACT: Polymer blends, mixtures, or block copolymers can be cross-linked in a homogeneous state forming a multicomponent network. Upon cooling such network, the repulsion between different components may lead to a microphase separation into regions rich in each of these components. The main difference of the microphase separation in multicomponent networks from, say, that in block copolymers is that there are quenched random elastic forces acting on the microphase regions from the cross-links of the network. We demonstrate that these forces destroy the long-range order of microstructures in undeformed or isotropically swollen network. The system is broken into correlation regions significantly larger than the period of microstructures. The long-range orientational order appears upon anisotropic deformation of the network.

1. Introduction

Blending chemically different polymers is an important practical way of making materials with improved properties.[1] The main problem in preparations of such materials is that polymers tend to macrophase separate due to their incompatibility. One possible way to prevent macrophase separation is to cross-link polymers in the mixed state. Cross-linked polymer blends can only microphase separate on length scales of the network mesh size.[2] This method of improving miscibility by cross-linking polymer blends has been discussed in a number of recent papers.[3−12] These works studied blends, cross-linked in a homogeneous state, and focused mainly on the stability of this state. It was demonstrated both theoretically[2−9] and experimentally[11,12] that cross-linking makes the homogeneous state significantly more stable. As the boundary of stability of this state (spinodal) is approached, the composition fluctuations increase at length scales of the order of the network mesh size. The corresponding peak in the scattering function was predicted theoretically[2] and observed in recent experiments.[11,12]

Thus, the onset of microphase separation from the homogeneous state of the cross-linked blends has been well understood. On the other hand, the structure of the microphase-separated state has been studied in much less detail. Computer simulation of microphase separation in interpenetrating binary polymer networks has been performed by Schulz et al.[13] The mean field theory of the microphase-separated state for such networks has been developed by Schulz[9] on the basis of the Leibler approach.[14] This class of theories predicts the formation of ordered periodic superstructures with different symmetries, such as lamellar, cylindrical, and spherical mesophases similar to those in melts and solutions of block copolymers. But there is a qualitative difference between translationally invariant solutions or melts and polymer networks with broken translational invariance due to randomness of cross-linking process. It is therefore very interesting to find out how this broken translational invariance affects the microphase separation process in networks. This important question is the subject of the present paper.

Consider a network, prepared from a mixture of chains A and B above their phase separation transition. If we cool the network below a certain temperature, the chains would tend to phase separate. Cross-links prevent macrophase separation, and chains can only move apart on microscopic scales of the order of network mesh size, forming domains of increased fractions of either chain A or B.[2] Below we demonstrate that these microscopic domains in an undeformed network organize themselves into a microstructure with only *finite-range order*, while the *long-range orientational order* appears upon anisotropic macroscopic deformation of the network.

The physical reason for such phenomenon is the existence of quenched random stresses in any real network. In the process of microphase separation a given chain is displaced, locally stretching the network. Thus, there is a returning force acting on this chain from the network through its cross-links. To form an ordered microstructure, different chains have to be displaced from their original average positions, determined during the random cross-linking process. Thus, *there are random forces acting on the microstructure from the network and destroying long-range order*.

In section 2 we present a theory of microphase separation in undeformed networks. In section 3 we propose a simple one-dimensional model which provides simple physical picture of the destruction of long-range order due to quenched random forces. The appearance of long-range orientational order in anisotropically deformed network is demonstrated in section 4. This interesting effect can be observed in scattering experiments. The scattering function from these deformed networks is presented in section 5. In section 6 we summarize our main results and propose experiments to verify them.

2. Undeformed Networks

If random forces in a network are neglected, the microphase separation results in an ordered microstruc-

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1996.

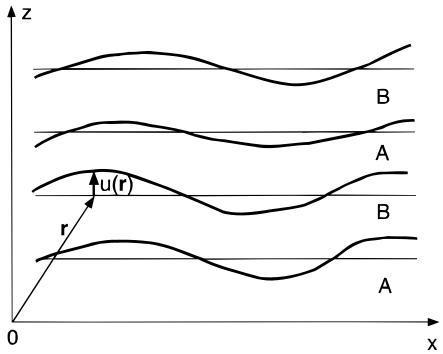

Figure 1. Displacement field $u(\mathbf{r})$, defined as a deviation in the z-direction of a lamella at point $\mathbf{r}$ from the ideal structure.

ture. For simplicity, we consider a strongly segregated lamellar mesophase which, in ideal state, is a one-dimensional lattice say, along the z-axis. The deformation of the lamellar structure from this ideal state can be described by the displacement field $u(\mathbf{r})$[16] that defines the deviation of a lamella at position $\mathbf{r}$ in the z-direction (see Figure 1). Obviously, this displacement field can only be defined in the regime where the superstructure does not deviate significantly from the ideal one. The free energy of such deformation can be expanded in powers of the displacement field and its derivatives.

We first consider the part of the free energy independent of the quenched disorder. First-order derivatives of $u(\mathbf{r})$ in directions parallel to lamellar planes correspond to mere rotations of the system. Since such rotations do not change the energy of an isotropic system, they do not contribute to the free energy of an undeformed or an isotropically deformed network. Thus, only the first-order derivative in the direction perpendicular to the planes ($\partial u/\partial z$), corresponding to compression or expansion of lamellar thickness, enters the free energy. The second-order derviatives ($\partial^2 u/\partial x^2 + \partial^2 u/\partial y^2$) correspond to the bending of the lamellar planes and thus cost energy. Therefore, the lowest order contributions to the free energy from the derivatives of u in the directions parallel and perpendicular to planes are

$$\frac{1}{2}\int \mathrm{d}\mathbf{r}\left[B\left(\frac{\partial u}{\partial z}\right)^2 + K\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}\right)^2\right] \tag{1}$$

This is the well-known form of the free energy of lamellar and smectic structures,[16] where B is the layer compressibility modulus and K is the splay elastic coefficient. The layer compressibility B is of the order of network modulus

$$B \simeq k_B T\rho/N \tag{2}$$

where k_B is the Boltzmann constant, T is the absolute temperature, ρ is the total monomer density, and N is the degree of polymerization between neighboring cross-links (we assume that N is the same for both chains of type A and B). The splay constant K is of the order of

$$K \approx Bd^2 \tag{3}$$

where the layer thickness d is of the order of the size of a typical chain[2] with N monomers each of length a

$$d \simeq aN^{1/2} \tag{4}$$

The main additional feature of the network is the presence of the forces acting on the displaced (stretched) chains from randomly placed cross-links.[17] The contribution of these random forces to the free energy is the term, linear in displacement field, u

$$-\int \mathrm{d}\mathbf{r}\, f(\mathbf{r})\, u(\mathbf{r}) \tag{5}$$

where $f(\mathbf{r})$ is the force per unit volume acting on the lamellar at a point $\mathbf{r}$. This density of force $f(\mathbf{r})$ can be taken to be a Gaussian random variable with zero average $\overline{f(\mathbf{r})} = 0$ and δ-function correlations

$$\overline{f(\mathbf{r})\, f(\mathbf{r}')} = g\delta(\mathbf{r}-\mathbf{r}') \tag{6}$$

The bar denotes the averaging over quenched randomness or, alternatively, averaging over the sample volume. The value of g is related to the mean-square fluctuations of the random force $F = \int \mathrm{d}\mathbf{r}\, f(\mathbf{r})$ acting on the mesh volume d^3, occupied by a chain. From eq 6 it is easy to see that $g \simeq F^2/d^3$. The typical magnitude of the random force F with zero average can be estimated as $(\rho d^3/N)^{1/2}(k_B T/d)$, where $\rho d^3/N$ is the average number of chains in the volume d^3 and $k_B T/d$ is the force necessary to stretch a typical chain of size d (mesh size) by approximately factor of 2, in order to place it into an appropriate lamella. Therefore

$$g \simeq (\rho/N)(k_B T/d)^2 \tag{7}$$

Combining the contributions to the free energy from the deformations of lamellar structure, eq 1, and random forces, eq 5, we obtain[15]

$$F = \int \mathrm{d}\mathbf{r}\left\{\frac{1}{2}\left[B\left(\frac{\partial u}{\partial z}\right)^2 + K\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}\right)^2\right] - f(\mathbf{r})\, u(\mathbf{r})\right\} \tag{8}$$

Note that the gradient terms in the free energy (square bracket in eq 8) tend to stabilize the order, while the random force term, eq 5, tends to disorder the lamellar structure. The resulting equilibrium displacement can be found by minimizing the free energy (eq 8). It is more convenient to carry out this minimization in Fourier space. Let us define the Fourier components of the displacement field u and of the random force density f

$$u_{\mathbf{q}} = \int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^3} u(\mathbf{r}) \exp(-i\mathbf{q}\mathbf{r}),$$
$$f_{\mathbf{q}} = \int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^3} f(\mathbf{r}) \exp(-i\mathbf{q}\mathbf{r}) \tag{9}$$

The free energy F (eq 8) can be rewritten in terms of these Fourier components

$$F = \int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^3}\left\{\frac{1}{2}(Bq_z^{\,2} + Kq_\perp^{\,4})u_{\mathbf{q}}u_{-\mathbf{q}} - f_{\mathbf{q}}u_{-\mathbf{q}}\right\} \tag{10}$$

where the projection $q_\perp$ of wave vector $\mathbf{q}$ into xy plane is defined by $q_\perp^2 = q_x^2 + q_y^2$. Minimizing this free energy with respect to displacement $u_{\mathbf{q}}$, we find

$$u_{\mathbf{q}} = \frac{f_{\mathbf{q}}}{Bq_z^{\,2} + Kq_\perp^{\,4}} \tag{11}$$

The degree of order (or disorder) in the lamellar structure can be characterized by the correlations between displacements at positions $\mathbf{r}$ and $\mathbf{r}'$. The displacement correlation function $\overline{[u(\mathbf{r}) - u(\mathbf{r}')]^2}$ is the average of the square of the relative displacement in the z-direction of lamellae at $\mathbf{r}$ and $\mathbf{r}'$ with respect to their ideal spacing. The displacement correlation function can be expressed in terms of Fourier components $u_{\mathbf{q}}$ as

$$\overline{[u(\mathbf{r}) - u(\mathbf{r}')]^2} = 2\int \frac{d\mathbf{q}}{(2\pi)^3}\overline{u_{\mathbf{q}}u_{-\mathbf{q}}}\{1 - \cos[\mathbf{q}(\mathbf{r}-\mathbf{r}')]\} \tag{12}$$

Using eq 11 for equilibrium displacement we obtain

$$\overline{[u(\mathbf{r}) - u(\mathbf{r}')]^2} = 2\int \frac{d\mathbf{q}}{(2\pi)^3}\frac{\overline{f_{\mathbf{q}}f_{-\mathbf{q}}}}{(Bq_z^{\ 2} + Kq_\perp^{\ 4})^2} \times \{1 - \cos[\mathbf{q}(\mathbf{r}-\mathbf{r}')]\} \tag{13}$$

From the δ-function correlations of random forces (eq 6) we find

$$\overline{[u(\mathbf{r}) - u(\mathbf{r}')]^2} = 2g\int \frac{d\mathbf{q}}{(2\pi)^3}\frac{1 - \cos[\mathbf{q}(\mathbf{r}-\mathbf{r}')]}{(Bq_z^{\ 2} + Kq_\perp^{\ 4})^2} \tag{14}$$

The fact that this integral diverges at small q implies that displacement correlations are lost at large distances. In order to define a displacement field u, one has to assume the existence of the meaningful reference ideal state. If the structure is disturbed very far from this ideal state, the displacement field u is ill-defined. The parts of the space where the displacement field is well-defined are called correlation regions. The sizes of these correlation regions $\xi_x^{or} \approx \xi_y^{or}$ and ξ_z^{or} determine the wavelengths of the cutoff of the integral in eq 14 along the corresponding directions. From the denominator of eq 14 we see that the cutoffs $q_x^{cut} \approx 1/\xi_x^{or}$ and $q_y^{cut} \approx 1/\xi_y^{or}$ are related by $B(q_z^{cut})^2 \approx K(q_x^{cut})^4$ (see page 354 of ref 16 for more detailed discussion). From the relation (3) between splay constant K and layer compressibility B we conclude that correlation regions are elongated along the z-direction

$$\xi_x^{or} \simeq \xi_y^{or} \simeq (\xi_z^{or}d)^{1/2} \tag{15}$$

Calculating the integral (14) with these cutoffs leads to the displacement correlation function proportional to the size ξ_z^{or} of the correlation region of the sample in the z-direction

$$\overline{[u(\mathbf{r}) - u(\mathbf{r}')]^2} \simeq (z - z')^2\frac{d}{l}\ln\frac{\xi_z^{or}}{|z - z'|} + [(x - x')^2 + (y - y')^2]\frac{\xi_z^{or}}{l'} \tag{16}$$

where

$$l \simeq dB^{3/2}K^{1/2}/g; \quad l' \simeq BK/g \tag{17}$$

Substituting the estimates of the random force correlator g (eq 7), layer compressibility B (eq 2), and splay constant K (eq 3), into eq 17 we get

$$l \simeq l' \simeq \rho d^4/N \simeq aN \tag{18}$$

From the displacement correlation function (16) we can estimate the sizes $\xi_x^{or} \simeq \xi_y^{or}$ and ξ_z^{or} of the correlation regions. These regions where the displacement field is well-defined are the parts of space where the normals to lamellar planes are rotated by the angles less than $\pi/2$ with respect to the ideal state (see Figure 2). Let us first analyze the displacement field in the x-direction. In order for layers to turn by the angle $\pi/2$ on the length scale ξ_x^{or}, the displacement has to be of the same order of magnitude $\overline{[u(\xi_x^{or}) - u(0)]^2} \simeq (\xi_x^{or})^2$. Therefore, from eq 16 we conclude that

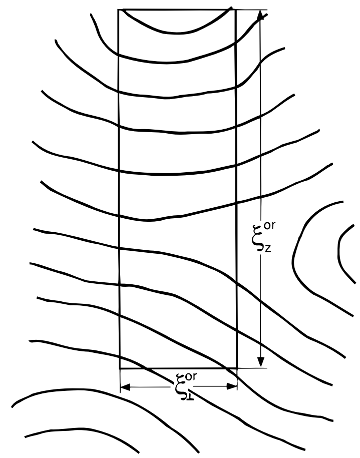

Figure 2. Distorted conformation of the lamellae under the influence of random forces from the network. The correlation region is sketched by the rectangle with dimensions ξ_z^{or} and $\xi_\perp^{or}$ (the orientational correlation lengths).

$$\xi_z^{or} \simeq l \simeq aN \tag{19}$$

From eqs 15 and 19 we get

$$\xi_x^{or} \simeq \xi_y^{or} \simeq aN^{3/4} \tag{20}$$

Let us describe the physical picture proposed above. The orientational order of lamellar planes is well-defined only in the asymmetric correlation regions of the size $\xi_x^{or} \simeq \xi_y^{or} < \xi_z^{or}$; see eqs 19 and 20. The lamellar planes are randomly rotated on larger length scales, and the directions of the normals to planes are uncorrelated between different correlation regions. The translational order exists only at distances along the normal at which the displacement correlation function is smaller than the square of the lamellar thickness. The condition $\overline{[u(\xi_z^{tr}) - u(0)]^2} \simeq d^2$ defines the correlation length of the translational order. Using eq 16 we find

$$\xi_z^{tr} \simeq [dl/\ln(l/d)]^{1/2} \simeq aN^{3/4}(\ln N)^{-1/2} \tag{21}$$

Thus, in undeformed polymer networks there are only short-range *orientational* and *translational orders* with the correlation lengths ξ_z^{or} and ξ_z^{tr}, respectively (in z-direction).

3. Simple Model

It is interesting to point out that the correlations on length scales smaller than ξ_z^{or} are affected by the size of the whole correlated region ξ_z^{or} (see eq 16). In order to understand this unusual dependence of the displacement correlation function on the size ξ_z^{or}, let us discuss a simple model with similar behavior. Consider a one-dimensional regular array of L beads equally spaced along the z-axis and connected to their nearest neigh-

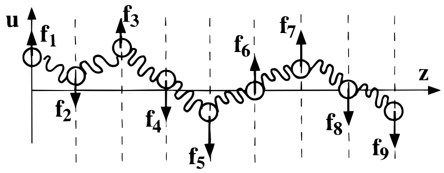

Figure 3. One-dimensional random force model.

bors by Gaussian springs with elastic constant B. There is a force f_j acting on bead j ($j = 1, ..., L$) in the direction normal to the z-axis (along the u-axis, see Figure 3). Beads can only move along the u direction. We assume that the forces $\{f_j\}$ are independent Gaussian random values with zero averge ($\overline{f_j} = 0$) and mean square deviation $\overline{f_j^2} = g$.

The Hamiltonian of this 1 + 1-dimensional model has the form

$$H = \frac{B}{2}\sum_{j=1}^{L-1}(u_{j+1} - u_j)^2 - \sum_{j=1}^{L} f_j u_j \tag{22}$$

The forces f_j tend to randomly displace the beads up and down along the u-axis. Their contribution to the Hamiltonian is given by the second sum in eq 22. The Gaussian springs connecting the neighboring beads tend to stabilize bead displacement (first sum in eq 22). Note the strong analogy of this simple one-dimensional model with our multicomponent network (eq 8).

Consider a section of the array, consisting of n beads, and let us first ignore its connection to the rest of the array. The mean square force acting on this section increases linearly with the size of the section

$$\overline{\left(\sum_{j=m}^{m+n} f_j\right)^2} = \sum_{j=m}^{m+n} \overline{f_j^2} = gn \tag{23}$$

The elastic modulus of the section of n beads decreases inversely proportional to the section size, $G_{m,m+n} \simeq B/n$. Therefore, the typical deformation of the section along the u-axis (the relative displacement of its ends in the u-direction) is the ratio of the root-mean-square force $(gn)^{1/2}$ and the modulus B/n:

$$\sqrt{\overline{(u_{n+m} - u_m)^2}} \approx \frac{\sqrt{g}}{B}\, n^{3/2} \tag{24}$$

The fact that the relative displacement of the ends of the section of n beads grows faster than linear is the reason that the tension in the array due to deformations on the largest length scale (the size of the whole array) controls the displacement on all length scales. Indeed, let us assume that our section is the whole array ($n = L$). Then the discussion above is correct and the typical relative displacement of the array ends is

$$\sqrt{\overline{(u_L - u_1)^2}} \simeq \frac{\sqrt{g}}{B}\, L^{3/2} \tag{25}$$

The tension $(gL)^{1/2}$ due to this formation forces the relative displacement of beads on smaller length scales

$$\sqrt{\overline{(u_{n+m} - u_m)^2}} \simeq \frac{\sqrt{gL}}{B}\, n \tag{26}$$

which is larger than the deformation due to the forces directly acting on this subsection (eq 24). Therefore, we conclude that the deformation on all length scales in this simple one-dimensional model depends on the system size

$$\overline{(u_{n+m} - u_m)^2} \approx \frac{g}{B^2} L n^2 \tag{27}$$

The reason for this unusual deformation is that the random forces deform the whole sample stronger than linear ($\sim L^{3/2}$), creating tension that dominates deformation on all length scales. We stress that this behavior is due to one-dimensional elasticity of our simple model.

Similarly, in the network with uncorrelated regions of size $L = \xi_z^{\text{or}}$ the displacement correlations on length scales down to the mesh size depend on the larger length scale ξ_z^{or}. The reason for this is that the lamellar structure displays one-dimensional-like layer compressibility with elastic modulus B (see eq 10). There is no *elastic moduli* in the directions along the lamellar planes. The stiffness of the system in these "soft" directions is related only to its resistance to lamellar bending with the splay modulus K.

4. Anisotropically Deformed Networks

The elastic moduli in the soft directions can be induced by the anisotropic deformation of the sample. Such deformation breaks the rotational symmetry of the system. Therefore, there are additional terms in the free energy (10) representing the system stiffness in such "soft" directions. The elastic moduli in these directions are thus proportional to the anisotropy of the network deformation[17]

$$\epsilon_x \simeq {\lambda_x}^2 - {\lambda_z}^2, \quad \epsilon_y \simeq {\lambda_y}^2 - {\lambda_z}^2 \tag{28}$$

where λ_α is the relative sample stretching (or compression) in the α-direction.

The free energy of the deformed network takes the form

$$F = \int \mathrm{d}\mathbf{r} \left\{ \frac{1}{2}B\left[\left(\frac{\partial u}{\partial z}\right)^2 + \epsilon_x\left(\frac{\partial u}{\partial x}\right)^2 + \epsilon_y\left(\frac{\partial u}{\partial y}\right)^2\right] + K\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}\right)^2 - f(\mathbf{r})\, u(\mathbf{r}) \right\} \tag{29}$$

For the stability of the system all the three elastic moduli in eq 29 have to be positive ($B > 0$, $\epsilon_x > 0$, $\epsilon_y > 0$) and therefore the system chooses the direction z normal to its layers to be directed along the smallest stretching axis ($\lambda_z < \lambda_x$ and $\lambda_z < \lambda_y$). The free energy of the anisotropically deformed network (29) can be expressed in terms of Fourier components of the displacement field $u_{\mathbf{q}}$ and the random force density $f_{\mathbf{q}}$ (eq 9) as

$$F = \int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^3} \left\{ \frac{1}{2}\left[B({q_z}^2 + \epsilon_x {q_x}^2 + \epsilon_y {q_y}^2) + K{q_\perp}^4\right] u_{\mathbf{q}} u_{-\mathbf{q}} - f_{\mathbf{q}} u_{-\mathbf{q}} \right\} \tag{30}$$

This free energy can be minimized with respect to the displacement $u_{\mathbf{q}}$ with the result

$$u_{\mathbf{q}} = \frac{f_{\mathbf{q}}}{B({q_z}^2 + \epsilon_x {q_x}^2 + \epsilon_y {q_y}^2) + K{q_\perp}^4} \tag{31}$$

The displacement correlation function (eq 12) for anisotropically deformed network takes the form

$$\overline{[u(\mathbf{r}) - u(\mathbf{r}')]^2} = 2g\int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1 - \cos[\mathbf{q}(\mathbf{r}-\mathbf{r}')]}{[B(q_z^{\ 2} + \epsilon_x q_x^{\ 2} + \epsilon_y q_y^{\ 2}) + Kq_\perp^{\ 4}]^2} \quad (32)$$

The integral in the right-hand side of eq 32 converges at small q (recall that the integral in eq 13 for $\epsilon_x = \epsilon_y = 0$ diverges at small q). The displacement correlation function has two different asymptotic behaviors at different length scales.

At small distances it is estimated in Appendix A for a general case $\epsilon_x \neq \epsilon_y$. In a simpler case $\epsilon_x = \epsilon_y = \epsilon$ the displacement correlation function at small distances takes the form

$$\overline{[u(\mathbf{r}) - u(\mathbf{r}')]^2} \simeq \frac{d}{l}\left\{(z - z')^2 \ln \frac{d}{\epsilon|z - z'|} + \frac{1}{\epsilon}[(x - x')^2 + (y - y')^2]\right\} \quad (33)$$

In order to understand the physical meaning of this expression, let us consider the rotation of an ideal lamellar structure around the y-axis by a small angle θ_x. This rotation can be described by the displacement $u = \hat{z} - z$. Here the new coordinate $\hat{z} = z \cos \theta_x - x \sin \theta_x$. For small rotations the displacement u can be expanded in angle θ_x as $u(\mathbf{r}) - u(\mathbf{r}') = \theta_x^2(z - z')/2 + \theta_x(x - x')$. Different parts of the structure are turned by a different angle θ_x. Therefore, we can express the mean square average displacement in terms of fluctuation of rotational angle θ_x

$$\overline{[u(\mathbf{r}) - u(\mathbf{r}')]^2} \simeq \frac{\overline{\theta_x^{\ 4}}}{4}(z - z')^2 + \overline{\theta_x^{\ 2}}(x - x')^2 \quad (34)$$

This description can be easily generalized to the case of local rotation by two angles θ_x and θ_y. Comparing the displacement correlation function obtained above (expression 33) with eq 34 we find the mean square angle of plane rotation

$$\overline{\theta_x^{\ 2}} \simeq \overline{\theta_x^{\ 2}} \simeq \frac{d}{l\epsilon} \simeq \frac{1}{\sqrt{N}\epsilon} \quad (35)$$

This picture is valid only as long as the mean square values of the angles $\overline{\theta_x^{\ 2}}$ and $\overline{\theta_y^{\ 2}}$ are small. The condition $\overline{\theta_x^{\ 2}} \simeq \overline{\theta_y^{\ 2}} \simeq 1$ is the onset of global orientational ordering of lamellar planes. This condition corresponds to stress anisotropy

$$\epsilon_c \simeq d/L \simeq N^{-1/2} \quad (36)$$

At higher anisotropy $\epsilon > \epsilon_c$ there is *a global orientational order* with lamella planes, on average, perpendicular to the z-axis (direction of the smallest elongation).

The displacement correlation function at large distances can be estimated from eq 32 by neglecting the term due to splay $\sim K$ (see Appendix A)

$$\overline{[u(\mathbf{r}) - u(\mathbf{r}')]^2} = \frac{d^2}{l\epsilon}\sqrt{(z - z')^2 + \frac{1}{\epsilon}[(x - x')^2 + (y - y')^2]} \quad (37)$$

The crossover between the two limiting behaviors of the displacement correlation function (eqs 33 and 37) occurs at length scales

$$\xi_z^{\mathrm{or}} \simeq d/\epsilon = aN^{1/2}/\epsilon \quad (38)$$

$$\xi_x^{\mathrm{or}} \simeq \xi_y^{\mathrm{or}} \simeq \xi_\perp^{\mathrm{or}} \simeq d/\sqrt{\epsilon} = aN^{1/2}\epsilon^{-1/2}$$

Note that at the threshold of the anisotropy effects $\epsilon \simeq \epsilon_c$ these crossover length scales (eq 38) coincide with the corresponding dimensions of the correlation volume, eqs 19 and 20, and eq 33 coincides with (16).

The two asymptotic expressions of the displacement correlation function (eqs 33 and 37) describe two different types of deformations of the lamella planes on different length scales. At distances shorter than the crossover lengths $\{\xi_z^{\mathrm{or}}, \xi_\perp^{\mathrm{or}}\}$ the relative displacement of the planes corresponds to their simple rotation (eq 34) by random angles. Deformation of the lamellar structure on larger length scales is a random bending of layers. On these length scales the normal to the lamellar planes fluctuates around the z-axis by a small angle. Thus the structure has a long-range orientational order.

The energy cost of rotation of the lamellar planes in anisotropically deformed network grows with the increasing size of rotated regions. This leads to the decrease of the average sizes ξ_z^{or} and $\xi_\perp^{\mathrm{or}}$ of these regions with increasing anisotropy parameter ϵ, which is described by eq 38. For extremely large anisotropy ($\epsilon \geq 1$) the rotation of lamellar planes is strongly suppressed and they are ordered in sandwich-like structure. Note that even in this case *there is no long-range translational order* because of fluctuations of domain widths with variations of local density of cross-links which is frozen-in during the process of network preparation.

We now discuss the limits of validity of our theory. In general, the free energy of the structure can be expanded in powers of displacement tensor, eq 29. The Gaussian character of displacement fluctuations is valid only for small values of $\partial u/\partial z$. Estimating the mean square of this value using eqs 14 and 33, we find $\overline{(\partial u/\partial z)^2} \approx d/l \approx N^{-1/2}$. This allows us to neglect the non-Gaussian character of the fluctuations.

5. Structure Factors

Consider, for simplicity, the symmetric composition of components A and B with uniform total density $\rho_A(\mathbf{r}) + \rho_B(\mathbf{r}) = \rho = \text{const}$, where $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$ are monomeric densities of the components A and B at position $\mathbf{r}$. Define the compositional deviation of component A (or B) from its average (over the whole sample) value $\rho/2$

$$\psi(\mathbf{r}) = \rho_A(\mathbf{r}) - \rho/2 = -(\rho_B(\mathbf{r}) - \rho/2) \quad (39)$$

In an ideal lamellar mesophase this compositional difference can be expanded in Fourier series as

$$\psi(z) = \sum_{n=-\infty}^{\infty} \psi_n e^{iQ(2n+1)z} \quad (40)$$

where the wave vector Q is related to the period d of the structure $Q = 2\pi/d$ and is directed along the z-axis. In the strong segregation limit the Fourier amplitudes ψ_n have the form

$$\psi_n = \frac{2i\rho}{\pi(2n+1)} \tag{41}$$

The scattering from such ideal structure produces δ-peaks at wave vectors $(2n + 1)Q$ with the amplitudes $|\psi_n|^2$.

Random forces, acting on the lamellae, cause displacements $u(\mathbf{r})$ from this ideal structure. The compositional deviation $\psi(\mathbf{r})$ in such nonideal state can be expressed in terms of this displacement field $u(\mathbf{r})$ through the Fourier series

$$\psi(\mathbf{r}) = \sum_{n=-\infty}^{\infty} \psi_n e^{iQ(2n+1)[z-u(\mathbf{r})]} \tag{42}$$

where the amplitudes ψ_n are still given by eq 41 in the strong segregation limit.

Since light, X-rays, and neutrons are scattered by composition deviations, we need to calculate the correlation function of these composition deviations. This calculation is described in detail in Appendix B with the result

$$\overline{\psi(\mathbf{r})\,\psi(\mathbf{r}')} = \sum_{n=-\infty}^{\infty} |\psi_n|^2 \exp\left\{iQ(2n+1)(z-z') - \frac{Q^2(2n+1)^2}{2}\overline{[u(\mathbf{r}) - u(\mathbf{r}')]^2}\right\} \tag{43}$$

The structure factor $S(\mathbf{q})$ is the Fourier component of this correlation function and is calculated in Appendix B in the general case of anisotropic deformation of the network ($\epsilon_x \neq \epsilon_y$). For simplicity, we limit our consideration below to a uniaxially compressed network with single anisotropy parameter $\epsilon_x = \epsilon_y = \epsilon$. There are three characteristic regions depending on this parameter.

1. In the case of small anisotropy of deformation ($\epsilon < \epsilon_c \simeq N^{-1/2}$) the scattering function

$$S_1(\mathbf{q}) \simeq \rho^2 d^2 \xi_z^{\mathrm{tr}} \exp\left[-(\xi_z^{\mathrm{tr}})^2 (q - Q)^2\right] \tag{44}$$

is spherically symmetric (does not depend on the direction of the wave vector $\mathbf{q}$). As can be seen from the 3D plot $S_1(q_z,q_\perp)$ in Figure 4a, it reaches its maximum at $q = Q$. This maximum is sharp with the width inversely proportional to the translational correlation length $\xi_z^{\mathrm{tr}} \simeq aN^{3/4}(\ln N)^{-1/2}$ (see eq 21).

2. In the case of intermediate anisotropy, $\epsilon_c < \epsilon < \epsilon_c^{1/2}$, the long-range lamellar order appears. In this regime the main contribution to the structure factor comes from random rotation of lamellar planes, eq 33, and the structure factor is

$$S_2(\mathbf{q}) = \rho^2 \xi_z^{\mathrm{tr}} (\xi_\perp^{\mathrm{tr}})^2 \sum_{n=-\infty}^{\infty} \frac{1}{(2n+1)^5} \times \exp\left[-\frac{(\xi_z^{\mathrm{tr}})^2 (q_z - (2n+1)Q)^2 - (\xi_\perp^{\mathrm{tr}})^2 q_\perp^{\,2}}{2(2n+1)^2}\right] \tag{45}$$

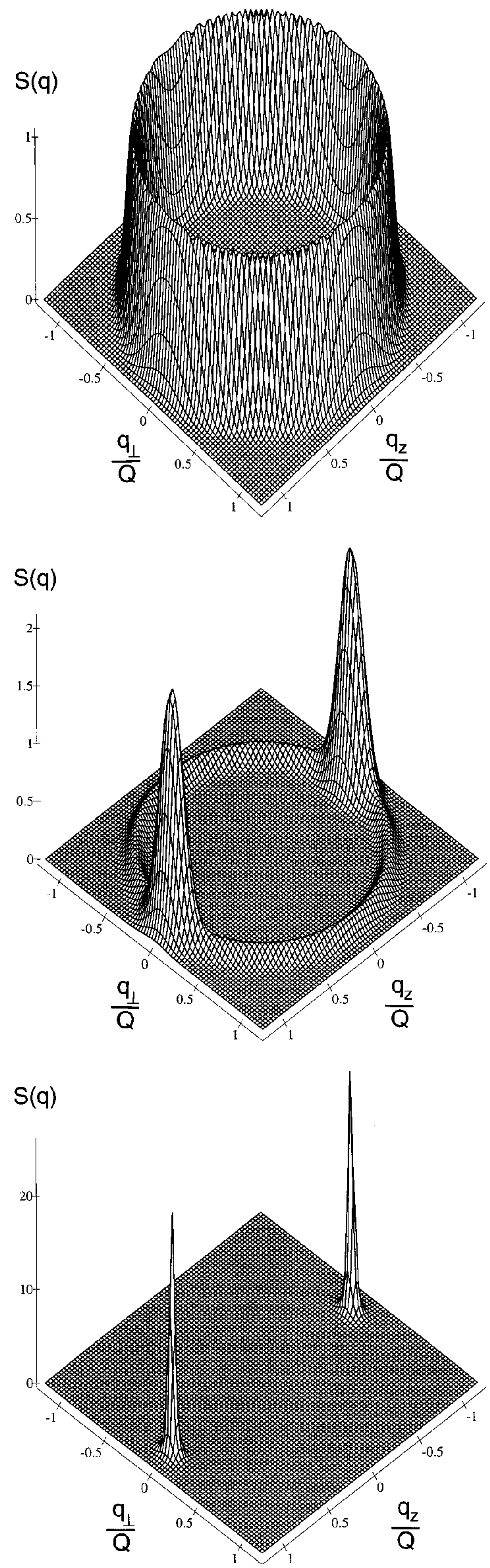

Figure 4. Three-dimensional plot of the structure factors $S(q_z, q_\perp)$ of the microphase-separated network. The number of monomers between cross-links is $N = 100$. (a, top) Undeformed network ($\epsilon = 0$); (b, middle) Intermediate anisotropy regime ($\epsilon = 0.2$); (c, bottom) Strong anisotropy regime ($\epsilon = 0.5$).

The translational correlation lengths along and perpendicular to the z-direction are

$$\xi_z^{tr} \simeq \left(dl\Big/\ln\frac{d}{l\epsilon^2}\right)^{1/2} \simeq aN^{3/4}\left(\ln\frac{1}{\sqrt{N}\epsilon^2}\right)$$

$$\xi_\perp^{tr} \simeq (dl\epsilon)^{1/2} \simeq aN^{3/4}\sqrt{\epsilon} \qquad (46)$$

At the threshold of the anisotropy effects, $\epsilon \simeq \epsilon_c$, the maxima of the structure factors at small and intermediate anisotropy coincide, $S_1(\mathbf{Q}) = S_2(\mathbf{Q})$. In the crossover region $\epsilon \sim \epsilon_c$ the structure factor can be written in the form

$$S(\mathbf{q}) = p(\epsilon)\, S_1(\mathbf{q}) + (1 - p(\epsilon))S_2(\mathbf{q}) \qquad (47)$$

Here $p(\epsilon) = e^{-\epsilon/\epsilon_c}$ is the probability that the directions of lamellar planes are pinned by random forces within the corresponding correlation regions (see Appendix C). The plot of the scattering function (47) is shown in Figure 4b. This picture clearly demonstrates the appearance of pronounced peaks at wavevectors $\pm\mathbf{Q}$. The height of these peaks grows linearly with the parameter of anisotropy ϵ. The width of the peaks in the direction normal to the wave vector of the structure is inversely proportional to the translational correlation length $\xi_\perp^{tr}$. This width is of the order of wave vector Q at the crossover between the weak and intermediate anisotropies ($\epsilon \simeq \epsilon_c$) and decreases with increasing anisotropy as $\epsilon^{-1/2}$.

3. In the case of strong anisotropy, $\epsilon_c^{1/2} < \epsilon$, only the random bending of lamellar layers, eq 37, contributes to the structure factor

$$S_3(\mathbf{q}) \simeq \frac{\rho^2}{l}\sum_{n=-\infty}^{\infty}\left[(q_z - (2n+1)Q)^2 + \epsilon q_\perp{}^2 + \frac{(2n+1)^4}{(\xi_z^{tr})^2}\right]^{-2} \qquad (48)$$

where the translational correlation length in the z-direction is

$$\xi_z^{tr} \simeq l\epsilon \simeq aN\epsilon \qquad (49)$$

The corresponding correlation length in the directions along the lamellar plate is

$$\xi_\perp^{tr} = \epsilon^{1/2}\xi_z^{tr} \simeq aN\epsilon^{3/2} \qquad (50)$$

Note that the higher order peaks at wave vectors $(2n + 1)\mathbf{Q}$ are hard to observe, as their heights fall off as $(2n + 1)^{-8}$ ($|2n + 1|^{-5}$ for intermediate anisotropies). The peaks at wave vectors $\pm\mathbf{Q}$ are extremely sharp as shown in Figure 4c. The height of these peaks is a strongly increasing function of anisotropy ($\sim\epsilon^4$). The width of the peaks is decreasing inversely proportional to the corresponding translational correlation lengths (eqs 49 and 50). The asymmetry of the peaks is decreasing as $\xi_z^{tr}/\xi_\perp^{tr} \simeq \epsilon^{-1/2}$ with anisotropy of deformation.

The orientational correlation lengths ξ_z^{or} and $\xi_\perp^{or}$ are decreasing functions of the parameter of anisotropy ϵ, while the translational correlation lengths ξ_z^{tr} and $\xi_\perp^{tr}$ are increasing functions of ϵ, as can be seen in Figure 5. At low and intermediate anisotropies (for $\epsilon < \epsilon_c^{1/2}$) the orientational correlation lengths ξ_z^{or} and $\xi_\perp^{or}$ determine the sizes of the correlation region. Inside this region the deformation of the structure is related to the rotations of the layers. These rotations lead to loss of translational correlations at distances ξ_z^{tr} and $\xi_\perp^{tr}$. The orientational and translational correlation lengths coincide at the crossover between intermediate and strong anisotropies

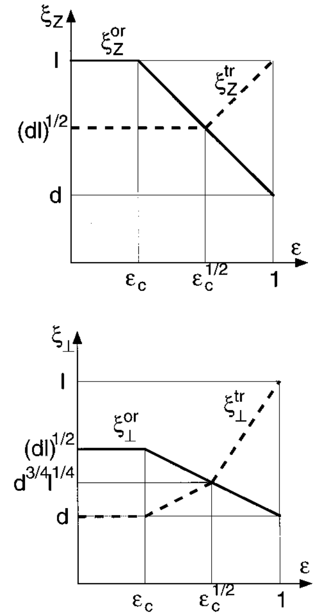

Figure 5. Double logarithmic plot of the orientational and translational correlation lengths as functions of anisotropy parameter ϵ: (a, top) Correlation lengths ξ_z^{or} and ξ_z^{tr} in the direction of weakest anisotropy; (b, bottom) Correlation lengths $\xi_\perp^{or}$ and $\xi_\perp^{tr}$ in the plane normal to the direction of weakest anisotropy.

$$\left.\begin{aligned}\xi_z^{or} \simeq \xi_z^{tr} \simeq (dl)^{1/2} \simeq aN^{3/4}\\ \xi_\perp^{or} \simeq \xi_\perp^{tr} \simeq d^{3/4}l^{1/4} \simeq aN^{5/8}\end{aligned}\right\} \text{ at } \epsilon \simeq \epsilon_c{}^{1/2} \simeq N^{-1/4} \qquad (51)$$

In the region of strong anisotropies (for $\epsilon > \epsilon_c^{1/2}$) the translational correlation lengths are longer than the orientational ones ($\xi_z^{tr} > \xi_z^{or}$, $\xi_\perp^{tr} > \xi_\perp^{or}$). The deformation on small length scales (up to orientational correlation length) corresponds to rotation of the layers. The displacement field u at length scales ξ^{or} is still small compared to layer spacing d. At larger length scales the directions of rotation are not correlated with each other. The mean square displacement field grows linearly with the distance and reaches d^2 at translational correlation length scales ξ^{tr}. Note that the pairs of orientational and translational correlation length have the same asymmetry (up to logarithmic corrections, see eqs 46, 49, 50, and 38)

$$\frac{\xi_z^{or}}{\xi_\perp^{or}} \simeq \frac{\xi_z^{tr}}{\xi_\perp^{tr}} \simeq \epsilon^{-1/2} \qquad (52)$$

6. Conclusion

Microphase separation in polymer networks is significantly different from that in block and graft copolymers. The main reason for this difference is the existence of quenched random forces acting on lamellar planes from the network, which are balanced by elastic deformations of the network. These forces destroy the long-range order in the microphase-separated networks. The short-range order is still presented, but the lamellar planes are rotated with respect to each other (see Figure

2). The length scales at which this rotation reaches angles of order unity define the orientational correlation lengths. At length scales larger than these orientational correlation lengths the lamellar planes are turned by random angles with respect to each other. The scattering from such structure is spherically symmetric with a peak independent of the direction of the scattering wavevector.

Upon anisotropic deformation of the network, normals to the lamella planes tend to turn into the direction of the weakest stretching. The deviations of the normals from this preferred direction decrease with increasing anisotropy. These deviations correspond to the rotation of lamella planes inside orientational correlation regions. On large length scales the correlations between these rotations are lost leading to random bending of lamella. The size of the orientational correlation volume decreases with increasing anisotropy. The scattering from these anisotropically deformed microphase-separated networks has two pronounced peaks in the weakest stretching direction. The height of these peaks rapidly increases and their width decreases with anisotropy. This is the signature of a long-range orientational order. The lamellar planes can be rotated by changing the direction of weakest stretching. These interesting effects can also be observed by transmission electron microscopy of freeze-dried samples.[18]

Note that the destruction of the lamellar order in polymer *solids* is different from that in polymer *liquids* subjected to an external quenched random field.[19] The random forces in polymer networks are an inevitable ingredient due to the random nature of the cross-linking process, while the random quenched field is not intrinsic to polymer liquids. To destroy the long-range order one has to place the block copolymer liquid into the random medium with the special correlation properties (with the correlation radius of the random field of the order of block size). Another difference is the presence of the long-range elastic stresses in polymer networks. These stresses restore the long-range order under the anisotropic deformation of the network.

The networks discussed in the present paper were assumed to be prepared (cross-linked) in the homogeneous state of the blend but studied in the microphase separated state of the network. The temperature difference between these two states can be quite large due to suppression of the microphase separation transition by cross-links.[2,3,6,11,12] This fact could make it quite difficult to find an experimental system with wide enough temperature window to include both of these states. One possible way to overcome this difficulty is to cross-link the network in a common solvent for both A and B polymers and to induce the microphase separation either by removing the solvent or by changing the relative quality of the solvent for the two polymers.

The first approach was recently used by Sakurai et al.[18] in a series of very interesting experiments. Triblocks of polystyrene−polybutadiene−polystyrene were cross-linked in a diocryl phthalate solvent in a homogeneous state. The solvent was later evaporated from the homogeneous gel, leading to microphase-separated network. This dry network was investigated by both transmission electron microscopy and small-angle X-ray scattering. These experiments clearly demonstrate that the cross-linking leads to the disorder of microphase-separated states in agreement with the predictions of the present paper. Unfortunately, the networks were not deformed in a controlled way to enable us to make a more quantitative comparison with our theory.

We hope that the future experiments will verify our predictions of the stress-induced ordering in microphase separated networks.

Acknowledgment. We are grateful to A. Dobrynin for useful discussions. The financial support of the NFS under Grants DMR 9409787 and 9696081 is gratefully acknowledged.

Appendix A

Calculation of Displacement Correlation Function. Here we calculate the displacement correlation function for the general case of anisotropically deformed network, eq 32, for both short and long distances $|\mathbf{r} - \mathbf{r}'|$. In the case of short distances we can expand $\cos[\mathbf{q}(\mathbf{r} - \mathbf{r}')]$ in powers of $\mathbf{r} - \mathbf{r}'$ to find

$$\overline{[u(\mathbf{r}) - u(\mathbf{r}')]^2} = (z - z')^2 I_z + (x - x')^2 I_x + (y - y')^2 I_y \quad \text{(A1)}$$

with

$$I_z \simeq \frac{g}{2\pi^3}\int_0^{\pi} \mathrm{d}\varphi \int_0^{\infty} \mathrm{d}q_\perp \int_0^{q_{\mathrm{cut}}} \mathrm{d}q_z \times \frac{q q_z^{\,2}}{\{B[q_z^{\,2} + q_\perp^{\,2}\,\epsilon(\varphi)] + K q_\perp^{\,4}\}^2} \quad \text{(A2)}$$

$$I_x = \frac{g}{2\pi^3}\int_0^{\pi} \mathrm{d}\varphi \int_0^{\infty} \mathrm{d}q_\perp \int_0^{\infty} \mathrm{d}q_z \times \frac{q^3 \cos^2\varphi}{\{B[q_z^{\,2} + q_\perp^{\,2}\epsilon(\varphi)] + K q_\perp^{\,4}\}^2} \quad \text{(A3)}$$

$$I_y = \frac{g}{2\pi^3}\int_0^{\pi} \mathrm{d}\varphi \int_0^{\infty} \mathrm{d}q_\perp \int_0^{\infty} \mathrm{d}q_z \times \frac{q^3 \sin^2\varphi}{\{B[q_z^{\,2} + q_\perp^{\,2}\epsilon(\varphi)] + K q_\perp^{\,4}\}^2} \quad \text{(A4)}$$

where $\epsilon(\varphi) \equiv \epsilon_x \cos^2\varphi + \epsilon_y \sin^2\varphi$ and we have replaced the integration variables

$$\mathbf{q} \equiv (q_x, q_y, q_z) = (q_\perp \cos\varphi, q_\perp \sin\varphi, q_z) \rightarrow (q_z, q_\perp, \varphi)$$

The cutoff $q_{\mathrm{cut}} \simeq |z - z'|^{-1}$ is determined by the limits of the validity of the expansion of $\cos[\mathbf{q}(\mathbf{r} - \mathbf{r}')]$. Performing the integration over q_z we find

$$I_z = \frac{g}{4\pi^3 B^{3/2}}\int_0^{\pi} \mathrm{d}\varphi \int_0^{\infty} \mathrm{d}q_\perp \times \left\{\frac{1}{[B\epsilon(\varphi) + K q_\perp^{\,2}]^{1/2}} \arctan \frac{B^{1/2} q_{\mathrm{cut}}}{q_\perp [B\epsilon(\varphi) + K q_\perp^{\,2}]^{1/2}} - \frac{q B^{1/2} q_{\mathrm{cut}}}{B\epsilon(\varphi)\, q_\perp^{\,2} + K q_\perp^{\,4} + B q_{\mathrm{cut}}^{\,2}}\right\} \quad \text{(A5)}$$

$$I_x = \frac{g}{8\pi^2 B^{1/2}}\int_0^{\pi} \mathrm{d}\varphi \int_0^{\infty} \mathrm{d}q_\perp \frac{\cos^2\varphi}{[B\epsilon(\varphi) + K q_\perp^{\,2}]^{3/2}} \quad \text{(A6)}$$

$$I_y = \frac{g}{8\pi^2 B^{1/2}}\int_0^{\pi} \mathrm{d}\varphi \int_0^{\infty} \mathrm{d}q_\perp \frac{\sin^2\varphi}{[B\epsilon(\varphi) + K q_\perp^{\,2}]^{3/2}} \quad \text{(A7)}$$

The integration over $q_\perp$ can be carried out in the above expressions with the result

$$I_z = \frac{g}{16\pi^2 B^{3/2} K^{1/2}} \int_0^{\pi} \mathrm{d}\varphi \ln \frac{4K^{1/2} q_{\mathrm{cut}}}{\mathrm{e}B^{1/2}\epsilon(\varphi)} \qquad \text{(A8)}$$

$$I_x = \frac{g}{8\pi^2 B^{3/2} K^{1/2}} \int_0^{\pi} \frac{\mathrm{d}\varphi \cos^2\varphi}{\epsilon(\varphi)} \qquad \text{(A9)}$$

$$I_y = \frac{g}{8\pi^2 B^{3/2} K^{1/2}} \int_0^{\pi} \frac{\mathrm{d}\varphi \sin^2\varphi}{\epsilon(\varphi)} \qquad \text{(A10)}$$

After the integration over φ we get

$$I_z = \frac{g}{16\pi B^{3/2} K^{1/2}} \ln \frac{16K^{1/2} q_{\mathrm{cut}}}{\mathrm{e}B^{1/2}(\epsilon_x^{1/2} + \epsilon_y^{1/2})^2} \qquad \text{(A11)}$$

$$I_x = \frac{g}{8\pi B^{3/2} K^{1/2}} \frac{1}{\epsilon_x^{1/2}(\epsilon_x^{1/2} + \epsilon_y^{1/2})} \qquad \text{(A12)}$$

$$I_y = \frac{g}{8\pi B^{3/2} K^{1/2}} \frac{1}{\epsilon_y^{1/2}(\epsilon_x^{1/2} + \epsilon_y^{1/2})} \qquad \text{(A13)}$$

Substituting these results (A11)–(A13) into eq A1 we obtain the expression for the displacement correlation function at short distances:

$$\overline{[u(\mathbf{r}) - u(\mathbf{r}')]^2} \simeq \frac{d}{l}\left[(z - z')^2 \ln \frac{d}{(\epsilon_x^{1/2} + \epsilon_y^{1/2})^2 |z - z'|} + \frac{(x - x')^2}{\epsilon_x^{1/2}(\epsilon_x^{1/2} + \epsilon_y^{1/2})} + \frac{(y - y')^2}{\epsilon_y^{1/2}(\epsilon_x^{1/2} + \epsilon_y^{1/2})}\right] \qquad \text{(A14)}$$

The displacement correlation function at long distances can be estimated from eq 32 by neglecting the term due to splay $\sim K$. The integration over $\mathbf{q}$ can be performed using the change of variables

$$\{\hat{z} = z, \hat{x} = x/\sqrt{\epsilon_x}, \hat{y} = y/\sqrt{\epsilon_y}\} \quad \text{and} \quad \{\hat{q}_z = q_z, \hat{q}_x = q_x\sqrt{\epsilon_x}, \hat{q}_y = q_y\sqrt{\epsilon_y}\}$$

In the new variables the displacement correlation function takes the form

$$\overline{[u(\mathbf{r}) - u(\mathbf{r}')]^2} = \frac{g}{B^2(\epsilon_x\epsilon_y)^{1/2}} \int \frac{\mathrm{d}\hat{\mathbf{q}}}{(2\pi^2)^3} \frac{1 - \cos[\hat{\mathbf{q}}(\hat{\mathbf{r}} - \hat{\mathbf{r}}')]}{\hat{q}^4} \simeq \frac{d^2}{l(\epsilon_x\epsilon_y)^{1/2}}\left[(z - z')^2 + \frac{(x - x')^2}{\epsilon_x} + \frac{(y - y')^2}{\epsilon_y}\right]^{1/2} \qquad \text{(A15)}$$

The crossover between the two limiting behaviors of the displacement correlation function (eqs A14 and A15) occurs at length scales ξ_z^{or}, ξ_x^{or}, and ξ_y^{or} in corresponding directions z, x, and y

$$\xi_z^{\mathrm{or}} \simeq \frac{d}{\sqrt{\epsilon_x\epsilon_y}}, \quad \xi_x^{\mathrm{or}} \simeq \xi_y^{\mathrm{or}} \simeq d\left(\frac{1}{\sqrt{\epsilon_x}} + \frac{1}{\sqrt{\epsilon_y}}\right) \qquad \text{(A16)}$$

Appendix B

Calculation of the Structure Factor. Below we calculate the correlation function $\overline{\psi(\mathbf{r})\,\psi(\mathbf{r}')}$ of the composition deviations $\psi(\mathbf{r})$ and the corresponding structure factor $S_{\mathbf{q}}$. Note that this function is normalized by the condition

$$\int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^3} S_{\mathbf{q}} = \overline{\psi^2(\mathbf{r})} = \rho^2 \qquad \text{(B1)}$$

which allows us to find the maximum $S_{\max}$ of the function $S_{\mathbf{q}}$ at $q = Q$ in the case of undeformed network. Using the fact that this function is spherically symmetric and depends only on the modulus of the wave vector q, we can rewrite the integral (B1) in the form

$$\int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^3} S_{\mathbf{q}} = \int \frac{\mathrm{d}q}{2\pi^2} q^2 S_{\mathbf{q}} \qquad \text{(B2)}$$

Since the scattering function $S_{\mathbf{q}}$ has a sharp maximum at $q = Q$ with the width $(\xi_z^{\mathrm{tr}})^{-1}$, we can approximate the integral by

$$\int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^3} S_{\mathbf{q}} \simeq Q^2(\xi_z^{\mathrm{tr}})^{-1} S_{\max} \qquad \text{(B3)}$$

Substituting this estimate into eq B1, we find that $S_{\max} \simeq \rho^2 d^2 \xi_z^{\mathrm{tr}}$. Neglecting non-Gaussian logarithmic dependence of the displacement correlation function, eq 16, we can represent the function $S_{\mathbf{q}}$ in the form (44).

The correlation function of the anisotropically deformed network requires more refined calculations. The composition deviations of a nonideal structure in the limit of strong segregation can be expressed through the displacement $u(\mathbf{r})$ from the ideal structure using the Fourier series representation (eq 42)

$$\psi(\mathbf{r}) = \sum_{n=-\infty}^{\infty} \psi_n \mathrm{e}^{iQ(2n+1)[z - u(\mathbf{r})]} \qquad \text{(B4)}$$

where the amplitudes ψ_n are those of the ideal structure (eq 41)

$$\psi_n = \frac{2i\rho}{\pi(2n + 1)} \qquad \text{(B5)}$$

The correlation function of composition deviations is

$$\overline{\psi(\mathbf{r})\,\psi(\mathbf{r}')} = \sum_{n=-\infty}^{\infty} \sum_{n'=-\infty}^{\infty} \psi_n \psi_{-n'} \exp\{iQ[(2n + 1)z - (2n' + 1)z']\}\, \overline{\exp\{-iQ[(2n + 1)u(\mathbf{r}) - (2n' + 1)u(\mathbf{r}')]\}} \qquad \text{(B6)}$$

Neglecting the non-Gaussian character of the fluctuations of the displacement field $u(\mathbf{r})$, we transform the average of an exponential into the exponential of the corresponding correlation function

$$\overline{\exp\{-iQ[(2n + 1)u(\mathbf{r}) - (2n' + 1)u(\mathbf{r}')]\}} = \exp\left\{-\frac{Q^2}{2}\overline{[(2n + 1)u(\mathbf{r}) - (2n' + 1)u(\mathbf{r}')]^2}\right\} \qquad \text{(B7)}$$

Thus, we need to calculate

$$\overline{[(2n + 1)u(\mathbf{r}) - (2n' + 1)u(\mathbf{r}')]^2} = (2n + 1) \times (2n' + 1)\, \overline{[u(\mathbf{r}) - u(\mathbf{r}')]^2} + 2(2n + 1)(n - n')\overline{u^2(\mathbf{r})} + 2(2n' + 1)(n' - n)\overline{u^2(\mathbf{r}')} \qquad \text{(B8)}$$

Since the averages are taken over the random force, acting on the lamellae (due to different possible ways of cross-linking the system) the value $\overline{u^2(\mathbf{r})}$ should not depend on coordinate ($\overline{u^2(\mathbf{r})} = \overline{u^2(\mathbf{r}')} = \overline{u^2}$) and we rewrite the correlation function (B6) as

$$\overline{\psi(\mathbf{r})\,\psi(\mathbf{r}')} = \sum_{n=-\infty}^{\infty}\sum_{n'=-\infty}^{\infty} \psi_n\psi_{-n'} \exp\{iQ[(2n+1)z - (2n'+1)z']\} \exp[-2Q^2(n-n')^2\overline{u^2}] \times \exp\left\{-\frac{Q^2}{2}(2n+1)(2n'+1)\overline{[u(\mathbf{r})-u(\mathbf{r}')]^2}\right\} \quad (B9)$$

Let us estimate the average value of the mean square displacement $\overline{u^2}$. The average over random forces at a given position $\mathbf{r}$ is equivalent to the average over the volume of the sample for a given quenched configuration of random forces. The relative positions of lamellae are well correlated only up to the distance ξ_z^{tr}:

$$|u(z+\xi_z^{\mathrm{tr}}) - u(z)| \sim d$$

For definiteness, we choose the value of u of the order of the lamellar thickness d near $z = 0$ (note that this choice is arbitrary but has to be made once for the sample). Then the mean square displacement grows linearly with the distance along the z-direction between this origin and the point of interest $u^2(z) \simeq d^2 z/\xi_z^{\mathrm{tr}}$ and at the sample boundary it is $u^2(L_z) \simeq d^2 L_z/\xi_z^{\mathrm{tr}}$. Therefore, the mean square value of the displacement averaged over the whole sample grows linearly with the sample thickness L_z:

$$\overline{u^2} \simeq d^2 L_z/\xi_z^{\mathrm{tr}} \quad (B10)$$

Thus we can neglect the terms with $n \neq n'$ in the double summation for the composition correlation function (B9) because

$$e^{-2Q^2(n-n')^2\overline{u^2}} \simeq e^{-8\pi^2(n-n')^2 L_z/\xi_z^{\mathrm{tr}}}$$

is exponentially small in the case $L_z \gg \xi_z^{\mathrm{tr}}$. Consequently, there is only single sum ($n = n'$) left in eq B9

$$\overline{\psi(\mathbf{r})\,\psi(\mathbf{r}')} = \sum_{n=-\infty}^{\infty} |\psi_n|^2 \exp\{iQ(2n+1)(z-z')\} \times \exp\left\{-\frac{Q^2}{2}(2n+1)^2\overline{[u(\mathbf{r})-u(\mathbf{r}')]^2}\right\} \quad (B11)$$

where ψ_n are defined in eq B5 and the displacement correlation function is given by eqs 33 and 37. The structure factor is the Fourier transform of the correlation function (which is only a function of the vector $\mathbf{r} - \mathbf{r}'$) $\overline{\psi(\mathbf{r})\,\psi(\mathbf{r}')} = \overline{\psi(\mathbf{r}-\mathbf{r}')\,\psi(0)}$

$$S_{\mathbf{q}} = \int d\mathbf{r}\, \overline{\psi(\mathbf{r})\,\psi(0)} e^{-i\mathbf{qr}} = \sum_{n=-\infty}^{\infty} |\psi_n|^2 \int d\mathbf{r}\, e^{-i\mathbf{qr}} \times \exp\left[iQ(2n+1)z - (2n+1)^2\frac{Q^2}{2}\overline{[u(\mathbf{r})-u(0)]^2}\right] \quad (B12)$$

We now estimate the integral in eq B12 for different degrees of anisotropy of the network deformation. In the case of weak anisotropy, $(\epsilon_x\epsilon_y)^{1/2} \ll d/l$, only small distances r contribute to the integral (B12):

$$|z| \sim \xi_z^{\mathrm{tr}} \simeq \left(dl\Big/\ln\frac{d}{l(\epsilon x^{1/2} + \epsilon_y^{1/2})^4}\right)^{1/2}$$

$$|x| \sim \xi_x^{\mathrm{tr}} \simeq [dl\epsilon_x^{1/2}(\epsilon_x^{1/2} + \epsilon_y^{1/2})]^{1/2} \ll \xi_x^{\mathrm{or}}$$

$$|y| \sim \xi_y^{\mathrm{tr}} \simeq [dl\epsilon_y^{1/2}(\epsilon_x^{1/2} + \epsilon_y^{1/2})]^{1/2} \ll \xi_y^{\mathrm{or}} \quad (B13)$$

The crossover lengths ξ_z^{or}, ξ_x^{or}, and ξ_y^{or} were defined in eq A16. With logarithmic accuracy we can make the substitution

$$\ln\frac{d}{(\epsilon_x^{1/2} + \epsilon_y^{1/2})^2|z|} \rightarrow \ln\frac{d}{(\epsilon_x^{1/2} + \epsilon_y^{1/2})^2\,\xi_z^{\mathrm{tr}}}$$

in expression A14 for the displacement correlation function. Substitution the resulting expression into eq B12, we can perform the Gaussian integration over $\mathbf{r}$. The result of this integration is

$$S_{\mathbf{q}} = \frac{\rho^2}{\xi_x\xi_y\xi_z}\sum_{n=-\infty}^{\infty}\frac{1}{(2n+1)^5} \times \exp\left[-\frac{(\xi_z^{\mathrm{tr}})^2(q_z-(2n+1)Q)^2 - (\xi_x^{\mathrm{tr}})^2 q_x^{\,2} - (\xi_y^{\mathrm{tr}})^2 q_y^{\,2}}{2(2n+1)^2}\right] \quad (B14)$$

where the translational correlation lengths ξ_z^{tr}, ξ_x^{tr}, and ξ_y^{tr} are defined by equations

$$\xi_x^{\mathrm{tr}} \simeq [dl\epsilon_x^{1/2}(\epsilon_x^{1/2} + \epsilon_y^{1/2})]^{1/2}$$

$$\xi_y^{\mathrm{tr}} \simeq [dl\epsilon_y^{1/2}(\epsilon_x^{1/2} + \epsilon_y^{1/2})]^{1/2}$$

$$\xi_z^{\mathrm{tr}} \simeq \left(dl\Big/\ln\frac{d}{l(\epsilon_x^{1/2} + \epsilon_y^{1/2})^4}\right)^{1/2} \quad (B15)$$

In the case of strong anisotropy $\epsilon \gg d/l$, the main contribution to the integral (B12) comes from the region $|z| \gg \xi_z^{\mathrm{tr}}$, $|x| \gg \xi_x^{\mathrm{tr}}$, and $|y| \gg \xi_y^{\mathrm{tr}}$. Therefore, we have to use the asymptotic expression (A15) for the displacement correlation function in eq B12. The integration over $\mathbf{r}$ can be performed using the change of variables

$$\{\hat{z} = z,\ \hat{x} = x/\sqrt{\epsilon_x},\ \hat{y} = y/\sqrt{\epsilon_y}\} \quad \text{and} \quad \{\hat{q}_z = q_z - (2n+1)Q,\ \hat{q}_x = q_x\sqrt{\epsilon_x},\ \hat{q} = q_y\sqrt{\epsilon_y}\}$$

In these new variables the structure factor takes the form

$$S_{\mathbf{q}} = \sum_{n=-\infty}^{\infty} |\psi_n|^2 \sqrt{\epsilon_x\epsilon_y}\int d\hat{\mathbf{r}}\, e^{-i\mathbf{qr}} \times \exp[-(2n+1)^2\xi_z^{-1}|\hat{\mathbf{r}}|] \quad (B16)$$

Integrating this expression over $\hat{\mathbf{r}}$ and substituting the value of the amplitude ψ_n into eq B16, we finally obtain

$$S_{\mathbf{q}} = g\left(\frac{2\rho Q}{\pi B}\right)^2 \sum_{n=-\infty}^{\infty} [(q_z - (2n+1)Q)^2 + \epsilon_x q_x^{\,2} + \epsilon_y q_y^{\,2} + (2n+1)^4/(\xi_z^{\mathrm{tr}})^2]^{-2} \quad (B17)$$

where the correlation length ξ_z^{tr} is given by the expression

$$\xi_z^{tr} = 8\pi B^2 d^2 (\epsilon_x \epsilon_y)^{1/2}/g \qquad (B18)$$

Appendix C

Pinning of Lamellar Planes. The anisotropy leads to the rotation of the direction normal to the lamellar planes into the direction of the smallest stretching. To describe this effect we consider the model in which there are only two types of correlation regions: rotated by the anisotropy or pinned by the random forces and estimate the probability for these correlation regions to be pinned

$$p(\epsilon) \approx \exp(-F_{anis}/\Delta F_{corr}) \qquad (C1)$$

Here F_{anis} is the energy of the anisotropy and ΔF_{corr} is the free energy difference of rotated and pinned correlation regions. The random forces, acting on the lamellar plates, are uncorrelated on length scales d. Thus, there are V_{corr}/d^3 independent random variables in the volume of the correlation region

$$V_{corr} = \xi_z^{or}(\xi_\perp^{or})^2 \simeq d^3/\epsilon_c^{\,2} \qquad (C2)$$

Here we used eqs 19 and 20 and the definition (36) of ϵ_c. Due to the Gaussian character of these variables, the variation of the free energy of correlation regions about its average $\bar{F}_{corr}$ under the rotation of lamellar planes can be estimated as $\Delta F_{corr} = \bar{F}_{corr}/(V_{corr}/d^3)^{1/2}$. Substituting this expression into eq C1 and estimating the energy of the anisotropy as $F_{anis} \simeq \epsilon \bar{F}_{corr}$ we finally find

$$p(\epsilon) \approx \exp(-\epsilon/\epsilon_c) \qquad (C3)$$

Note that the rotation of lamellar planes could be very slow due to high energy barriers and it would take a long time for the system to reach the equilibrium.

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MA960721B