Theory of the nematic–smectic-A transition in a melt of macromolecules consisting of a rigid and a flexible block

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(Submitted 12 December 1985)
Zh. Eksp. Teor. Fiz. **90**, 124–140 (January 1986)

A simple theoretical approach is proposed that makes it possible to describe smectic ordering in melts of block copolymers containing flexible and rigid blocks. It is shown that for such systems the Ginzburg parameter is very small, which ensures that the mean-field approximation is applicable. It is found that 1) the nematic–smectic-*A* transition can be either a second-order transition (if the volume fraction of the flexible component is small), or a first-order transition (in the opposite case); 2) in the smectic phase, with decrease of the temperature (increase of the parameter χ) one or two structural transitions can occur (the latter case is always associated with a doubling of the period of the smectic phase). The phase diagram for the system under consideration is constructed. The parameters of the smectic structures are related to molecular characteristics of the polymer. The situation in which the appearance of a smectic-*C* phase should be expected is indicated.

1. INTRODUCTION

Numerous observations of liquid-crystalline phases in polymer melts[1–3] have recently stimulated intensive development of theoretical ideas in this area. The special interest in smectic liquid-crystal polymers is connected both with the fact that they are a good model for illustrating general concepts in condensed-matter physics and biology, and with the application of materials based on them in new areas of technology.

The smectic mesophase is the most complicated and so least studied of the possible liquid-crystalline phases. The theoretical papers in which smectic liquid crystals are investigated mainly use phenomenological methods of the Landau-expansion type.[4–6] In a recent paper,[7] Dowell proposed that a lattice model be used to describe the smectic ordering of a melt of particles that consist of a rigid rod and a flexible part. A number of nonrigorous assumptions in Ref. 7 lead to what is, in our view, the qualitatively incorrect conclusion that a stable smectic phase can exist in the absence of energy of attraction between the particles.

The aim of the present paper is to give a theoretical analysis of smectic ordering in liquid-crystalline melts of two-block macromolecules with one rigid and one flexible block (Fig. 1a). The choice of this system for investigation is the most natural as a first step on the road to studying more-complicated polymer systems, such as many-block and branched polymers (Figs. 1b,c), and is at the same time of obvious interest in its own right (see, e.g., Refs. 8 and 9, in which it is proposed that films of the block copolymer polybutadiene with poly-γ-benzyl-L-glutamate be used as a model of biological membranes, etc.).

The model of the macromolecule is represented in Fig. 2a. The polymer chain is constructed from a rigid and a flexible fragment, linked together. The rigid fragment is a strongly asymmetric rod of length L and diameter d ($L/d \gg 1$). The flexible fragment is a uniform filament of length L', of diameter d', and characterized by a rigidity segment l (the distance over which substantial bending of the filament can occur); $L' \gg l \gg d'$. We shall assume that a rigid and a flexible block are incompatible and therefore tend to become spatially separated. Since separation of the system into two macroscopic phases is prevented by the chemical bonding of the blocks into a chain, a structure consisting of microdomains enriched alternately in the rigid and flexible components should be stabilized in the melt. In accordance with Ref. 10 we shall describe the effective repulsion between unlike blocks (or the equivalent attraction between like blocks) by an interaction parameter $\chi > 0$.

We also formulate the following additional statements concerning the model under consideration. First of all we use the fact that the orientational order of the rods in the region of the nematic-smectic transition should be very high. We shall assume, in the zeroth approximation, that the orientational disorder can be neglected completely, and that all the rods are strictly oriented along one axis (the z axis). As regards the flexible block, the description of its conformations is simplified substantially if we replace the uniform chain by the equivalent chain of beads on a nonmaterial fila-

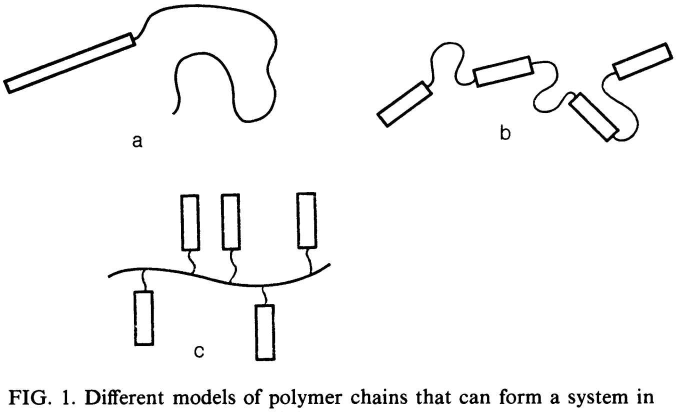

FIG. 1. Different models of polymer chains that can form a system in which smectic ordering is possible.

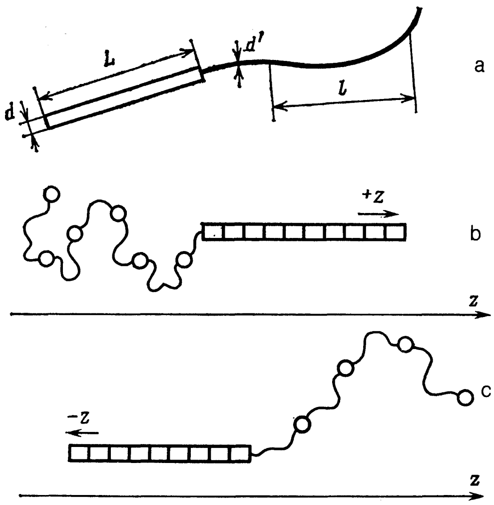

FIG. 2. a) Copolymer consisting of a rigid and a flexible block; b) macromolecule orientation corresponding to f_1; c) orientation corresponding to f_2.

ment (the standard Gaussian model; for the rules for going over to this model, consult Ref. 11). It is assumed that the beads each have volume v, the total number of beads in one macromolecule is N, and the mean square distance between neighboring beads is equal to $6a^2$ (Fig. 2b). Of course, the beads model should ensure both the correct mean square distance between the ends of the flexible filament and the correct volume of a flexible block[11]:

$$6Na^2=L'l, \qquad Nv=L'd'^2. \tag{1.1}$$

From the quantities a, d, v, N, and L we can construct two important dimensionless parameters:

$$\lambda\equiv\frac{\varphi}{1-\varphi}=\frac{Nv}{Ld^2}=\frac{L'd'^2}{Ld^2}, \qquad \varkappa=\frac{Na^2}{L^2}=\frac{L'l}{6L^2}. \tag{1.2}$$

An important role is played by their ratio

$$\nu=\varkappa/\lambda\equiv(l/6L)\,(d^2/d'^2). \tag{1.3}$$

As a rule, $d\sim d'$ and $L\gg l$, and therefore $\nu\ll 1$. This is the limiting case that will be considered in the following.

The results of the work are described in the following sequence. First we write out the free energy of the melt in the formalism of the mean-field method and discuss the character of the nematic-smectic transition and the possible structural transitions within the smectic phase in this approximation. In the last Section we analyze the density correlation function of one of the components in the region of the nematic-smectic transition.

2. THE FREE ENERGY OF THE SYSTEM

Each macromolecule can be found in two essentially different conformational states associated with the orientation of the macromolecule relative to the z axis. To these states (which are shown in Figs. 2b and 2c) correspond different distributions $\tilde{f}_1(\mathbf{r})$ and $\tilde{f}_2(\mathbf{r})$—the concentrations of the points of attachment between the rods and the flexible parts. The volume fraction occupied by rods near the point $\mathbf{r}$ is obviously equal to

$$\eta(\mathbf{r})=\int_0^L f_1(\mathbf{r}-t\mathbf{e}_z)\,dt+\int_0^L f_2(\mathbf{r}+t\mathbf{e}_z)\,dt, \tag{2.1}$$

where $f_1=d^2\tilde{f}_1, f_2=d^2\tilde{f}_2$, and $\mathbf{e}_z$ is the unit vector along the z axis. Henceforth it will be convenient to take the length L of the rod as the unit of length. Since we are considering spatial variation only along the z coordinate, we can rewrite (2.1) in the form

$$\eta(z)=\int_0^1 \sigma(z-t)\,dt, \qquad \sigma(z)=f_1(z)+f_2(z+1). \tag{2.2}$$

The volume fraction occupied by flexible blocks in the layer z is equal to

$$g(z)=c(z)v,$$

where $c(z)$ is the total concentration of beads.

The condition that the melt be incompressible has the form

$$\eta(z)+g(z)=1. \tag{2.3}$$

The average volume fractions are equal to

$$\langle\eta(z)\rangle=1-\varphi, \qquad \langle g(z)\rangle=\varphi,$$

where

$$\varphi=Nv/(Nv+Ld^2)=L'd'^2/(L'd'^2+Ld^2). \tag{2.4}$$

The free energy F of the system per area d^2 in the xy plane can be separated into four terms

$$F=F_{id}+F_{at}+F_{st}+F_{fl},$$

where

$$F_{id}=T\int\left\{f_1\ln\frac{f_1}{e}+f_2\ln\frac{f_2}{e}\right\}dz \tag{2.5}$$

is the ideal-gas term, F_{at} corresponds to the energetic interaction (the attraction between like blocks), F_{st} corresponds to the steric interaction of the rods, and F_{f1} describes the change of the free energy on account of the restriction on the number of possible conformations of the flexible fragments in the microstratified system. We shall write the term F_{at} in the customary form[10]:

$$F_{at}=-\chi T\int\eta^2\,dz. \tag{2.6}$$

To find F_{st} we shall use the lattice-packing model, i.e., we shall assume that the rods are arranged on a lattice with spacing d such that each rod occupies L/d successive cells along the z axis. It is necessary to find the number of ways in which the rods can be placed on the lattice without self-intersections for a given distribution $\sigma(z)$. This can be done by generalizing the well known arguments of Flory[12] to the case of a nonuniform system. We shall denote the number of cells in one layer of the lattice (in the xy plane) by n. Let N_1 be the number of rods that begin in the first layer (and end in the layer with label L/d), let N_2 be the number of rods that begin in the second layer, and so on. The total number of ways of placing the rods for given N_1, N_2,... is equal to

$$\mathcal{N}=C_n^{N_1}C_{n-N_1}^{N_2}C_{n-N_1-N_2}^{N_3}\dots .$$

The term $F_{\rm st} = -Tn^{-1}\ln(\mathcal{N}/\mathcal{N}_0)$, where $\mathcal{N}_0$ is the number of ways of placing the rods when self-intersections are not forbidden:

$$\mathcal{N}_0=C_n^{N_1}C_n^{N_2}C_n^{N_3}\dots .$$

Taking into account that $N_j = n(d/L)\sigma(z_j)$ and taking the thermodynamic limit, we find

$$F_{st}=T\int\Big\{\sigma(z)+\frac{L}{d}[1-\eta(z)]\ln[1-\eta(z)]$$

$$-\frac{L}{d}\left[1-\eta(z)+\frac{d}{L}\sigma(z)\right]\ln\left[1-\eta(z)+\frac{d}{L}\sigma(z)\right]\Big\}dz. \quad (2.7)$$

For a uniform system, (2.7) goes over into the corresponding formula of Ref. 13. Since $L/d\gg 1$, formula (2.7) can be simplified:

$$F_{st}=T\int\sigma(z)\ln\frac{1}{1-\eta(z)}dz. \quad (2.8)$$

We turn to the calculation of the last term in the free energy:

$$F_{fl}=-d^2TS[c(z),\tilde{f}(z)],$$

where S is the conformational entropy of the flexible parts for a given total concentration $c(z)$ of all the beads and a given concentration of the end beads adjacent to the rigid rods: $\tilde{f}(z)=\tilde{f}_1(z)+\tilde{f}_2(z)$. We have not succeeded in obtaining an exact analytical expression for $S[c,\tilde{f}]$ in the general case. We shall investigate the limiting cases of short-wavelength and long-wavelength variations of the concentrations. If the characteristic length scale b of variation of the concentrations c and $\tilde{f}$ is considerably smaller than the characteristic spatial size of a flexible block ($b\ll N^{1/2}a$), end effects can be neglected completely. In this case, $S=S[c]$ depends only on the total concentration of beads. Under the condition that the variation of the concentration $c(z)$ is not too rapid ($b\gg a$), the entropy $S[c(z)]$ can be written in the form[11]

$$S_1[c]=-\frac{a^2}{4}\int\frac{(\nabla c)^2}{c}dz, \qquad a\ll b\ll N^{1/2}a, \quad (2.9)$$

where ∇ is the spatial gradient.

We shall consider the opposite limiting case $b\gg N^{1/2}a$. We shall assume that the stretching of the flexible blocks is small (the relative change in the distance between the ends of a flexible block is much less than unity). Then, as shown in Appendix A, the conformational entropy is equal to (cf. Ref. 13)

$$S_2[c,\tilde{f}]=-\frac{1}{2}\int\frac{D^2}{\varepsilon}dz, \qquad b\gg N^{1/2}a, \quad (2.10)$$

where $\varepsilon = 2a^2c/3$, and the quantity $\mathbf{D}$ is determined from equations analogous to the equations of electrostatics:

$$\mathbf{D}=-\varepsilon\nabla\psi, \qquad \nabla\mathbf{D}=\tilde{f}-c/N; \quad (2.11)$$

the function ψ is proportional to the potential of the self-consistent field acting on the beads. As a reasonable approximation for S we can take the sum of the expressions (2.9) and (2.10). This sum describes the behavior of S asymptotically exactly in the short-wavelength and long-wavelength limits, and, as shown by analysis, even in intermediate cases gives an error less than 20%.

Using the notation (1.2) we can write the formula for $F_{\rm fl}$ in the form

$$F_{fl}=\frac{\varkappa}{4\lambda}T\int\frac{(d\eta/dz)^2}{1-\eta}dz+\frac{3}{4}T\frac{\lambda}{\varkappa}\int\frac{\mathcal{D}^2}{1-\eta}dz, \quad (2.12)$$

where

$$\mathcal{D}=Dd^2, \qquad \mathbf{D}=\mathbf{D}l_z, \qquad d\mathcal{D}/dz=f_1+f_2-g/\lambda. \quad (2.13)$$

Thus, formulas (2.5), (2.6), (2.8), and (2.12) determine the free energy F of the system as a functional of f_1 and f_2. The polymer melt is a weakly fluctuating system,[14] and therefore to find its thermodynamic characteristics it is necessary simply to minimize the functional F with respect to f_1 and f_2. The nematic phase corresponds to uniform distributions: $f_1=f_2=(1-\varphi)/2$. The smectic-A phase corresponds to periodic functions $f_1(z)$ and $f_2(z)$. In Secs. 3–5 we investigate the conditions of formation and the properties of the smectic-A phase.

3. THE SPINODAL OF THE SYSTEM. THE MONOLAYER-BILAYER PHASE TRANSITION

We shall investigate the stability of the nematic melt against the formation of a smectic structure, which, for the system under consideration, corresponds to microphase stratification of the lamellar type (cf. Ref. 13). For this, in accordance with the general scheme of Ref. 15, we specify increments:

$$f_1={}^1/_2(1-\varphi)+\delta f_1(z), \qquad f_2={}^1/_2(1-\varphi)+\delta f_2(z),$$

go over to Fourier components, and write $\delta F = F - F_0$ with quadratic accuracy:

$$\delta F=\int\{C_{11}|f_{1\mathbf{q}}|^2+C_{22}|f_{2\mathbf{q}}|^2+2\,\mathrm{Re}\,(C_{12}f_{1\mathbf{q}}f_{2\mathbf{q}}^*)\}\frac{dq}{2\pi}, \quad (3.1)$$

where C_{11}, C_{22}, and C_{12} depend on $\mathbf{q}$.

It is easy to show that $C_{11} = C_{22}$, and therefore the condition for stability against smectic ordering has the form $C_{11} > |C_{12}|$ for all $\mathbf{q}$. The spinodal equation is

$$\min_{\mathbf{q}}\{C_{11}-|C_{12}|\}=0. \quad (3.2)$$

The formulas of the preceding Section permit us to calculate C_{11} and C_{12}. After certain transformations Eq. (3.2) takes the form $\chi=\chi_c$, where

$$\chi_c=\min_{\alpha}\frac{1}{2(1-\varphi)}\Big\{\Big(1+\frac{2\varkappa}{\lambda^2}\Big)\alpha^2+\Big(\frac{1}{\lambda}+\frac{\alpha}{\mathrm{tg}\,\alpha}\Big)^2$$

$$\Big(1+\frac{1}{\sin^2\alpha+8\alpha^2\varkappa/3}\Big)\Big\}, \quad (3.3)$$

$$\alpha=qL/2.$$

If $\lambda\ll 1$ (i.e., $\varphi\ll 1$), minimization with respect to α in (3.3) in the leading approximation leads to the equation

$$1/\lambda+\alpha/\mathrm{tg}\,\alpha=0,$$

whence $\alpha_c \cong \pi(1-\lambda)$. Thus, when the volume fraction φ of flexible blocks is small, the instability appears when

$$\chi_c \approx {}^1/_2\pi^2(1+2\varkappa/\lambda^2) \tag{3.4}$$

and corresponds to a density modulation with period (in units of L)

$$P=\frac{\pi}{\alpha}\approx 1+\lambda-{}^1/_3\pi^2\lambda^3. \tag{3.5}$$

In the opposite limit $\lambda \gg 1$ (i.e., $1-\varphi \ll 1$) and $\varkappa \ll 1$ (the case $\varkappa \gg 1$ will be considered separately), formula (3.3) reduces to

$$\chi_c=\frac{1}{2(1-\varphi)}\min_{\alpha}\frac{\alpha^2}{\sin^4\alpha}, \tag{3.6}$$

whence $\alpha_c = 1.17$, and

$$\chi_c=0.95/(1-\varphi), \quad P=2.69. \tag{3.7}$$

Thus, if the flexible blocks occupy most of the volume, density modulations with a period comparable to L arise near the spinodal.

In order to elucidate the character of the nematic-smectic transition it is necessary to take into account the next terms (after the quadratic term (3.1)) in the expansion of the free energy. The cubic term in the expansion plays no role;[4] the quartic term is calculated in Sec. 6, and is found to be positive on the spinodal (both for $\lambda \ll 1$ and for $\lambda \gg 1$). In addition, analysis shows that for $\lambda \ll 1$, $v \ll 1$ and for $\lambda \gg 1$, $\varkappa \ll 1$ smectic ordering is not favored for $\chi < \chi_c$. Consequently, in these cases the nematic-smectic transition is a second-order transition and occurs at $\chi = \chi_c$, i.e., on the spinodal.

We now investigate the phase transition between smectic structures that occurs at large values of the incompatibility parameter $\chi \gg \chi_c$. Here there arises competition between two structures, of the monolayer (Fig. 3a) and bilayer (Fig. 3b) types.

In the former the rods densely occupy layers of thickness L, which alternate with layers of thickness λL occupied by flexible blocks. The domain walls between the layers have a small thickness Δ. We draw attention to the fact that the period of this structure almost coincides with (3.5). Let $\varkappa \ll \lambda^2$; then the flexible blocks have to be strongly extended, in order to fill the layer of thickness λ. The corresponding free energy, calculated from formula (2.12) (only the second term in this formula is important), is equal to

$$\frac{F_1}{(\mathscr{L}T)}=\frac{1}{16}\frac{\lambda^2}{\varkappa(1+\lambda)}, \tag{3.8}$$

where $\mathscr{L}$ is the total extent of the system along the z axis. The energy of a domain wall is calculated in Appendix B, and is equal to

$$\sigma=(\varkappa\chi/2\lambda)^{1/2},$$

which corresponds to the following contribution to the free energy:

$$F_2/\mathscr{L}T=\sigma/(1+\lambda). \tag{3.9}$$

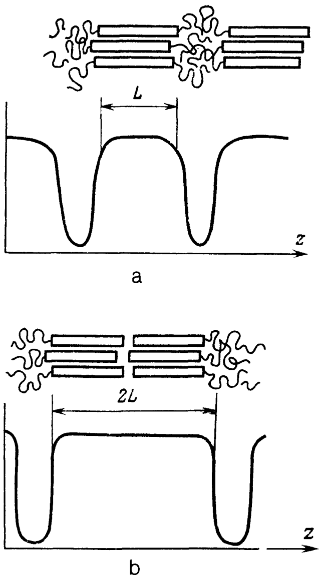

FIG. 3. a) Structure of the monolayer type; b) structure of the bilayer type.

The structure of the bilayer type is formed by layers of twice the thickness, and therefore the flexible blocks are extended twice as much, with a corresponding increase in the free energy of stretching F_1 by a factor of four. On the other hand, there are half as many domain walls in this structure. For large values of χ the latter circumstance is decisive and a first-order monolayer-bilayer transition occurs. The transition point $\chi = \chi^*$ is determined by the equation

$$F_1+F_2=4F_1+F_2/2,$$

whence

$$\chi^*={}^9/_{128}\lambda^5/\varkappa^3. \tag{3.10}$$

4. STRUCTURE OF THE SMECTIC PHASES FOR $\lambda \ll 1$

We proceed to a systematic study of the properties of the smectic order in the case when the rigid blocks occupy most of the volume of the system. For $\chi \gg \chi_c$ the volume occupation $g(z)$ of space by the flexible blocks should have the form depicted schematically in Fig. 4a. From this Figure it is already clear that the period of the structure should be exactly equal to $P = 1+\lambda$. In fact, the space between the domains that are enriched in the flexible component is entirely occupied by rods. This means that there is exactly one rod per period (along the z axis) and per area d^2 in the plane of the layer (the xy plane). Consequently, by virtue of the close-packing condition (2.3), the volume Pd^2 should be equal to the volume

$$Ld^2+L'd'^2=d^2(1+\lambda)$$

of a macromolecule, i.e., $P = 1+\lambda$. Therefore,

$$\int_0^P \sigma(z)\,dz=P(1-\varphi)=1. \tag{4.1}$$

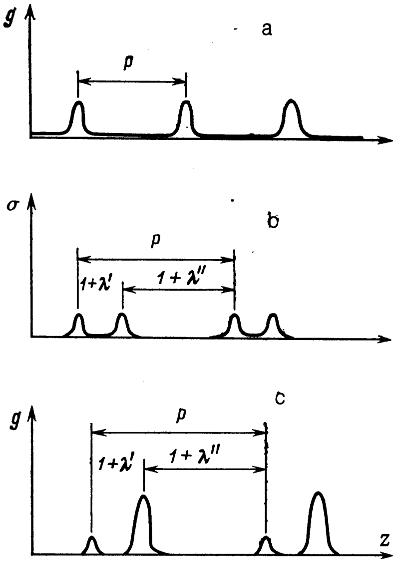

FIG. 4. a) Dependence of the concentration of flexible fragments on the coordinate z in the case $\varphi \ll 1$; b) distribution of the starting points of rigid blocks in the smectic phase with doubled period.

Taking into account (4.1) and the definition of the function $\eta(z)$, we find

$$g(z) \equiv 1-\eta(z)=\int_{z}^{z+\lambda} \sigma(z)\,dz$$

$$=\lambda\sigma(z)\left[1+\frac{\lambda}{2}\frac{\sigma'}{\sigma}+\frac{\lambda^2}{6}\frac{\sigma''}{\sigma}+\ldots\right], \qquad (4.2)$$

$$\sigma(z)=f_1(z)+f_2(1+z)=f_1(z)+f_2(z-\lambda). \qquad (4.3)$$

Substituting (4.2) into (2.8), expanding in the small parameter λ, and retaining the leading terms we arrive at the expression

$$\frac{F_{el}}{T}=\int \sigma \ln\frac{1}{\lambda\sigma}\,dz+\frac{\lambda^2}{8}\int\frac{\sigma'^2}{\sigma}\,dz. \qquad (4.4)$$

An analogous procedure enables us to simplify the expressions for $F_{\rm at}$ and $F_{\rm fl1}$ ($F_{\rm fl1}$ corresponds to the first term in formula (2.12), and $F_{\rm fl2}$ corresponds to the second term):

$$\frac{F_{at}}{T}=-\chi\lambda^2\int \sigma^2\,dz, \qquad \frac{F_{fl1}}{T}=\frac{\varkappa}{4}\int\frac{\sigma'^2}{\sigma}\,dz. \qquad (4.5)$$

From (4.3) follows the expansion

$$f_1+f_2=\sigma+\lambda f_2'-{}^1/_2\lambda^2 f_2''.$$

Expressing f_1 and f_2 in terms of $\psi \equiv f_2-f_1$ and σ, and substituting the result into (2.5) and (2.12), we find

$$\frac{F_{id}}{T}=\int\left\{\sigma\ln\frac{\sigma}{2e}+\frac{1}{2\sigma}\left(\psi-\frac{\lambda\sigma'}{2}\right)^2\right\}dz; \qquad (4.6)$$

$$\frac{F_{fl2}}{T}=\frac{3}{16}\frac{\lambda^2}{\varkappa}\int \sigma^{-1}\left(\psi-\frac{\lambda\sigma'}{3}\right)^2 dz. \qquad (4.7)$$

Combining all the terms and minimizing with respect to ψ, we obtain the final expression for the free energy:

$$\frac{F}{T}=\int\left(\ln\frac{1}{2e\lambda}+Q\frac{\sigma'^2}{\sigma}-\chi\lambda^2\sigma^2\right)dz, \qquad (4.8)$$

where

$$Q=\frac{\lambda^2}{8}\left(1+\frac{2\varkappa}{\lambda^2}+\frac{1}{24}\frac{\lambda^2}{\varkappa+3\lambda^2/8}\right).$$

We note that the first term in the brackets in (4.8) corresponds to the free energy of the nematic phase.

It should be noted that the expression (4.8) is valid for any χ, and not only for $\chi \gg \chi_c$, if the period of the structure is exactly equal to $P_0 = 1+\lambda$. We shall see what the expression (4.8) gives for the spinodal. For this we minimize the expression (4.8) with respect to σ for a given period P_0 and with the additional condition (4.1). As a result we obtain the equation of the spinodal:

$$\chi_c=\frac{\pi^2}{2}\left(1+\frac{2\varkappa}{\lambda^2}+\frac{1}{24}\frac{\lambda^2}{\varkappa+3\lambda^2/8}\right). \qquad (4.9)$$

The slight difference between (4.9) and the exact solution (3.4) is connected with the fact that the true period of the structure on the spinodal differs slightly from P_0.

The density function is specified by the following relation (see the calculations in Appendix B):

$$g(z)=\frac{\lambda k_0}{2\,\mathrm{ch}^2 k_0 z}, \qquad k_0=\frac{\lambda^2}{8Q}\chi. \qquad (4.10)$$

Let $\varkappa \ll \lambda^2$; then $k_0 = \chi$, and with increase of χ the domains enriched in the flexible component become narrower and at the same time the density of the flexible component in these domains increases. For $\chi \sim 1/\lambda$ this density becomes of the order of unity, and the size of the domain becomes of the order of λ. Above these values of χ formula (4.8) ceases to be valid, since gradient expansions of the type (4.2) become inapplicable. Further analysis shows that for $\chi \geqslant 1/\lambda$ the structure practically does not change. In this stable structure the density function $g(z)$ has a rectangular shape. In this state, $\rho = f_1 + f_2 - g/\lambda$, i.e., the flexible parts of the macromolecules are not extended (they are similar in shape to a "Gaussian ball"), and, therefore, by analogy with the electrostatic problem, such a structure can be called neutral.

The transition to the monolayer-type structure (in which the period does not change, but the domains acquire a rectangular shape) occurs as a first-order phase transition at

$$\chi=\chi_1 \gg \lambda/16\varkappa \gg 1/\lambda. \qquad (4.11)$$

Finally, at $\chi = \chi^* \gg \chi_1$ the final, first-order, monolayer-bilayer transition occurs (see formula (3.10)).

In the case $\chi \gg \lambda^2$, still in the stage of growth of the domains, a transition to a phase with doubled period occurs. We shall investigate this transition. It is clear that the function $\sigma(z)$ should have the form depicted in Fig. 4b: It consists of identical waves $\sigma(z) = U(z - z_j)$ (z_j is the average coordinate of the wave), separated alternately by intervals of length $1+\lambda' \equiv 1+\lambda(1-\alpha)$ and $1+\lambda'' \equiv 1+\lambda(1+\alpha)$, where α is an asymmetry parameter; the period of the structure is equal to $P = 1+\lambda'+1+\lambda'' = 2P_0$.

The density function of the flexible component corresponds to alternating waves of different amplitudes (Fig. 4c). The domain corresponding to the lower wave is described by the formula

$$g(z)=1-\eta(z)=1-\int\limits_{z-1}^{z}\sigma(z)\,dz=\int\limits_{z}^{z+\lambda}U(z-z_j)\,dz\approx\lambda U(z-z_j). \tag{4.12}$$

Analogously, for the other domain,

$$g(z)\approx\lambda''U(z-z_j). \tag{4.13}$$

From the condition $\rho\cong 0$ we find

$$f_1\approx f_2\approx g/2\lambda. \tag{4.14}$$

Substituting now (4.12)–(4.14) into (2.5), (2.6), (2.8) and (2.12) and performing the same expansions as in the derivation of formula (4.8), we find the free energy of the system per period $P=2P_0$:

$$\frac{F}{T}=\frac{\varkappa}{2}\int\frac{U'^2}{U}dz-2\chi\lambda^2(1+\alpha^2)\int U^2\,dz+2\ln\frac{1}{2e\lambda}+S(\alpha), \tag{4.15}$$

where

$$S(\alpha)=\alpha\ln\frac{1+\alpha}{1-\alpha}=2\alpha^2+\frac{2\alpha^4}{3}+\dots. \tag{4.16}$$

Minimizing (4.15) with the additional condition (cf. (4.1))

$$\int U(z)\,dz=1$$

and for fixed α, we find

$$U(z)=\frac{k_0}{2\operatorname{ch}^2 k_0 z},\qquad k_0=\frac{\lambda^2}{2\varkappa}\chi(1+\alpha^2). \tag{4.17}$$

For $\alpha=0$ (4.17) agrees with (4.10). We substitute (4.10) into (4.15):

$$\frac{F}{T}=2\ln\frac{1}{2e\lambda}+S(\alpha)-\frac{1}{6}\frac{\lambda^4\chi^2}{\varkappa}(1+\alpha^2)^2. \tag{4.18}$$

Minimization of (4.18) with respect to α shows that the doubling of the period occurs by a first-order phase transition at

$$\chi=\chi_1=2.42\varkappa^{1/3}/\lambda^2\gg\chi_c, \tag{4.19}$$

and the asymmetry parameter α at the transition point is equal to

$$\alpha=0.52. \tag{4.20}$$

As χ increases for $\chi>\chi_1$ the amplitude of the weaker waves rapidly decreases practically to zero, while the sharp waves grow yet more and gradually become narrower. At $\chi\sim\varkappa/\lambda^3\gg\chi_1$ a smooth transition occurs to a bilayer-type structure, characterized by a rectangular dependence $g(z)$.

5. PHASE TRANSITIONS FOR $\lambda\gg 1$

We shall consider the properties of the smectic order in the case when the flexible blocks occupy most of the volume ($\lambda\gg 1$; it is assumed, of course, that $\nu=\varkappa/\lambda\ll 1$).

First let $\varkappa\ll 1$. As shown in Sec. 3, the nematic-smectic transition in this case is a second-order phase transition and occurs on the spinodal at $\chi=\chi_c$ (formula (3.7)). It is not difficult to show that for $\chi\gg\chi_c$ a neutral structure ($\rho=0$), analogous to that considered in the preceding Section for $\lambda\ll 1$ and $\varkappa\ll\lambda^2$, is stabilized.

We note that

$$\rho=f_1+f_2-\frac{1-\eta}{\lambda}\approx f_1+f_2-\frac{1}{\lambda},$$

since $\langle\eta\rangle=1-\varphi\ll 1$, and therefore the condition $\rho=0$ gives $f_1+f_2=1/\lambda$, i.e.,

$$f_1=\frac{1}{2\lambda}[1+V(z)],\qquad f_2=\frac{1}{2\lambda}[1-V(z)], \tag{5.1}$$

where $V(z)$ can vary between the limits -1 and 1. If $\chi\gg\chi_c$, the main contribution to the free energy is given by the term (2.6), which we write in the form

$$\frac{F_{at}}{T}=-\chi\mathscr{L}(1-\varphi)^2-\chi\int\tilde{\eta}^2\,dz, \tag{5.2}$$

where $\tilde{\eta}=\eta-\langle\eta\rangle$ can be represented, with allowance for (5.1), in the form

$$\tilde{\eta}(z)=\frac{1}{2\lambda}\int\limits_0^1[V(z-t)-V(z+t)]\,dt. \tag{5.3}$$

The expression (5.2), with the condition (5.3), must be minimized with respect to $V(z)$. In order of magnitude, the answer is clear in advance:

$$F_{at}/\mathscr{L}T=-\chi\lambda^{-2}(1+\beta), \tag{5.4}$$

where β is a numerical coefficient. By taking the trial function $V(z)$ in the form depicted in Fig. 5a, we obtain

$$\beta_{max}={}^1/_3,\quad 2<P<4.$$

For the trial function $B(z)=\cos kz$, we obtain

$$\beta(k)=\frac{1}{2k}(1-\cos k),\qquad \beta_{max}=0.362,\qquad P=\frac{2\pi}{k}=2.69. \tag{5.5}$$

From these results it is clear that the true dependence $V(z)$ should have the form depicted approximately in Fig. 5b, and the parameters of the structure should be close to (5.5).

For sufficiently large values of χ the neutral structure becomes less favored than the structure depicted in Fig. 6: The rigid rods form domains of thickness 1, separated by an interval S, $1+S$. The packing factor of the rods in the domains is obtained from the condition $\langle\eta\rangle=1/\lambda$:

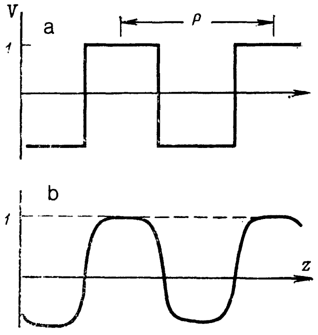

FIG. 5. a) Trial function $V(z)$; b) true solution for $U(z)$.

$$\eta_{max}=(1+S)/\lambda.$$

The free energy is determined mainly by the terms F_{at} and F_{fl2}. It is not difficult to find that the free energy per unit length is equal to

$$\frac{F}{\mathscr{L}T}=\frac{F_{at}+F_{fl2}}{\mathscr{L}T}=-\frac{\chi}{\lambda^2}(1+S)+\frac{1-S+S^2}{16\varkappa\lambda}. \qquad (5.6)$$

Minimizing with respect to S, we find

$$\frac{F}{\mathscr{L}T}=-\frac{\chi}{\lambda^2}\left(\frac{3}{2}+\frac{4\varkappa\chi}{\lambda}-\frac{3}{64}\frac{\lambda}{\varkappa\chi}\right), \quad S=\frac{1}{2}+\frac{8\varkappa\chi}{\lambda}. \qquad (5.7)$$

Comparing (5.7) with (5.4)–(5.5), we find that a first-order phase transition occurs at

$$\chi=\chi_1=0{,}09\lambda/\varkappa\gg\chi_c \qquad (5.8)$$

with the formation of a structure of the type shown in Fig. 6; the period of this structure at the transition point is

$$P=1+S=2.24, \qquad (5.9)$$

i.e., is somewhat smaller than the period in the neutral phase.

With increase of χ the period P increases in accordance with the law

$$P={}^3/_2+8\varkappa\chi/\lambda, \quad \eta_{max}={}^3/_2\lambda+8\varkappa\chi/\lambda^2.$$

This growth ceases when $\bar{\eta}_{\max}$ becomes equal to 1, i.e., when $\chi=\chi_2=\lambda^2/8\varkappa$. For large values of $\chi>\chi_2$ the system has a structure of the monolayer type. The final, first-order, monolayer-bilayer phase transition occurs at

$$\chi=\chi^*=\frac{9}{128}\frac{\lambda^5}{\varkappa^3}\gg\chi_2.$$

We now consider the situation when $\varkappa\gg1$. In this case the smectic ordering occurs directly with the formation of a structure of the type shown in Fig. 6, omitting the neutral phase. To investigate the corresponding transition it is necessary to add to the free energy (5.6) the ideal-gas term (2.5), which, in the logarithmic approximation, is equal to

$$F_{id}/\mathscr{L}T=\lambda^{-1}\ln S, \quad S\gg1. \qquad (5.10)$$

Minimizing the free energy of the smectic phase (the sum of the expressions (5.6) and (5.10)) with respect to S and equating it to the energy of the nematic phase ($F/\mathscr{L}T=-\chi/\lambda^2$), we find that the nematic-smectic transition for $\varkappa\gg1$ occurs as a first-order phase transition at

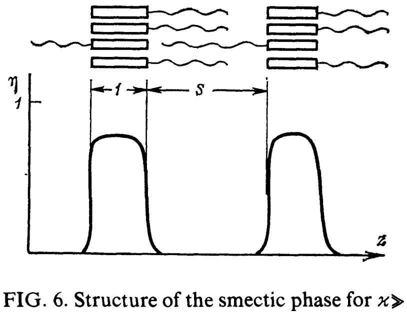

FIG. 6. Structure of the smectic phase for $\varkappa\gg1$.

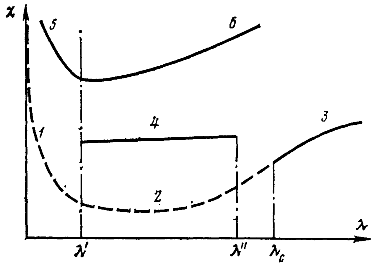

FIG. 7. Schematic phase diagram of the system for a fixed value of $\nu=\varkappa/\lambda\ll1$. The solid lines correspond to a first-order transition, and the dashed lines to a second-order transition; $\lambda_c\cong0.3/\nu$, $\lambda'\sim\nu$, $\lambda''\sim\lambda_c$. The numbers indicate the following dependences: 1) $\chi=4.93(1+2\nu/\lambda)$, $\lambda\ll1$; 2) $\chi=0.95\lambda$, $1/\nu\gg\lambda\gg1$; 3) $\chi=\gamma(\lambda/\nu)^{1/2}$, $\lambda\gg1/\nu$, and γ is determined by Eq. (5.12); 4) $\chi\cong0.09/\nu$; 5) $\chi=2.42\nu^{1/2}/\lambda^{3/2}$, $\lambda\ll\nu$; 6) $\chi=0.07\lambda^2/\nu^3$, $\lambda\gg\nu$.

$$\chi=\chi_1=\lambda/\varkappa^{1/2}\gamma, \qquad (5.11)$$

the period of the smectic structure at the transition point being equal to

$$P\approx S=8\varkappa^{1/2}\gamma,$$

where the parameter γ is determined from the equation

$$(8\gamma)^{-1}e^{4\gamma}=\varkappa^{1/2}. \qquad (5.12)$$

As χ increases in the region $\chi>\chi_1$ the same changes of the smectic structure occur as in the case $\varkappa\ll1$.

Joining the line (5.11) of the first-order transitions with the line of second-order transitions, which is determined by the spinodal equation (3.3) and has the form

$$\chi_c=\lambda\min_{\alpha}\left\{\frac{\alpha^2}{2\sin^2\alpha}\frac{1+8\alpha^2\varkappa/3}{\sin^2\alpha+8\alpha^2\varkappa/3}\right\}, \quad \lambda\gg1,$$

we obtain the critical point of the second-order transitions:

$$\varkappa_c\approx0.3, \quad \chi_c\approx0.9\lambda. \qquad (5.13)$$

For $\varkappa<\varkappa_c$ the smectic ordering occurs as a second-order phase transition, while for $\varkappa>\varkappa_c$ it occurs as a first-order transition.

The results obtained in Secs. 3–5 make it possible to construct the phase diagram of the system for a fixed value of $\nu=\varkappa/\lambda\ll1$.[1)] This diagram is depicted schematically in Fig 7 in the variables λ and χ. The solid lines on the diagram correspond to first-order transitions, and the dashed lines to second-order transitions. Nematic-smectic transitions occur on the line 1–2–3, and the critical point of the second-order transitions has the parameters $\lambda_c\cong0.3/\nu$, $\chi_c\cong0.27/\nu$. The line 4 corresponds to transitions from the neutral phase to the phase with the monolayer-type structure; $\lambda'\sim\nu$, $\lambda''\sim\lambda_c$. Finally, the line 5–6 describes the monolayer-bilayer transitions. The numbers correspond to the following asymptotic regimes: 1) $\lambda\ll1$, formula (3.4); 2) $1/\nu\gg\lambda\gg1$, formula (3.7); 3) $\lambda\gg1/\nu$, formula (5.11); 4) formulas (4.11) and (5.8); 5) $\lambda\ll\nu$, formula (4.19); 6) $\lambda\gg\nu$, formula (3.10).

6. DENSITY CORRELATION FUNCTION NEAR THE NEMATIC-SMECTIC TRANSITION

In this Section we shall consider the density correlation function of one of the components in the melt:

$$G(\mathbf{r})=\langle\delta\eta(0)\,\delta\eta(\mathbf{r})\rangle,\quad \delta\eta=\eta(\mathbf{r})-\langle\eta\rangle \tag{6.1}$$

near second-order transitions from the nematic to the smectic phase. The interest in this function is connected with the fact that the structures with one-dimensional periodicity that were considered in the preceding Sections can exist only in the framework of the mean-field approximation; in reality, over large scales they are washed out by fluctuations.[15] But the correlation function does have direct physical meaning; it can be measured in experiments on x-ray scattering.

The correlation function near the transition from the nematic phase can be found in the standard way. We write the free energy $\mathscr{F}$ per unit volume of the system in the form of an expansion in powers of $\delta\eta$:

$$\mathscr{F}=T\left(\frac{L}{d}\right)^2\left\{\frac{1}{4}\sum_q a(\mathbf{q})\,|\delta\eta_{\mathbf{q}}|^2 + \frac{1}{12}\sum b(\mathbf{q}_1,\mathbf{q}_2)\,\delta\eta_{\mathbf{q}_1}\delta\eta_{\mathbf{q}_2}\delta\eta_{\mathbf{q}_3} + \frac{1}{48}\sum b(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3)\,\delta\eta_{\mathbf{q}_1}\delta\eta_{\mathbf{q}_2}\delta\eta_{\mathbf{q}_3}\delta\eta_{\mathbf{q}_4}\right\}, \tag{6.2}$$

where the summation over the wave vectors is performed with $\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3=0$ and $\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3+\mathbf{q}_4=0$ in the second and third terms, respectively, and

$$\delta\eta_{\mathbf{q}}=V^{-1}\int\delta\eta(\mathbf{r})\,e^{-i\mathbf{q}\mathbf{r}}\,d^3r.$$

If χ is close to χ_c, then $a(q)$ has a minimum near q_0e_z; for

$$\mathbf{q}=(q_0+q_1)\mathbf{e}_z+q_2\mathbf{e}_y,\quad q_1,\ q_2\ll q_0, \tag{6.3}$$

we have

$$a(\mathbf{q})=a_0\tau+c_1q_1^2+c_2q_2^2, \tag{6.4}$$

where $\tau=1-\chi/\chi_c$. Let

$$\delta\eta(\mathbf{r})=2\,\mathrm{Re}\,(\varepsilon e^{i\mathbf{q}\mathbf{r}});$$

then

$$\mathscr{F}=T(L/d)^2\{{}^1/_2(a_0\tau+c_1q_1^2+c_2q_2^2)\,|\varepsilon|^2+{}^1/_8b|\varepsilon|^4\}, \tag{6.5}$$

where $b=b(\mathbf{q}_0,\mathbf{q}_0,-\mathbf{q}_0)$, and ε is a small parameter. Consequently, the nematic-smectic transition can indeed be second-order,[4] and the Ginzburg parameter for this transition is equal to[16]

$$\zeta=(2\pi)^{-6}\left(\frac{d}{L}\right)^4\frac{b^2}{a_0c_1c_2^2}. \tag{6.6}$$

The correlation function for $\tau\gg\zeta$, as can be seen from (6.5), is equal to

$$G(\mathbf{q})=G(-\mathbf{q})=2(d/L)^2(a_0\tau+c_1q_1^2+c_2q_2^2)^{-1}, \tag{6.7}$$

where $\mathbf{q}$ is defined by formula (6.3). In the coordinate representation (6.7) gives

$$G(\mathbf{r})=\left(\frac{d}{L}\right)^2\frac{1}{\pi c_2}\left(\frac{a_0\tau}{c_1}\right)^{1/2}\frac{e^{-S}}{S}\cos q_0z,$$

$$S^2\equiv\left[\frac{a_0\tau}{c_1}z^2+\frac{a_0\tau}{c_2}(x^2+y^2)\right].$$

Omitting the details of the calculations, we give the values of the parameters a_0, b, c_1, and c_2 for our model:

$$\begin{gathered}a_0=2\pi^2(1+2\varkappa/\varphi^2),\quad \varphi\ll1,\\ b=(8\pi^2/\varphi^2)(1+2\varkappa/\varphi^2),\quad \varphi\ll1,\\ c_1=(\varphi^{-6}/2\pi^4)(1+8\varkappa/3\varphi^2)^{-1},\quad \varphi\ll1,\\ c_2=\frac{\varkappa}{\lambda\varphi}\left\{1-\frac{4}{3}\lambda^2\left(\frac{\alpha}{\operatorname{tg}\alpha}+\frac{1}{\lambda}\right)^2\left(\sin^2\alpha+\frac{8\varkappa\alpha^2}{3}\right)^{-2}\right\},\end{gathered} \tag{6.8}$$

where $\alpha=q_0L/2$. The most important consequence of (6.8) is that c_2 becomes negative for $\varphi>\varphi_c$, where $\varphi_c=0.639$, if $\nu\ll1$. Consequently, for $\varphi>\varphi_c$ the structure of the smectic-*A* phase is found to be unstable against rotation of the director. A more complicated structure (evidently, a smectic-*C* phase) should be stable. We shall not investigate this question here, but shall confine ourselves to the case $\varphi<\varphi_c$.

Substituting (6.8) into (6.6), we see that for $\varphi\ll1$ the Ginzburg parameter is small both in d/L and in φ. To estimate ζ when φ is not too small we can assume that $\varkappa\ll\varphi^2$; then (6.6) and the generalization of the expressions (6.8) (for brevity, we omit them here) give

$$\zeta=(d/L)^4\nu^{-2}\psi(\varphi)=(d/L)^2(\nu L/d)^{-2}\psi(\varphi),$$

where $\psi(\varphi)=\varphi^4$ for $\varphi\lesssim0.2$; $\psi(0.4)=0.0046$; $\psi(\varphi_c)=\infty$. A typical value of the parameter $\nu L/d=ld/6d'^2$ (see formula (1.3)) is 0.28 ($l=7$ Å, $d=5$ Å, $d'=4.5$ Å). If we choose the value $L/d=4$, which is typical for low-molecular-weight substances (for polymers, as a rule, this quantity is much greater), then for $\varphi=0.4$ the Ginzburg parameter is still found to be very small:

$$\zeta=0.9\psi(\varphi)=0.004.$$

Thus, the fluctuation region should be very narrow, even for low-molecular-weight smectics, and so should be still narrower for polymer systems.

In the smectic phase the principal role for the correlation function is played by elastic distortions of the layers, which smear out the periodic structure. If $u(\mathbf{r})$ is the displacement of a layer along the director (along the z axis), the free energy of distortion is equal to[17,18]

$$\mathscr{F}=\frac{1}{2}\bar{B}\left(\frac{\partial u}{\partial z}\right)^2+\frac{1}{2}K_1\left(\frac{\partial^2u}{\partial x^2}+\frac{\partial^2u}{\partial y^2}\right)^2. \tag{6.9}$$

If the equilibrium (in the framework of mean-field theory) structure has the form $\delta\eta_0=2\varepsilon\cos q_0z$, and $P=2\pi/q_0$ is the period of this structure, then, as shown on the basis of (6.9) in Ref. 19, the correlation function has the form 2)

$$G(r)\approx2\varepsilon^2\left(\frac{4\Lambda z+\rho^2}{P^2}\right)^{-x(\tau)}\cos q_0z, \tag{6.10}$$

where

$$\Lambda=(K_1/\bar{B})^{1/2},\quad r^2=z^2+\rho^2,\quad x(\tau)=Tq_0^2/8\pi(K_1\bar{B})^{1/2}. \tag{6.11}$$

We shall investigate how $x(\tau)$ varies in the smectic phase near the transition. As follows from (6.5),

$$\varepsilon^2=2a_0\tau/b,\ \bar{B}=T(L/d)^2c_1\varepsilon^2q_0^2. \tag{6.12}$$

The coefficient K_1 near the transition is equal to the transverse-bending constant for the nematic. To estimate this quantity we shall make use of scaling considerations:

$$K_1=\beta(T/L)(L/d)^2, \tag{6.13}$$

where β is a numerical coefficient that depends weakly on the temperature. We estimate the quantity β starting from data for para-azoxy anisole (PAA). For $T = 370$ K, $L = 20$ Å, $d = 6$ Å, and $K_1 = 0.7\cdot10^{-6}$ dyne (Ref. 17) we obtain $\beta\cong1/4$. We substitute (6.12) and (6.13) into (6.11):

$$x(\tau)=(d/L)^2(q_0/8\pi)(b/2\beta c_1a_0)^{1/2}|\tau|^{-1/2},$$

whence, for $\varphi\ll1$, we have

$$x(\tau)={}^1/_2\pi^2\beta^{-1/2}\nu(1+2\varkappa/\varphi^2)^{-1/2}(\zeta/|\tau|)^{1/2}. \tag{6.14}$$

Consequently, already on the boundary of the fluctuation region (at $|\tau| = \zeta$) we have $x(\tau)\lesssim1$; with increase of $|\tau|$ the quantity $x(\tau)$ decreases as $(\zeta/|\tau|)^{1/2}$. For $|\tau|\gg\zeta$ the length scale over which the smectic structure is washed out by fluctuations is exponentially large in the parameter $1/x(\tau)\gtrsim(|\tau|/\zeta)^{1/2}$.

CONCLUSION

Thus, we have investigated the properties of the smectic ordering in melts of two-block copolymers by the mean-field method. The applicability of the theory is ensured by the smallness of the Ginzburg parameter ζ. It is shown that the nematic-smectic transition should be a second-order transition if the length of the flexible fragment is small, and a first-order transition otherwise. As the parameter χ increases and (the temperature decreases) a structural transition of the monolayer-bilayer type between two smectic phases should occur.

These conclusions agree qualitatively with the experimental data for low-molecular-weight and polymer smectics. In most cases the nematic–smectic-A transition is found to be a first-order transition, but in the case of short flexible fragments it has been established that this transition can be second-order.[21–23] In low-molecular-weight systems cybotactic structures are known[24] in which layer smectic order is observed only over small scales (of the order of a few layers). Such structures have also been observed recently in systems of polymers with strongly interacting cyan-containing mesogenic groups.[25] The nematic-cybotactic transition is usually second-order. As follows from the analysis given in Sec. 6, the cybotactic structure is very similar to the smectic structure near the point of the second-order transition to the nematic phase.

A monolayer-bilayer transition when the temperature drops has been observed in a melt of cholesterol-containing polymers.[26]

The authors are grateful to V. P. Shibaev for fruitful discussions of the results of this paper.

APPENDIX A

To calculate the conformational entropy $S[c,\tilde{f}]$ we shall make use of the well known method of Ref. 11. We specify the concentration $\tilde{f}(\mathbf{r})$ of end links in a system of identical flexible chains and place this system in an external field $\Phi(\mathbf{r})$ acting on each bead-link. We assume that the length scale B over which $\tilde{f}(\mathbf{r})$ and $\Phi(\mathbf{r})$ change substantially is much greater than the size $N^{1/2}a$ of a ball. In the zeroth approximation we can assume that the total concentration $c(\mathbf{r})$ of all the beads has the same form as the distribution of the end beads:

$$c(\mathbf{r})\approx N\tilde{f}(\mathbf{r}). \tag{A.1}$$

Over the scale of one chain the field $\Phi(\mathbf{r})$ can be assumed to be uniform and to act on each bead of the chain with a force $\mathbf{R} = -\nabla\Phi$. If F_1 and U_1 are the free energy and energy of one chain in the uniform external field, the entropy of the chain is obviously equal to $S_1 = (U_1 - F_1)/T$. The calculation of F_1 and U_1 is trivial (it reduces to the calculation of Gaussian integrals). As a result we obtain

$$S_1=-a^2N^3(\mathbf{R}/T)^2/3,$$

i.e., the total entropy is equal to

$$S=\int S_1\tilde{f}\,d^3r=-\frac{a^2N^3}{3T^2}\int\tilde{f}(\nabla\Phi)^2d^3r. \tag{A.2}$$

We shall assume that the field $\Phi(\mathbf{r})$ is sufficiently weak that the difference between $\tilde{f}$ and c/N is due to the "polarization" of the chains in the external field:

$$c/N-\tilde{f}=-\nabla D, \tag{A.3}$$

where

$$D(\mathbf{r})=\tilde{f}(\mathbf{r})\sum_{n=1}^{N}(\mathbf{r}_n-\mathbf{r}),$$

in which $\mathbf{r}_n$ is the mean position of the link with label n in a chain with origin at the point $\mathbf{r}$. It is not difficult to show that

$$D(\mathbf{r})=-{}^2/_3a^2N^2\tilde{f}(\mathbf{r})\nabla\Phi/T. \tag{A.4}$$

Substituting (A.4) into (A.2), we obtain

$$S=-\frac{1}{2}\int\frac{D^2}{\varepsilon}d^3r,\qquad \varepsilon(\mathbf{r})=\frac{2}{3}a^2N\tilde{f}(\mathbf{r})\approx\frac{2}{3}a^2c(\mathbf{r}). \tag{A.5}$$

The formulas (A.5) and (A.3) solve the problem posed.

APPENDIX B

The energy of the domain wall is made up of two contributions: the energetic term F_{at} (formula (2.6)), which must be written in the form

$$\frac{F_{at}}{T}=\chi\int\eta(1-\eta)\,dz, \tag{B.1}$$

and the conformational term F_{fl1} (the first term in formula (2.12)):

$$\frac{F_{fl1}}{T}=\frac{\varkappa}{4\lambda}\int\frac{dz}{1-\eta}\left(\frac{d\eta}{dz}\right)^2. \tag{B.2}$$

It is not difficult to see that if the shape $\eta(z)$ of the domain wall on one boundary of the domain is specified, then on the other boundary the corresponding dependence should have the form (with a shift through L) $\tilde{\eta}(z) = 1 - \eta(z)$. The two domain walls should, obviously, have the same energy, and therefore the expressions (B.1) and (B.2) should be made symmetric with respect to the replacement $\eta \rightarrow 1 - \eta$. The final expression for the energy has the form

$$\frac{F}{T} = \chi \int \eta(1-\eta)\,dz + \frac{\varkappa}{8\lambda} \int \frac{dz}{\eta(1-\eta)} \left(\frac{d\eta}{dz} \right)^2. \qquad \text{(B.3)}$$

Minimizing (B.3) with respect to all functions $\eta(z)$ satisfying

$$\eta(-\infty)=0, \ \eta(\infty)=1, \qquad \text{(dd)}$$

we find

$$\eta_0(z) = \frac{1}{2}\left(1 + \operatorname{th}\frac{2^{1/2}z}{\Delta}\right), \quad \Delta = \left(\frac{\varkappa}{\lambda\chi}\right)^{1/2}, \qquad \text{(B.4)}$$

$$\sigma = F_{min}/T = 2^{-1/2}(\varkappa\chi/\lambda)^{1/2}. \qquad \text{(B.5)}$$

[1)] As follows from formula (2.15), the condition ν = const implies that we can change the length of the flexible blocks while leaving the rigid blocks unchanged.

[2)] We neglect the logarithmic corrections.[20]

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Translated by P. J. Shepherd