Contribution to the theory of microphase layering in block-copolymer melts

A. N. Semenov

M. V. Lomonosov Moscow State University

(Submitted 5 November 1984)
Zh. Eksp. Teor. Fiz. **88**, 1242–1256 (April 1985)

A theory is proposed that enables one to study microphase layering in a melt of diblock copolymers with highly incompatible blocks. The structure of an isolated spherical domain (micelle) is studied. It is established that the interaction of micelles can be described by an electrostatic analogy. The interaction energy of two micelles is shown to have a minimum at a finite distance between them. Hence the transition to the microdomain state is of first order; at distances $r \ll N^{1/2}a$ (N is the number of links in the polymer chain and a is the dimension of a single link) two micelles interact according to a Coulomb law; the equilibrium packing of spherical micelles is body-centered cubic; and the characteristic period of the microdomain structure is $b \sim \chi^{1/6}N^{2/3}$ (χ is a parameter characterizing the mutual repulsion of the blocks). Upon taking account of the results of Ref. 5, the complete phase diagram of the melt is constructed, with the regions indicated of existence of spherical, cylindrical, and lamellar microphases.

1. INTRODUCTION

A polymer chain is called a block copolymer if it consists of links of several types, with the links of each type collected into large-scale blocks (Fig. 1a). Solutions and melts of block copolymers have long attracted the attention of polymer specialists, owing to the ability of these systems to transform to a microlayered state. If the links of types A and B have a positive heat of mixing, then a tendency to layering arises. However, since the blocks A and B are linked into a single chain, layering can occur only on certain scales. Consequently a microdomain structure arises, which gives rise to many valuable properties of the system. The individual domains can have the shape of plane layers (Fig. 2a), lamellar structure), of cylinders (Fig. 2b), or spheres (Fig. 2c). The structures of the two latter types rise whenever the blocks A and B strongly differ in dimensions.

The effects of layering in polymer mixtures are applied, e.g., in preparing composite materials with high resistance to cracking. On the other hand, they are sometimes undesirable, since the inhomogeneous structures that arise scatter light. Therefore the growing interest toward study of microdomain structures in polymers is not amazing, both on the part of theoreticians[1–10] and experimentalists.[11–13]

However, despite the wealth of publications, the physical properties of systems of block copolymers have not yet been studied enough theoretically. A number of the theoretical studies on this problem have employed the Landau expansion, which has restricted applicability. Thus, the results of Ref. 5, in which the phase diagram was constructed (Fig. 3) of a melt of diblock copolymers (Fig. 1b), are valid only in a small region near the critical point $\alpha = \alpha_c = 2.62$, $f = f_c = 0.5$. Here α is the characteristic interaction energy per block (the exact definition will be given below), and f is the fraction of links of type A in the system. Consequently, the region $\alpha \gg 1$ is not studied in this paper. Other studies[4,7] have either employed ungrounded assumptions, or, beyond certain stages, they involve computer calculations. As a result, even for the simplest system—a melt of diblock copolymers—many problems remain unelucidated.

This study proposes a relatively simple, rigorously analytical approach that enables one to study the equilibrium structure of a melt of diblock copolymers far from the critical point where the interaction parameter $\alpha \gg 1$.

As is known,[14] a polymer melt is a weakly fluctuating system to which one can apply the mean-field approximation. In line with the approach of Liftshitz,[15] one can separate the free energy F of the system into two components: an energy component arising from the interaction of links remote along the chain (or links of different chains), and a conformational component, which takes account of the connection of the links into polymer chains. The main difficulty is faced in calculating the conformational term (cf. the studies on the theory of globules[16–18]). We shall start analyzing this problem with studying the simplest case in which the A blocks are considerably shorter than the B blocks, and hence must form spherical domains during microlayering. Section 2 will treat one such domain—an isolated spherical micelle. The next section will study the interaction of two micelles and establish an electrostatic analogy that describes this interaction. Section 4 will study the most stable structure having spherical domains, and will show that the transition to the microdomain state occurs jumpwise as a first-order transition. Finally, Sec. 5 will treat transitions between microphases having different symmetry (with plane, cylindrical, and spherical domains).

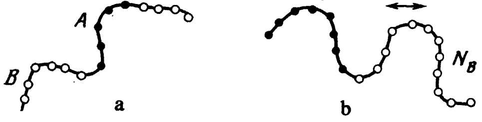

FIG. 1. Triblock copolymer (a) and diblock copolymer (b); N_A and N_B are the numbers of links of types A and B.

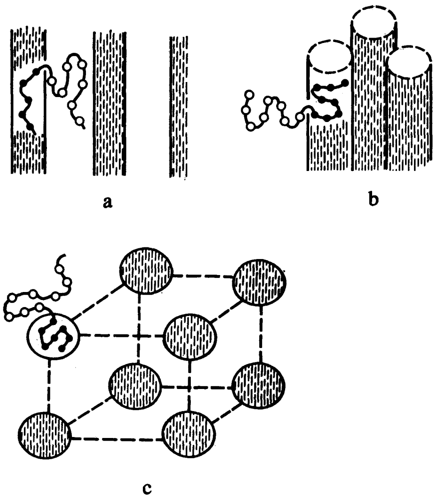

FIG. 2. Microdomain structures: lamellar (a), cylindrical (b), spherical (c).

2. STRUCTURE OF AN ISOLATED SPHERICAL MICELLE

Let us study a melt of diblock copolymers with a fixed number of links in the chain $N = N_A + N_B$ ($N_A \gg 1$, $N_B \gg 1$) and fixed fraction of links of type A, $f = N_A/N \ll 1$ (see Fig. 1b). The mean square of the distance between the ends of the polymer chain without interaction is $\langle R^2 \rangle = 6Na^2$, where a is the effective radius of gyration of a single link. For the sake of definiteness, let us assume that the links of the two blocks (A and B) have the same radii of gyration a.

To good accuracy, we can consider the polymer melt to be incompressible.[2] Let us choose a system of units in which the volume per link is $v = 1$. Then the condition of incompressibility acquires the form

$$\Phi_A(\mathbf{r}) + \Phi_B(\mathbf{r}) = 1. \qquad (2.1)$$

Here $\Phi_A(\mathbf{r})$ and $\Phi_B(\mathbf{r})$ are the local concentrations of links of types A and B, whose mean values are

$$\langle \Phi_A(\mathbf{r}) \rangle = f, \quad \langle \Phi_B(\mathbf{r}) \rangle = 1 - f.$$

Below we shall take the concentration to mean the concentration of links of type A: $\Phi \equiv \Phi_A$.

We can write the free energy of interaction of the links in the following form[14,19]:

$$F_{int} = \chi T \int \Phi_A(\mathbf{r}) \Phi_B(\mathbf{r})\, d^3r.$$

Apart from inessential constant terms, using Eq. (2.1), we can represent $F_{\rm int}$ in a more convenient form:

$$F_{int} = -\chi \int (\Phi - f)^2 d^3r \qquad (2.2)$$

(hereinafter we take the temperature $T = 1$). For most pairs of polymers the Flory parameter χ is positive ($\chi = 10^{-3}$–10^{-1}). This corresponds to effective repulsion between the A and B links.

For given spatial distributions $\Phi_A(r)$ and $\Phi_B(r)$, many ways exist of connecting the links into block copolymers. This is taken into account by the extra conformational term $F_{\rm conf}[\Phi(\mathbf{r})]$, which reflects the polymer character of the problem. Thus, the total free energy of the system is divided into two components.

$$F = F_{int}[\Phi] + F_{conf}[\Phi], \qquad (2.3)$$

The first of these describes the system of separated, interacting links, and the second describes the system of noninteracting links connected into polymer chains. We note that the quantity $\chi a^{-6} \lesssim a^{-6}$ plays the role of the Ginzburg parameter G for the system being studied.[17,18] In practice the condition $a^{-6} \ll 1$ is always fulfilled. Therefore we have $G \ll 1$, and the separation in (2.3) is quantitatively regular.

If $\chi = 0$, the links of both types are uniformly distributed throughout the volume of the system. As χ increases, the contacts between the links of different types become ever less favorable. Therefore the melt will tend to layer into regions enriched in links of a single type. In the simplest case a single isolated spherical domain is formed, filled with links of type A (formation of a B domain is less favorable, since even in a homogeneous melt the fraction of B links is close to unity). The structure of this spherical domain (or micelle) is shown in Fig. 4. It includes: 1) a nucleus of radius $R \gg R_A$ filled with A blocks ($R_A = N_A^{1/2} a$ is the unperturbed radius of gyration of an A block); 2) a surface layer of thickness $\Delta \ll R_A$, in which the junctions of the A and B blocks are concentrated; 3) a coat of B blocks surrounding the nucleus.[1] Correspondingly we shall divide the free energy of the micelle into three components—internal, surface and external: $F = F_1 + F_2 + F_3$.

The A blocks are seemingly attached at one end to the surface of the micelle, while the other, free end must lie near

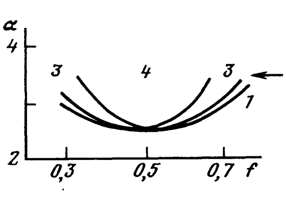

FIG. 3. Phase diagram of a melt of diblock copolymers near the critical point $\alpha \equiv \chi N f(1-f) = \alpha_c = 2.62$, $f = f_c = 0.5$ (according to Ref. 5): *1*—homogeneous phase, *2*—body-centered-cubic phase, *3*—hexagonal phase, *4*—lamellar phase.

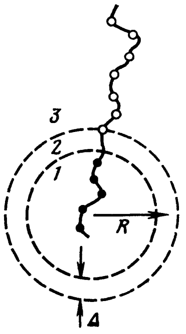

FIG. 4. Structure of an isolated micelle: *1*—core, *2*—surface layer, *3*—coat.

its center. Therefore the mean distance between ends of an A block is of the order of $R \gg R_A$. That is, these blocks prove to be highly extended. The corresponding "elastic" free energy is calculated in Appendix A (A.11):

$$F_e = \frac{\pi^2}{160} Q \frac{R^2}{R_A{}^2}, \tag{2.4}$$

Here $Q = 4\pi R^3/(3N_A)$ is the number of chains forming the micelle. As Eq. (2.2) shows, the main component of the interaction energy in the micelle belongs to the nucleus. Upon neglecting quantities of the order of $f \ll 1$, we find

$$F_{int} = -4\pi R^3 \chi/3. \tag{2.5}$$

Thus the free energy of the nucleus is $F_1 = F_e + F_{\text{int}}$.

The B blocks surrounding the micelle must be extended similarly to the A blocks: otherwise the concentration of B links in a certain neighborhood of the nucleus would considerably exceed the maximum possible ($\Phi_B = 1$). Evidently the most favorable arrangement of the B blocks is radial (see Fig. 4). Let the nth link of a B block (counting from the junction point) lie on the average at the distance r from the center of the micelle. The condition of incompressibility implies that

$$(4\pi/3)(r^3 - R^3) = Qn. \tag{2.6}$$

If a region of the chain containing ΔN links is extended so that its ends lie at the distance Δr from one another, then this corresponds to the elastic free energy[14]

$$\Delta F = \frac{1}{4a^2} \Delta N \left(\frac{\Delta r}{\Delta N}\right)^2.$$

Therefore the free energy of the entire coat is

$$F_3 = \frac{Q}{4a^2} \int_0^\infty \left(\frac{dr}{dn}\right)^2 dn = \frac{1}{12} Q \frac{R^2}{R_A{}^2}. \tag{2.7}$$

Only those regions of the chain will appreciably affect the properties of the thin surface layer that directly adjoin the junction point. The extension of the chains (of both A and B blocks) and the end effects begin to have an appreciable effect at scales considerably exceeding the thickness Δ of the layer. Therefore, in calculating the surface tension we can assume that both blocks, A and B, are of infinite length, while the junction points lie near the surface $x = 0$. If the blocks are incompatible, then links of one type (A) will lie in the half-space $x > 0$, and those of the other type (B) in the half-space $x < 0$. The surface tension for this system is calculated in Appendix B. The answer is:

$$\sigma = \sigma_0 + \sigma_1, \quad \sigma_1 = \rho_s \ln(\rho_s/\pi e \Delta), \quad \sigma_0 = a\chi^{1/2}. \tag{2.8}$$

Here ρ_s is the number of chains per unit of surface, and the thickness of the surface layer is

$$\Delta = a\chi^{-1/2}. \tag{2.9}$$

We must take two circumstances into account in order to go to a real micelle. First, we must take account for the translational entropy of the chains not bound to the micelle. One can do this automatically by replacing the ideal-gas term $\rho \ln(\rho/e)$ in Eq. (B.9) with

$$\rho \ln(\rho/e\bar{\rho}) + \bar{\rho}, \tag{2.10}$$

Here $\bar{\rho} = 1/N$ is the mean concentration of chains. In the surface tension, this leads to the substitution $\sigma_1 \to \sigma_1 - \rho_s \ln \bar{\rho}$ (the term $\bar{\rho}$ in (2.10) gives a negligibly small contribution after integrating over the volume of the micelle). Second, the calculation of F_1 in Appendix A did not take account of the logarithmic corrections: it was assumed that the A block is strictly extended in the direction toward the center of the micelle. One can easily show that actually the links of the A block can deviate from their radius by a distance of the order of R_A. Therefore, in particular, the end of the A block proves to be seemingly included in a volume $V_1 \sim RR_A^2$. In the free state this end can lie within the limits of a volume $V_1 \sim R_A^3$. Hence the logarithmic correction to the free energy per link is $\Delta F = -\ln V_1/V_0 = \ln R_A/R$. Upon including also this correction in σ_1, we finally obtain (with logarithmic accuracy):

$$\sigma_1 = \rho_s \ln(\rho_s R_A/\bar{\rho} R \Delta), \tag{2.11}$$

$$F_2 = 4\pi R^2(\sigma_0 + \sigma_1) = 4\pi R^2 \sigma_0 + Q \ln(\alpha^{1/2} f^{-1}), \tag{2.12}$$

Here we have defined $\alpha \equiv \chi N_A$.

Upon combining Eqs. (2.4), (2.5), (2.7), and (2.12), we find the free energy of the micelle:

$$F = F_1 + F_2 + F_3 = \frac{4\pi}{3} \frac{R_A{}^3}{N_A} \left\{ -\varepsilon x^3 + 3\alpha^{1/2} x^2 + \frac{1}{16}\left(\frac{\pi^2}{10} + \frac{4}{3}\right) x^5 \right\}, \tag{2.13}$$

Here we have $\varepsilon = \alpha - \ln(\alpha^{1/2} f^{-1})$, and $x = R/R_A$. Upon minimizing (2.13) with respect to x, we can show that the free eneregy of the micelle first becomes negative at $\varepsilon = 2.06\alpha^{1/3}$, $x = 2.18\alpha^{1/6}$. Hence the threshold for forming a single micelle is

$$\alpha_c = \ln(1/f) + {}^1/_2 \ln \alpha_c + 2.06\alpha_c^{1/3} \gg 1. \tag{2.14}$$

Its radius is

$$R = 2.18\alpha_c^{1/6} R_A. \tag{2.15}$$

We note that, if the A and B blocks were not linked into a single copolymer, the threshold for layering would be $\alpha_c = \ln(1/f)$,[20] which corresponds to the first principal term in (2.14). Hence the second and third terms in (2.14) describe the elevation of the threshold α_c owing to the linkage between the blocks.

Now we shall verify the assumptions that we have accepted without proof in the course of the presentation. As Eq. (2.15) implies, the radius of the micelle at the instant of creation is $R \gg R_A$. Therefore the A blocks and the initial regions of the B blocks are actually highly extended. On the other hand, for regions of the chain whose dimension is smaller than $r_b \sim R_A^2/R$, the extension will no longer be appreciable. Therefore we can neglect the extension in studying the surface layer, whose thickness is $\Delta = R_A \alpha_c^{-1/2} \ll r_b \sim R_A \alpha_c^{-1/6}$.

Let us estimate the dimensions of the coat of B blocks, i.e., find the distance D up to which the concentration of B links bound to the micelle exceeds the concentration of links of "foreign" chains. The condition (2.6) implies that $r \sim (Qn)^{1/3} \sim R\,(n/N_A)^{1/3}$. An unextended region of the chain containing n links has the spatial dimension $r' \sim n^{1/2}a$. Upon equating r and r', we find

$$D \sim R^3/R_A{}^2 \gg R. \tag{2.16}$$

At distances $r \gg D$, the presence of the micelle only slightly alters the concentration of the links of both types.

Thus, a micelle for $\alpha = \alpha_c$ consists of

$$Q = 4\pi R^3/3N_A \sim \alpha_c^{1/2} N_A^{1/2} a^3$$

chains that form an A core of radius R and a B coat of radius $D \gg R$, separated by a thin spherical layer. In this layer of thickness $\Delta \ll R$, the concentration of links of the two types undergoes a jump practically from 0 to 1 according to the law (B.4)

$$\Phi(x) = {}^1/_2 (1 + \operatorname{th}(x/\Delta)).$$

(Here the x coordinate is measured along the radius of the micelle from its surface to its center). In this same layer all the junction points are concentrated of the A and B blocks, which are distributed with the following density (B.12):

$$\rho(x) = \rho_s/\pi\Delta \operatorname{ch}(x/\Delta), \quad \rho_s = Q/4\pi R^2.$$

3. INTERACTION OF TWO MICELLES

As was shown at the end of the previous section, the perturbation caused by a micelle at distances $r \gg D$ from it is small. Therefore, if we are interested in the interaction of two micelles at distances $r \gg D$, then we can use an expansion of the free energy in powers of the small deviation in concentration $\delta\Phi = \Phi_A - f$, and restrict the expression to the leading quadratic term. Let $\rho(\mathbf{r})$ be the deviation of the concentration of junction points from the mean value $1/N$. Since $\delta\Phi(\mathbf{r})$ in the region of interest to us varies on scales considerably exceeding D, while the dimension of an A block is much smaller than D, then we have

$$\rho(\mathbf{r}) = \delta\Phi(\mathbf{r})/N_A.$$

Let us write the free energy for a given $\rho(r)$ in the form[21]

$$F = \frac{N}{2}\int \frac{d^3k}{(2\pi)^3} B(\mathbf{k})\,|\rho_{\mathbf{k}}|^2. \tag{3.1}$$

Here $\rho_{\mathbf{k}}$ is the Fourier transform of the function $\rho(\mathbf{r})$ while the coefficient has been set in front of the integral for convenience. We can easily associate the quantity $B(\mathbf{k})$ with the correlation function of the density of A links. In turn, we can calculate the latter by the method of Ref. 8. The answer is:

$$B(\mathbf{k}) = 1 + \Lambda^{-1}(\mathbf{k}) = 1 + \frac{(1-e^{-u})^2}{2(u+e^{-u}-1)-(1-e^{-u})^2} - 2\alpha f. \tag{3.2}$$

Here we have $u = k^2Na^2 = k^2R_A^2/f$. If $\alpha f \ll 1$, then we have

$$\Lambda(\mathbf{k}) = 2\frac{u+e^{-u}-1}{(1-e^{-u})^2} - 1 = \begin{cases} 2u/3, & u \ll 1 \\ 2u-3, & u \gg 1 \end{cases}. \tag{3.3}$$

We can easily verify that the separation $B(\mathbf{k}) = 1 + \Lambda^{-1}(\mathbf{k})$ corresponds to separation of the free energy into an ideal-gas component (corresponding to independent translational motion of the chains) and a component corresponding to interaction of the chains. Let several micelles exist at the points $\mathbf{r}_1, \mathbf{r}_2, \ldots$ They form a certain trial distribution of junction points

$$\rho^{(0)}(\mathbf{r}) = Q_1\delta(\mathbf{r}-\mathbf{r}_1) + Q_2\delta(\mathbf{r}-\mathbf{r}_2) + \ldots.$$

The free energy can reach a minimum in the case in which the free chains not bound to micelle are arranged somehow to give rise to the distribution $\delta\rho(\mathbf{r})$. We must take account of the translational component of the free energy only for free chains. Hence we can rewrite (3.1) in the form

$$F = \frac{N}{2}\int \frac{d^3k}{(2\pi)^3}\{|\delta\rho_{\mathbf{k}}|^2 + \Lambda^{-1}(\mathbf{k})\,|\rho_{\mathbf{k}}^{(0)} + \delta\rho_{\mathbf{k}}|^2\}. \tag{3.4}$$

Upon minimizing (3.4), we obtain

$$\delta\rho_{\mathbf{k}} = -\rho_{\mathbf{k}}^{(0)}/[1+\Lambda(\mathbf{k})], \tag{3.5}$$

$$F = \frac{N}{2}\int \frac{d^3k}{(2\pi)^3}\frac{|\rho_{\mathbf{k}}^{(0)}|^2}{1+\Lambda(\mathbf{k})}. \tag{3.6}$$

Equation (3.5) shows that the free ends of the chain completely screen the trial "charge" $Q^{(0)} = \int\rho^{(0)}d^3r$, since $\Lambda(0) = 0$. A single micelle gives rise to the trial distribution $\rho^{(0)}(\mathbf{r}) = Q\delta(\mathbf{r})$, so that

$$\delta\rho(\mathbf{r}) = -Q\int \frac{d^3k}{(2\pi)^3}\frac{e^{i\mathbf{kr}}}{1+\Lambda(\mathbf{k})} = -\frac{Q}{R_N{}^3}\varphi\left(\frac{r}{R_N}\right). \tag{3.7}$$

Here we have $R_N = Na^2$. Thus the "charge" of the micelle is screened on the scale of R_N, which corresponds to the unperturbed dimension of the copolymer and considerably exceeds the maximum dimension D of the micelle.

The dependence of φ on r/R_N is shown schematically in Fig. 5; it has the following asymptotics:

$$\varphi(s) = \frac{1}{8\pi s}\begin{cases} 1, & s \ll 1 \\ e^{-\lambda_1 s}[(\lambda_1{}^2-\lambda_2{}^2)\cos\lambda_2 s - 2\lambda_1\lambda_2\sin\lambda_2 s], & s \gg 1 \end{cases}, \tag{3.8}$$

Here we have $\lambda_1 = 1.682$, $\lambda_2 = 2.218$.

If two micelles lie at a distance $r_{12} \gg D$, then we have $\rho^{(0)}(\mathbf{r}) = Q\delta(\mathbf{r}-\mathbf{r}_1) + Q\delta(\mathbf{r}-\mathbf{r}_2)$. We can find from (3.6) their interaction energy:

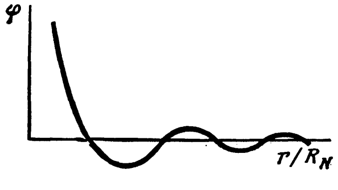

FIG. 5. Dependence of the interaction energy of two micelles on the distance between them.

$$U_{int}(r)=\frac{NQ^2}{R_N{}^3}\varphi\left(\frac{r}{R_N}\right). \qquad (3.9)$$

Upon comparing (3.9) and (3.8), we find that two spherical micelles at distances $D \ll r \ll R_N$ interact according to the Coulomb law

$$U_{int}(r)=\frac{1}{8\pi a^2}\frac{Q^2}{r}. \qquad (3.10)$$

Equation (3.10) justifies the term "charge," which we have employed up to now to denote $\int\rho(\mathbf{r})d^3r$. The function $\rho(\mathbf{r})$ itself can be called the charge density here. Interestingly, the entire charge of the micelle is concentrated in the surface layer.

At the greatest distances $r \gg R_N$, the interaction energy declines exponentially while oscillating. The quantity $U_{\rm int}$ has an absolute minimum $U_{\rm int} < 0$ at $r \sim R_N$.

Now let us study the interaction of two micelles at small distances: $R \ll r \ll D$. The fundamental effects in this region affect the coat of B blocks associated with the micelle. In the coat the chains are strongly extended. Hence each chain is characterized by a certain average trajectory $\mathbf{r}(n)$, where n is the order number of the monomer (see Appendix A). Let $\mathbf{E} = d\mathbf{r}(n)/dn$. Let us single out a small oriented area $d\mathbf{S}$. Owing to the condition of incompressibility (2.1), the product $\mathbf{E}d\mathbf{S}$ must equal the number of chains crossing this area. Consequently, if we integrate the form $\mathbf{E}d\mathbf{S}$ over the closed surface, we obtain the number of junction points in the region bounded by this surface[2)]:

$$\oint \mathbf{E}\,d\mathbf{S}=Q, \quad \operatorname{div}\mathbf{E}=\rho. \qquad (3.11)$$

Thus, if Q is the charge, then we must identify $\mathbf{E}$ with the electric field intensity.

The elastic free energy of the extended chains in (cf. (2.7)):

$$F=\frac{1}{4a^2}\sum_n \mathbf{E}_n{}^2,$$

Here the summation is performed over all the links. Upon taking account of the constant density, we find

$$F=\frac{1}{4a^2}\int \mathbf{E}^2\,d^3r. \qquad (3.12)$$

The principle that Eq. (3.12) should be minimized under the additional condition (3.11) leads to the following system of electrostatic equations:

$$\mathbf{E}=-\nabla\varphi, \quad \nabla^2\varphi=-\rho, \quad \mathrm{F}=\frac{1}{4a^2}\int\varphi\rho\,d^3r.$$

Consequently, the "external" component of the energy of an isolated micelle is the energy of a charged sphere of radius R:

$$F_3=(1/16\pi a^2)\,(Q^2/R), \qquad (3.13)$$

This coincides with (2.7) as it should. The interaction energy of two micelles in the region $R \ll r \ll D$ varies according to the Coulomb law:

$$U_{int}=(1/8\pi a^2)\,(Q^2/r). \qquad (3.14)$$

We call attention to the fact that (3.14) does not differ from (3.10).

We note that the conformation of the chains forming the coat coincides with the lines of force of the "electric" field $\mathbf{E}$. Hence, for an isolated micelle the chains will lie radially (Fig. 6a) and for two micelles—along the lines of force of a system of two identical charges (Fig. 6b).

Thus, both in the region $r \gg D$ and when $R \ll r \ll D$, the interaction of micelles can be described by using an electrostatic analogy.

4. ORDERED STRUCTURES FORMED BY SPHERICAL MICELLES

Let us turn to studying the thermodynamically most stable structures that can be constructed of spherical micelles. As was shown in the last section, the interaction energy of micelles has a negative minimum at $r \sim R_N$. This means that the threshold for formation of a single micelle is lowered if it lies in the field of another micelle. Evidently, even before a single micelle can appear under equilibrium conditions (i.e., when $\tau \equiv \alpha - \alpha_c < 0$), the formation of an ordered structure constructed of micelles with the characteristic period $b \sim R_N$ will be thermodynamically favored. Equation (2.13) implies that the free energy of an isolated micelle at small τ will be $F_0 = -Q\tau$. On the other hand, the depth of the minimum in the interaction energy of the micelles (cf. (3.9)) is of the order of $U_{\rm int} \sim -Q^2/R_N a^2$. Consequently, an ordered structure will arise when $\tau \sim -Q/R_N a^2 \sim -\alpha_c^{1/2} f^{1/2}$. Here the corresponding transition will occur jumpwise, i.e., will be a first-order transition.

Ultimately all these conclusions are based on the idea that a region exists in which the micelles *attract one another*. The authors of Ref. 7, who also studied the problem of micelle formation, arrived at contrary conclusions: first a rarefied gas of micelles appears, and only at a certain stage (with increasing density), it becomes ordered. This is explained by the fact that Ref. 7 introduced a repulsion between micelles without any proof (Eq. (3.6) of Ref. 7).

With increasing τ the period b of the structure begins to decline. Let us study the region $\tau \gg \alpha_c^{1/2} f^{1/2}$ in which $b \ll R_N$. In this region the micelles interact according to the Coulomb law. While using (3.6), let us expand the interaction energy in a three-dimensional Fourier series. As calculated per unit cell we have

$$\mathcal{F}_{int}=\frac{Nc}{2}\sum_{\mathbf{k}}\left|\frac{1}{n}\sum_{s=1}^{n}(\exp i\mathbf{k}\mathbf{r}_s)\right|^2\frac{Q^2}{1+\Lambda(\mathbf{k})}, \qquad (4.1)$$

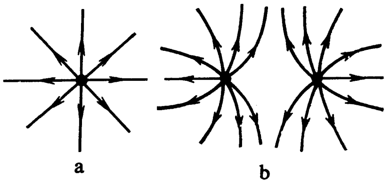

FIG. 6. Conformation of chains in the coat: isolated micelle (a); two interacting micelles (b).

Here c is the concentration of micelles, n is the number of them per unit cell, and the $\mathbf{r}_s$ are the coordinates of the micelles, while the summation is performed over all vectors $\mathbf{k}$ of the reciprocal lattice.

Since the size of the unit cell $b \ll R_N$, all the nonzero reciprocal-lattice vectors considerably exceed R_N^{-1} in modulus: $|\mathbf{k}| \gg R_N^{-1}$. Hence we have (cf. (3.3)):

$$1+\Lambda(\mathbf{k})=\begin{cases} 1, & \mathbf{k}=0 \\ 2k^2R_N^2, & \mathbf{k}\neq 0 \end{cases} . \tag{4.2}$$

Upon substituting (4.2) into (4.1), we find $\mathscr{F}_{\text{int}} = \mathscr{F}_1 + \mathscr{F}_2$, with

$$\mathscr{F}_1=NcQ^2/2, \tag{4.3}$$

$$\mathscr{F}_2=\frac{NcQ^2}{4R_N^2}\sum_{\mathbf{k}\neq 0}\frac{1}{k^2}\left|\frac{1}{n}\sum_{s=1}^{n}\exp i\mathbf{k}\mathbf{r}_s\right|^2 . \tag{4.4}$$

In order to determine the type of packing, we must minimize $\mathscr{F}_2$ for a fixed concentration c. We obtain as the result:

$$\mathscr{F}_2=\varkappa\frac{NQ^2}{4R_N^2}c^{1/3}. \tag{4.5}$$

Here the coefficient $\varkappa$ for the most widespread types of packing is: $\varkappa = -8.913634$ (simple cubic), $\varkappa = -9.073806$ (face-centered cubic (fcc)), $\varkappa = -9.074370$ (body-centered cubic (bcc)), $\varkappa = -9.073446$ (hexagonal close-packed (hcp)).

Thus the bcc structure proves most stable. We call attention to the fact that the relative difference of the coefficient $\varkappa$ does not exceed 10^{-4} for three types of packing—bcc, fcc, and hcp. For this reason alone, the relaxation of the melt into the most stable state must be very slow.

Now let us find how the period b of the structure varies with increasing τ (we assume for definiteness that $b = c^{-1/3}$). One can easily show that the main component of the interaction energy of the micelles always corresponds to the screening background, or in other words, to the free energy of translational motion of the unbound chains (the term $\mathscr{F}_1$). In the general case in which $\delta\rho \sim \bar{\rho}$, we must modify (4.3):

$$\mathscr{F}_1=\int_v\left(\rho\ln\frac{\rho}{e\bar{\rho}}+\bar{\rho}\right)d^3r. \tag{4.6}$$

Here $v=c^{-1}$ is the volume per micelle, while $\rho = \bar{\rho}(1-cQN)$ is the concentration of free chains. The free chains are uniformly distributed throughout the space outside the micelles, whose volume we can neglect.[3)]. Hence we can convert (4.6) into the form

$$\mathscr{F}_1=\frac{1}{Nc}f(cQN), \quad f(y)=(1-y)\ln(1-y)+y. \tag{4.7}$$

Let us rewrite the equation (2.13) for the intrinsic free energy of a micelle in the form

$$\mathscr{F}_0=\frac{1}{Nc}y[\varphi(x)-\tau], \quad x=R/R_A. \tag{4.8}$$

Here we have

$$\varphi(x)=3\alpha^{1/2}x^{-1}+\beta x^2-\gamma\alpha_c^{1/3},$$

$$\beta={}^1/_{16}(\pi^2/10+{}^4/_3), \quad \gamma=3(9\beta/4)^{1/3}.$$

Thus the free energy per unit volume is

$$F=c(\mathscr{F}_0+\mathscr{F}_1)=\frac{1}{N}\{f(y)+y[\varphi(x)-\tau]\}. \tag{4.9}$$

Upon minimizing (4.9) with respect to x and y and allowing for the fact that we always have $\varphi(x) \ll \omega$, we find

$$x=(2\beta/3)^{-1/3}\alpha^{1/6}, \quad y=1-e^{-\tau}.$$

Consequently, the radius of the nucleus of the micelle is

$$R=xR_A=2.18aN^{2/3}f^{2/3}\chi^{1/6}, \tag{4.10}$$

The characteristic period of the structure is

$$b=c^{-1/3}=3.50aN^{2/3}f^{1/3}\chi^{1/6}(1-e^{-\tau})^{-1/3}. \tag{4.11}$$

Thus, both characteristic scales R and b for $\tau \gg 1$ prove proportional to $aN^{2/3}$. That is, with increasing degree of polymerization N they increase more rapidly than the dimension of the chain $aN^{1/2}$. Further, with increasing τ the period b of the structure initially varies according to the law

$$b\sim aN^{1/3}\chi_c^{-1/6}(\alpha/\alpha_c-1)^{-1/3}\infty\tau^{-1/3}, \tag{4.12}$$

and then begins to increase:

$$b\sim aN^{2/3}f^{1/3}\chi^{1/6}. \tag{4.13}$$

When $\tau \gg 1$, we note that the melt now contains practically no free chains: they all participate in forming domains. If $\tau \ll 1/f$, the inequality $D \ll b \ll R_N$ is satisfied. That is, the fraction of the volume occupied by micelles (including their coats) is small. When $\tau \gg 1/f$, when the inverse relationship holds, $D \gg b \gg R_N$, the micelles strongly overlap in their coats. In this region Eqs. (4.10) and (4.11) continue to hold, but the character of the interaction of micelles that determines the type of packing changes. The point is that the dimensions D of the coat become larger than the dimension R_N of the chain. Hence one can no longer neglect the effects involving the free ends of the B blocks. Therefore, one can only assume that the bcc packing is conserved in this region.

5. TRANSITIONS BETWEEN SPHERICAL, CYLINDRICAL, AND LAMELLAR STRUCTURES

Up to now we have been treating structures with spherical domains. However, microphase layering can also involve formation of cylindrical domains (see Fig. 2b) and lamellae (plane layers, see Fig. 2a). Let us find out when the corresponding structures will be the most stable for a melt with strongly incompatible blocks: $\alpha = \chi N_A \gg 1$. As we shall show below, the transitions between these structures occur in the region $f \sim 1$, in which all the chains belong to micelles (i.e., to spheres, cylinders, or layers), while the micelles strongly overlap in their coats, and hence all the chains are strongly extended. One can easily show that the macromolecules associated with a given micelle densely fill the corresponding Wigner-Seitz cell. Let us fix the concentration of micelles (and hence also the volume of a cell). Evidently, the free energy of extension of the chains becomes less as the Wigner-Seitz cell approaches a spherical form (or circular in the case of cylindrical domains). Since the corresponding structures will be the most favorable, it is reasonable to use a spherical (circular) approximation for the Wigner-Seitz cell.

Let R be the radius of the nucleus of the micelle. Then the outer radius of the Wigner-Seitz cell is $R_2 = Rf^{-1.d}$, where $d = 3$ for spherical domains, $d = 2$ for cylindrical domains, and $d = 1$ for lamellae. The elastic free energy $\mathscr{F}_e$ is separated into two componente: an internal component U_{in} corresponding to the nucleus of the domains (filled with A links), and an external component U_{ex}, i.e., $\mathscr{F}_e = U_{\text{in}} + U_{\text{ex}}$. The energy U_{in} is calculated exactly in Appendix A, Eq. (A.11):

$$U_{in}=\lambda_d\frac{\pi^2}{32a^2}R^{d+2}N_A^{-2},\qquad \lambda_1={}^4/_3,\quad \lambda_2=\pi/3,\quad \lambda_3=4\pi/15. \tag{5.1}$$

The energy U_{ex} for lamellae ($d = 1$) is calculated exactly as for U_{in}: in the cases $d = 2$ and $d = 3$ the quantity U_{ex} is found approximately in Appendix A (with an accuracy no worse than 20%). As a result we have

$$U_{ex}=\varkappa_d\frac{\pi}{4a^2}R^{d+2}N_A^{-2},\quad \varkappa_1=(\pi/6)(1/f-1),\quad \varkappa_2=({}^1/_4)\ln(1/f),\quad \varkappa_3=({}^4/_9)(1-f^{1/3}). \tag{5.2}$$

The surface free energy of a micelle is (see (B.3)):

$$\mathscr{F}_s=a\chi^{1/2}S_d,\quad S_1=2,\quad S_2=2\pi R,\quad S_3=4\pi R^2. \tag{5.3}$$

In the region being studied, the A and B blocks are completely separated. Therefore the bulk component of the interaction energy of the links and the free energy of translational motion of the chains do not depend on the concentration of micelles nor on their arrangement. Consequently, these components of the free energy can be neglected during minimization. Thus the free energy per unit volume is

$$F=fV_d^{-1}(\mathscr{F}_e+\mathscr{F}_s),\quad V_1=2R,\quad V_2=\pi R^2,\quad V_3=4\pi R^3/3. \tag{5.4}$$

Upon substituting (5.1)–(5.3) into (5.4) and minimizing, we find that the transition from a spherical structure to cylindrical occurs at $f_{c1} = 0.12$, and from cylindrical to lamellar at $f_{c2} = 0.28$.

Thus the phase diagram of a melt for $\alpha \gg 1$ has the form shown in Fig. 7. The same diagram shows the results of Leibler,[5] which are valid in the region $\alpha \sim \alpha_c = 2.62$. The results of this section and those of Ref. 5 mutually supplement one another. The corresponding phase-transition lines smoothly join one another (dotted regions in Fig. 7). Consequently one obtains an approximate complete phase diagram of the melt of diblock copolymers: if the fraction of links of one type $f < f_c(\alpha)$, then the system remains homogeneous. When $f_c(\alpha) < f < f_{c1}(\alpha)$ spherical domains arise and are packed in a bcc lattice. When $f_{c1}(\alpha) < f < f_{c2}(\alpha)$, the most stable structure is one made of cylindrical domains packed in a hexagonal lattice. The region $f_{c2}(\alpha) < f < 1 - f_{c2}$ corresponds to a lamellar structure. With further increase in f the transitions are repeated in reverse order. As Eq. (2.14) implies, when $\alpha \gg 1$, we have $f_c(\alpha) \sim e^{-\alpha}$.

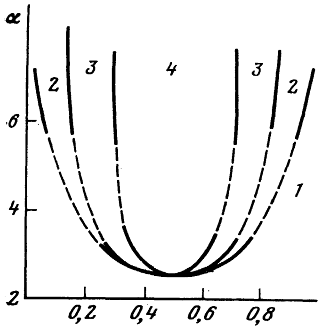

FIG. 7. Complete phase diagram of a melt of diblock copolymers in the variables $\alpha = \chi N f(1 - f)$ and f: *1*—homogeneous phase, *2*—body-centered-cubic phase, *3*—hexagonal phase, *4*—lamellar phase.

One can find from (5.4) that the characteristic period b for all three types of structures is of the order of

$$b \sim aN^{2/3}\chi^{1/6}. \tag{5.5}$$

In particular, the exact result for a lamellar structure is:

$$b=4(3/\pi^2)^{1/3}aN^{2/3}\chi^{1/6}. \tag{5.6}$$

Let us turn attention to the fact that the period of a lamellar structure proves independent of f.

The relationship $b \propto N^{2/3}$ has been found experimentally for a lamellar structure[11] and for a cylindrical structure.[13] This relationship has been derived theoretically[22] for a lamellar structure in a polymeric solution.

Thus we have been studying the equilibrium structures that arise in the melt of diblock copolymers with highly incompatible blocks. We note certain lines along which this study might be generalized. First, it is interesting to study melts of macromolecules of more complex architecture (triblock copolymers, etc.). Second, in practice one often encounters solutions of block copolymers—in a substance of low molecular weight or in some homopolymer—rather than melts. Finally, it is very important to study the dynamics of formation of microdomain structures. As a rule, polymer systems have very long relaxation times. Hence the thermodynamically more favored structure may prove inaccessible from the kinetic standpoint. We can expect that the dynamics of microphase layering of polymer stystems will prove very distinctive.

APPENDIX A

As was shown in Sec. 2, the A blocks in a micelle are highly extended: one end of the block (the junction point with the B block) is "attached" to the surface of the micelle, whereas the other end must lie in the vicinity of the center of the micelle, i.e., at a distance $\sim R \gg R_A$. Therefore each chain can be characterized by a definite trajectory about which it fluctuates weakly (the magnitude of the fluctuations is $\sim R_A$). We can describe this trajectory with the functions $\mathbf{r}(n)$, where n is the order number of the monomer unit. The transition from describing in terms of the probability $P[\mathbf{r}(n)]$ to describe with the trajectory recalls the transition from quantum mechanics to classical mechanics.

Let the free end of the A block lie at the distance r_0 from the surface of the micelle. Evidently, the chain lies along the radius of the micelle and hence is characterized by the scalar function $r(n)$—the distance from the surface, $r(N_A) = r_0$. Let $g(r_0)dr_0$ be the number of chains whose ends lie in the interval dr_0, while $E = d\mathbf{r}/dn$ is the local extension of the chain. We can write the free energy corresponding to the nucleus of the micelle in the following form (cf. (2.7)):

$$U=\frac{1}{4a^2}\int_0^R dr_0\int_0^{r_0} dr E(r,r_0)\,g(r_0). \tag{A.1}$$

Two additional conditions are imposed on the unknown functions $E(r, r_0)$ and $g(r_0)$:

$$\int_0^{r_0}\frac{dr}{E(r,r_0)}=N_A, \tag{A.2}$$

$$\int_r^R dr_0\frac{g(r_0)}{E(r,r_0)}=S_d(R-r), \tag{A.3}$$

where

$$S_1(r)=2,\qquad S_2(r)=2\pi r,\qquad S_3(r)=4\pi r^2;$$

$d = 3$ corresponds to a spherical micelle, $d = 2$ to a cylindrical micelle, and $d = 1$ to a lamelle. The condition (A.2) fixes the number of links in each chain, while the conditions (A.3) expresses the constancy of the density of the nucleus of the micelle.

The minimization of (A.1) under the additional conditions (A.2) and (A.3) leads to the equation

$$E(r,r_0)=[\varphi(r_0)-\varphi(r)]^{1/2},$$

Here φ is an unknown function. Let $dr/d\varphi = f(\varphi)$. Then we can rewrited (A.2) in the form

$$\int_{\varphi^*}^{\varphi_0}\frac{f(\varphi)\,d\varphi}{(\varphi_0-\varphi)^{1/2}}=N. \tag{A.4}$$

Here we have $\varphi_0 = \varphi(r_0)$ and $\varphi^* = \varphi(0)$. The solution of Eq. (A.4) has the form

$$f(\varphi)=\pi^{-1}N_A(\varphi-\varphi^*)^{-1/2}, \tag{A.5}$$

Hence, upon taking account of the definition of the function $f(\varphi)$, we find

$$E(r,r_0)=\pi(r_0^2-r^2)^{1/2}/2N_A. \tag{A.6}$$

Upon substituting (A.6) into (A.3), we obtain the equation

$$\int_u^1\frac{h(t)\,dt}{(t-u)^{1/2}}=\pi S_d(1-u^{1/2}), \tag{A.7}$$

where

$$g(r_0)=\frac{R^{d-2}r_0}{N_A}h\left(\frac{r_0^2}{R^2}\right).$$

The right-hand side of Eq. (A.7) contains a polynomial of no higher than second order in $u^{1/2}$. One can easily show that $S = 1$ corresponds to $h(t) = (1-t)^{-1/2}$, $S = u^{1/2}$ corresponds to $h = (1-t)^{-1/2} - \tanh^{-1}(1-t)^{1/2}$, and $S = u$ corresponds to $h = (2t-1)(1-t)^{-1/2}$.

Thus for $d = 3$ we have

$$g(r)=8\pi R^2N_A^{-1}x\{\operatorname{arth}(1-x^2)^{1/2}-(1-x^2)^{1/2}\}, \tag{A.8}$$

where $x = r/R$. Here number density of ends in the micelle is

$$\rho(x)=\frac{2}{N_A}\frac{x}{(1-x^2)}\{\operatorname{arth}(1-x^2)^{1/2}-(1-x^2)^{1/2}\},$$

and the $\rho(x)$ relationship is shown in Fig. 8a. For $d = 2$ we have

$$\begin{gathered} g(r)=2\pi RN_A^{-1}x\operatorname{arth}(1-x^2)^{1/2},\\ \rho(x)=N_A^{-1}\frac{x}{1-x}\operatorname{arth}(1-x^2)^{1/2}. \end{gathered} \tag{A.9}$$

Finally, for $d = 1$ (see Fig. 8b) we have:

$$g(r)=\frac{2}{N_A}\frac{x}{(1-x^2)^{1/2}},\qquad \rho(x)=x/[(1-x^2)^{1/2}N_A]. \tag{A.10}$$

Upon substituting the solutions (A.8)–(A.10) into (A.1), we find the elastic energy of the nucleus of the micelle[4]:

$$U_d=\frac{\pi^2}{32a^2}\lambda_d\frac{R^{d+2}}{N_A^2}, \tag{A.11}$$

where

$$\lambda_1={}^4/_3,\qquad \lambda_2=\pi/3,\qquad \lambda_3=4\pi/15.$$

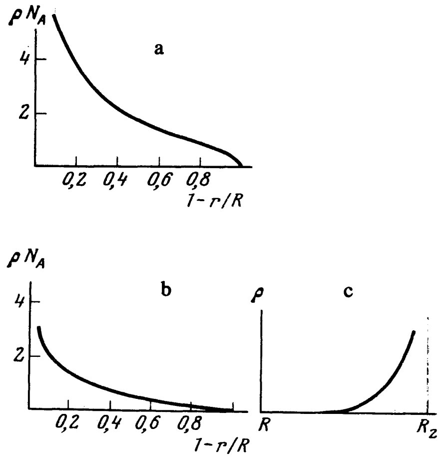

FIG. 8. Distribution of the free ends inside the nucleus of a spherical micelle (a), inside a plane layer (b), and in the outer part (the coat) of a spherical or cylindrical domain (c).

Now let us calculate the elastic energy of the outer part of the micelle, while assuming it spherical in form: the B blocks fill the spherical layer $R < r < R_2$, where r is the distance from the center of the micelle. If $d = 1$, then the problem reduces to one already solved. For $d = 2$ and $d = 3$ the ends of the B blocks, as it turns our, do not fill the entire spherical layer, but only a certain zone that adjoins the outer surface $r = R_2$ (Fig. 8c). Consequently the integral equation (A.7) is greatly complicated. However, an approximation works very well here that has the ends of the chains attached to the surface $r = R_2$. In fact, for the inner regions this approximation elevates the free energy for $d = 3$ by a factor of $40/\pi^2 \approx 4$, for $d = 2$ by a factor of $24/\pi^2 \approx 2.5$, and for $d = 1$ by a factor of $12/\pi^2 \approx 1.2$. For the outer regions for $d = 2$ and $d = 3$, the error will be even smaller than for $d = 1$, i.e., smaller than 20%. Thus, the elastic free energy of the outer part is[5]

$$d=3: \quad U_{ex}=(16\pi a^2)^{-1}Q^2(1/R-1/R_2), \tag{A.12}$$

$$d=2: \quad U_{ex}=(16\pi a^2)^{-1}2Q^2\ln(R_2/R). \tag{A.13}$$

Here Q is the number of chains in the micelle.

APPENDIX B

Let us study a melt of diblock copolymers with blocks of infinite length. The free energy of interaction of the blocks has the form (2.2) under the additional condition (2.1). If $\chi > 0$, the system becomes layered: the half-space $x > 0$ is filled with A blocks, and $x < 0$ with B blocks. Then the junction of the A and B blocks here proves to be somewhere near the plane $x = 0$. Let us find the surface free energy of the system and the distribution of junction points.

Let the inhomogeneous distribution of the links of type A be fixed: $\Phi_A = \Phi(x)$. In the zero-order approximation we can neglect the end effects (in particular, the fact that the ends of the A and B blocks are joined) and can calculate the conformational component of the free energy by the following formula (see Ref. 17):

$$F^A_{conf} = \frac{a^2}{4}\int d^3r \frac{(\nabla\Phi_A)^2}{\Phi_A}. \tag{B.1}$$

Upon summing the contributions from the A and B blocks, we obtain the following expressions for the total free energy per unit surface:

$$\mathscr{F}_0 = \chi\int \Phi(1-\Phi)\,dx + \frac{a^2}{4}\int \frac{(\Phi')^2}{\Phi(1-\Phi)}\,dx. \tag{B.2}$$

Upon minimizing (B.2) while using the substitution $\Phi = \sin^2 y$, we find the surface tension[1]:

$$\sigma_0 = a\chi^{1/2} \tag{B.3}$$

and the density profile

$$\Phi(x) = \frac{1}{2}\left(1 + \mathrm{th}\frac{x}{\Delta}\right). \tag{B.4}$$

Here the thickness of the surface layer is $\Delta = a\chi^{-1/2}$. The applicability of (B.2) is restricted by the condition $\Delta \gg a$. Hence the interaction parameter must be small: $\chi \ll 1$.

Let us take into account the end corrections. We can do this by the method of Ref. 23. The partition function of a chain (referring to one of the blocks) whose ends lie at the points $\mathbf{r}_1$ and $\mathbf{r}_2$ is

$$Z = Z_0\psi(\mathbf{r}_1)\psi(\mathbf{r}_2). \tag{B.5}$$

Here Z_0 is the partition function in the zero-order approximation, and $\psi(r)$ is the *a priori* distribution function of the ends as normalized by the condition:

$$\int \psi^2(\mathbf{r})\,d^3r = 1 \tag{B.6}$$

and as connected to $\Phi(\mathbf{r})$:

$$\psi^2(\mathbf{r}) = \mathrm{const}\,\Phi(\mathbf{r}). \tag{B.7}$$

Thus, if the second ends of the chains are free, while the first ends are distributed with the concentration $\rho(r)$, then the end corrections have the form

$$\Delta F = \int\left\{\rho\ln\frac{\rho}{e} - \rho\ln\psi - \rho\ln\left[\int\psi(\mathbf{r})\,d^3r\right]\right\} d^3r. \tag{B.8}$$

Here the first term in the curly brackets is the ideal-gas term.

Now let us take account of the contributions from the two blocks of the copolymer. The first ends of the A and B blocks are joined and have the same distribution function $\rho(x)$, while the other ends are free. Upon adding the expresions (B.8) corresponding to the A and B blocks, we obtain

$$F = F_0 + \int\left\{\rho\ln\frac{\rho}{e} - \rho\ln\psi_A\psi_B - \rho\ln\left(\int\psi_A\,d^3r\right) - \rho\ln\left(\int\psi_B\,d^3r\right)\right\} d^3r. \tag{B.9}$$

Upon taking account of (B.6) and (B.7) and transforming to the free energy per unit surface, we convert (B.9) into the form

$$\mathscr{F} = \mathscr{F}_0 + \int\left[\rho\ln\frac{\rho}{e} - \rho\ln(\Phi_A\Phi_B)^{1/2}\right] dx. \tag{B.10}$$

Upon minimizing (B.10) with respect to $\rho(x)$, we find $\sigma = \sigma_0 + \sigma_1$,

$$\sigma_1 = \rho_s\ln(\rho_s/\pi e\Delta), \tag{B.11}$$

$$\rho(x) = \rho_s/[\pi\Delta\,\mathrm{ch}(x/\Delta)]. \tag{B.12}$$

Here ρ_s is the number of copolymers per unit surface. Equation (B.12) shows that the junction points are concentrated in a surface layer of thickness Δ.

---

[1] These statements, which we have thus far taken on faith, will be substantiated below.

[2] The free ends of the B blocks lie far outside the coat (at a distance $\gg D$ from the micelle). Hence we can neglect them.

[3] One must not neglect the volume of the micelles only for very large τ, for which the micelles begin to overlap. However, in this case the term $\mathscr{F}_1$ is already inessential.

[4] The energy of a cylindrical domain or a plane layer is infinite. Therefore we cite below the values per unit of length of the cylinder or unit area of the plane layer.

[5] The calculation of the free energy is performed in exactly the same way as in deriving Eq. (2.7).

[1] E. Helfand and Y. Tagami, J. Chem. Phys. **56**, 3592 (1971).
[2] E. Helfand, Macromolecules **8**, 552 (1975).
[3] E. Helfand, J. Chem. Phys. **62**, 999 (1975).
[4] E. Helfand and Z. R. Wasserman, Macromolecules **9**, 879 (1976); **11**, 960 (1978); **13**, 994 (1980).
[5] L. Leibler, Macromolecules **13**, 1602 (1980).
[6] L. Leibler, Marcrmolecules **15**, 1283 (1982).
[7] L. Leibler, H. Orland, and J. C. Wheeler, J. Chem. Phys. **79**, 3550 (1983).
[8] I. Ya. Erukhimovich, Vysokomol. Soedin. **24**, 1942, 1950 (1982).
[9] K. M. Hong and J. Noolandi, Macromolecules **16**, 1083 (1983).
[10] J. Noolandi and K. M. Hong, Macromolecules **16**, 1443 (1983).
[11] T. Hashimoto, M. Shibayama, and H. Kawai, Macromolecules **13**, 1237, 1660 (1980).
[12] T. Hashimoto, M. Shibayama, and H. Kawai, Macromolecules **16**, 1093 (1983).
[13] K. Mori, H. Hasegawa, T. Hashimoto, and H. Kawai, to be submitted to Macromolecules.
[14] P. De Gennes Scaling Concepts in Polymer Physics, Cornell Univ. Press, Ithaca, N. Y., 1979 (Russ. Transl., Mir, M,. 1982).
[15] I. M. Liftshitz, Zh. Eksp. Teor. Fiz. **55**, 2408 (1968) [Sov. Phys. JETP **28**, 1280 (1969)].
[16] I. M. Liftshitz and A. Yu. Grosberg, *ibid.* **65**, 2399 (1973) [Sov. Phys. JETP **38**, 1198 (1974)].
[17] I. M. Liftshitz, A. Yu. Grosberg, and A. R. Khokhlov, Rev. Mod. Phys. **50**, 683 (1978).
[18] I. M. Liftshitz, A. Yu. Grosberg, and A. R. Khokhlov, Usp. Fiz. Nauk **127**, 353 (1979) [Sov. Phys. Usp. **22**, 123 (1979)].
[19] P. J. Flory, Principles of Polymer Chemistry, Cornell Univ. Press, Ithaca, N.Y., 1971.
[20] L. Scott, J. Chem. Phys. **17**, 279 (1949).
[21] E. M. Liftshitz and L. P. Pitaevskiĭ Statisticheskaya fizika, Ch. 1 (Statistical Physics, Part 1), Nauka, M., 1976 [Pergamon, 1980)].
[22] T. M. Birshteĭn, Abstracts of the 3rd All-Union Conference "Mathematical Methods for Studying Polymers", Pushchino, 1983.
[23] A. R. Khokhlov and A. N. Semenov, Physica (Utrecht) A **112**, 605 (1982).

Translated by M. V. King