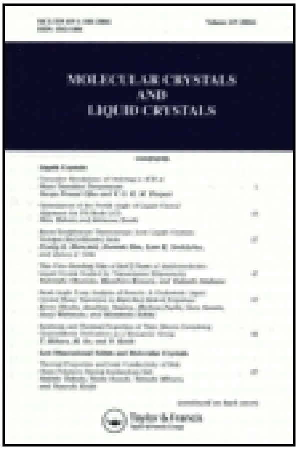

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Smectic Ordering in Block-Copolymer Melts

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Smectic Ordering in Block-Copolymer Melts

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Microscopic theory of smectic ordering in melts of rod-coil copolymers is proposed. It is shown that a second-order phase transition nematic-smectic A or a first-order transition nematic-smectic C may occur in the system as Flory's parameter of incompatibility of the blocks, χ is increased. A number of phase transitions between different smectic A and C phases are also predicted. The most stable structure for large χ is always SmA_2, implying head-to-head arrangement of rigid rods in double lamellar sheets.

Keywords: smectic ordering, block-copolymers

1. INTRODUCTION

It is well known that one-dimensional lamellar structures are often formed by flexible block-copolymers.[1] On the other hand, layered structures are also characteristic for thermotropic low molecular weight (LMW) smectogens.[2] These smectogenic molecules typically consist of a rigid core and one or two flexible tails. LMW smectogen systems were studied theoretically using microscopic lattice models[3,4] and phenomenological Landau type approaches.[5,6] Obviously, rod-coil copolymer systems should reveal features of both flexible block-copolymers and LMW smectic liquid-crystals. These copolymer systems allow a simpler theoretical description (in comparison with LMW smectogens) in terms of asymptotic properties[7–9] since the lengths of both rigid and flexible blocks are usually much larger than the characteristic width of polymer chains.

From a purely "polymeric" point of view the rod-coil macromolecules are the simplest objects which form smectic structures, and study of them can be considered as a first step before passing to polyblock-copolymers or comblike macromolecules (containing rigid and flexible blocks). Besides, rod-coil copolymer layered films can be considered as a model for biological membranes.[10–11] A smectic C order of such copolymer films was observed.[12]

A general theoretical "asymptotic" method for a microscopic study of rod-coil copolymer systems was proposed.[7] However, only Sm A phases were considered there. The aim of the present work is to study Sm A-Sm C phase transitions using the method. The model and the main relevant results of Reference 7 are considered in the following section, the particular new results being collected in the third section.

2. THE MODEL

Let us consider a melt of diblock-copolymers consisting of one rigid rodlike block of length L and diameter d, $L >> d$, and one flexible block. Let N be the number of polymer links per flexible block (coil), v the volume and a the size of a link (the "ideal" m.s. distance between the ends of a coil being $\langle R^2 \rangle = 6Na^2$). A perfect orientational order of rigid rods is assumed for simplicity: the rod axes are aligned along some director $\mathbf{u}$ ($|\mathbf{u}| = 1$). Thus, two orientations of rods are possible (Figure 1).

The (local) volume fraction occupied by the rigid component near the point $\mathbf{r}$ is

$$\eta(\mathbf{r}) = d^2 \int_0^L [c_1(\mathbf{r} + \zeta\mathbf{u}) + c_2(\mathbf{r} - \zeta\mathbf{u})]\, d\zeta, \tag{2.1}$$

where $c_1(\mathbf{r})$ and $c_2(\mathbf{r})$ are the local concentrations of junction points between rigid and flexible blocks corresponding to "parallel" (1) and "antiparallel" (2) orientations (see Figure 1). The incompressibility condition can be written as

$$\eta(\mathbf{r}) + \phi(\mathbf{r}) = 1, \tag{2.2}$$

where $\phi(\mathbf{r})$ is the volume fraction of flexible blocks. Obviously,

$$\langle \eta \rangle = 1/(1 + \lambda), \qquad \langle \phi \rangle = \lambda/(1 + \lambda), \tag{2.3}$$

where

$$\lambda \equiv Nv/Ld^2. \tag{2.4}$$

In the following it is assumed that

$$\nu \equiv Na^2/\lambda L^2 = a^2d^2/vL << 1. \tag{2.5}$$

The free energy of the system can be represented as[7]

$$F = F_{\mathrm{id}} + F_{\mathrm{attr}} + F_{\mathrm{ster}} + F_{\mathrm{conf}} \tag{2.6}$$

where

$$F_{\mathrm{id}} = T \int \{c_1(\mathbf{r})\ln[c_1(\mathbf{r})/e] + c_2(\mathbf{r})\ln[c_2(\mathbf{r})/e]\}\, d^3\mathbf{r} \tag{2.7}$$

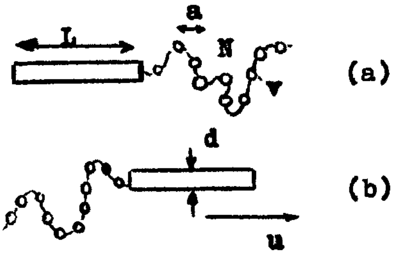

FIGURE 1 "Parallel" orientation of a block-copolymer (a); "anti-parallel" orientation (b).

is the ideal gas contribution; F_{attr} is the free energy of mixing of flexible and rigid blocks; F_{ster} is due to steric interactions of rigid rods; F_{conf} is the conformational free energy of flexible blocks (conformational entropic losses due to inhomogeneity of the system). It is assumed that the characteristic scale of inhomogeneity, $\tilde{l}$, is much larger than d and a. The free energy of mixing can be written as[13]

$$F_{\text{attr}} = \chi T \int \eta(\mathbf{r})\phi(\mathbf{r})d^3\mathbf{r}/Ld^2, \tag{2.7}$$

where the factor $(1/Ld^2)$is introduced for convenience. The term F_{ster} can be obtained using a generalization[7] of the well-known Flory result for a homogeneous system of rods[14]:

$$F_{\text{ster}} = (T/d^3) \int \{\sigma + (1 - \eta)\ln(1 - \eta) \\ - (1 - \eta + \sigma)\ln(1 - \eta + \sigma)\}\, d^3\mathbf{r}, \tag{2.8}$$

where

$$\sigma(\mathbf{r}) = d^3[c_1(\mathbf{r}) + c_2(\mathbf{r} - L\mathbf{u})]. \tag{2.9}$$

Taking into account that $d << L$ and $\sigma << \eta$, we have

$$F_{\text{ster}} = -(T/d^3) \int \sigma(\mathbf{r})\ln[1 - \eta(\mathbf{r})]\, d^3\mathbf{r}. \tag{2.10}$$

The last term, F_{conf}, is

$$F_{\text{conf}} = (Ta^2/4v) \int \phi^{-1}(\nabla\phi)^2 d^3\mathbf{r} + (T/2) \int (\mathbf{D}^2/\varepsilon)\, d^3\mathbf{r}, \tag{2.11}$$

where $\phi = \phi(\mathbf{r})$, $\varepsilon(\mathbf{r}) \equiv 2a^2\phi(\mathbf{r})/3v$; the vector-field $\mathbf{D}(\mathbf{r})$ satisfies the equations

$$\nabla \times (\mathbf{D}/\varepsilon) = 0, \qquad \nabla\mathbf{D} = c_1(\mathbf{r}) + c_2(\mathbf{r}) - \phi(\mathbf{r})/Nv. \tag{2.12}$$

Equation (2.11) is exact in the limits of "large-scale" and "short-scale" inhomogeneities, $\tilde{l} >> N^{1/2}a$ and $\tilde{l} << N^{1/2}a$; in the intermediate case an error of order 20% is expected.[7]

In order to obtain the equilibrium structure of the system one should minimize the free energy F (Equation (2.6)) as a functional of $c_1(\mathbf{r})$ and $c_2(\mathbf{r})$. The equilibrium free energy and equilibrium distributions $c_1(\mathbf{r})$ and $c_2(\mathbf{r})$ can be obtained as a result.

Let us consider briefly the main results of Reference 7 corresponding to small volume fraction of flexible component, $\lambda << 1$. A homogeneous (nematic, N) state of the system corresponds to sufficiently small values of the incompatibility parameter χ. For larger χ a second-order transition N-Sm A_1 was predicted at

$$\chi_1 = (\pi^2/2)(1 + 2\nu/\lambda), \qquad \lambda << 1. \tag{2.13}$$

The period of a one-dimensional (lamellar) structure appearing at the transition point is

$$P_1 = L(1 + \lambda). \tag{2.14}$$

The plot $\eta(z)$ for the Sm A_1 is shown schematically in Figure 2 (the axis z is normal to lamellar sheets).

As χ is further increased, a first-order phase transition between two different smectic phases (Sm $A_1 \rightarrow$ Sm A_2) occurs at

$$\chi_2 \simeq 2.42\, \nu^{1/2}\lambda^{-3/2}, \qquad \lambda \lesssim \nu. \tag{2.15}$$

This transition is accompanied by the doubling of the spatial period: $P_1 \rightarrow P_2$,

$$P_2 \simeq 2L(1 + \lambda). \tag{2.16}$$

As was already mentioned in Reference 7, a smectic A structure may become unstable in the region $\lambda \gtrsim 1$ so that a tilting of rod axes with respect to the z-axis may be favoured. Thus, Sm A-SmC transitions are expected in this region. These are considered in the next section.

3. N-C AND A-C PHASE TRANSITIONS

Let us consider a smectic C phase, i.e., a one-dimensional lamellar structure, where the rigid rod axes form an angle γ with the normal to lamellar sheets (z-axis) (Figure 3). A simple analysis of the free energy of the system (see Equations (2.6), (2.7), (2.9)-(2.12)) shows that

$$F([c_1(\mathbf{r}), c_2(\mathbf{r})], L, d, \gamma) = F([c_1(\mathbf{r}), c_2(\mathbf{r})], L\cos\gamma, d/\sqrt{\cos\gamma}, 0), \tag{3.1}$$

where $F([c_1, c_2], L\ d, \gamma)$ is the free energy as a functional of $c_1(\mathbf{r})$, $c_2(\mathbf{r})$ and a function of length L, diameter d and angle γ (other parameters N, a, v, χ are assumed to be fixed). Thus the free energy for smectic C structure reduces to that for smectic A provided that the renormalization $L \rightarrow \tilde{L} = L\cos\gamma$ and $d \rightarrow \tilde{d} = d(\cos\gamma)^{-1/2}$ is performed. Let Tf be the equilibrium free energy per one block-

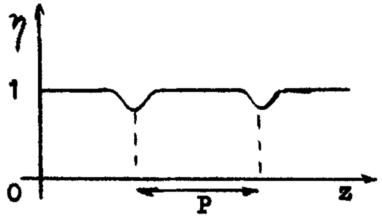

FIGURE 2 The dependence of volume fraction of rigid component, η on z (z-axis is normal to lamellar sheets) for a "weak" smectic A_1.

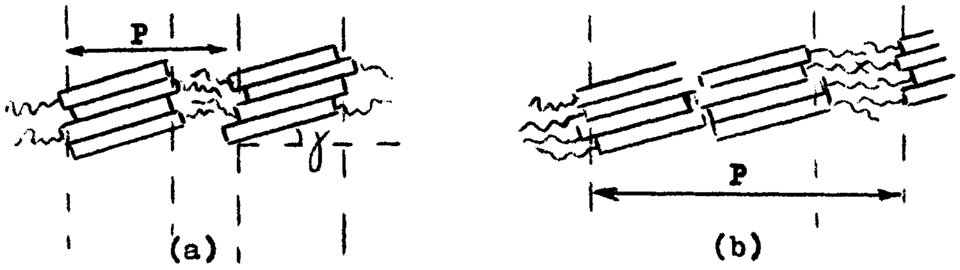

FIGURE 3 The structures of "sharp" smectic C_1 (a) and smectic C_2 (b).

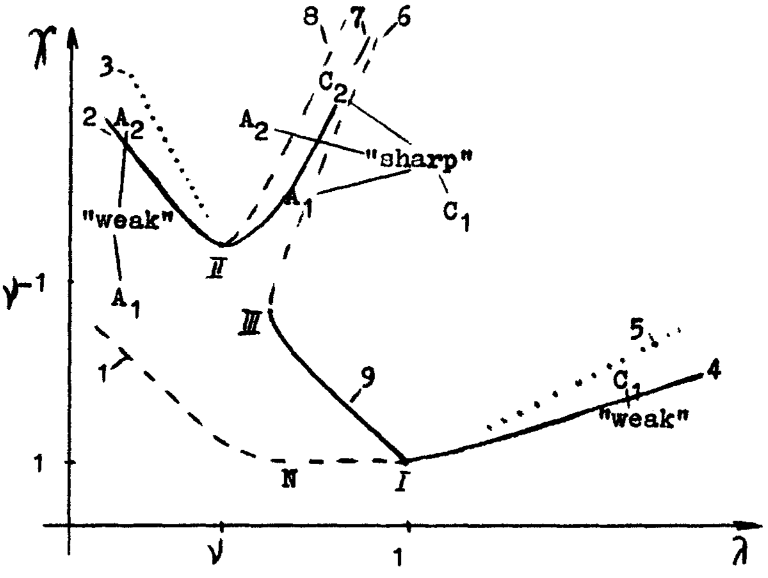

FIGURE 4 The λ-χ phase diagram of a rod-coil block-copolymer melt (in double logarithmic scale), where χ is the Flory parameter and λ is the ratio of the volumes of the flexible component and the "rigid" component. Solid lines correspond to first-order phase transitions, dashed lines to second-order phase transitions, dotted lines to crossover transitions. Lines 1–9 are characterized by the following equations: $\chi_1 \simeq (\pi^2/2)(1 + 2\nu/\lambda)$, $\lambda \lesssim 1$; $\chi_2 \simeq 2.42\,\nu^{1/2}\lambda^{-3/2}$, $\lambda \lesssim \nu$; $\chi_3 \sim \nu/\lambda^2$, $\lambda \lesssim \nu$; $\chi_4 \simeq \lambda^{1/3}$, $\lambda \gtrsim 1$; $\chi_5 \sim \lambda^{1/2}$, $\lambda \gtrsim 1$; $\chi_7 \simeq \chi_6 \simeq \lambda^2/128\,\nu^3$, $\lambda \gtrsim \nu$; $\chi_8 \simeq \lambda^2/2\nu^3$, $\lambda \gtrsim \nu$; $\chi_9 \sim 1/\lambda$, $\nu \lesssim \lambda \lesssim 1$. I and II are the triple points; III is the critical point for the second-order transitions.

copolymer (for a given γ). Note that f is a dimensionless function of dimensionless parameters ν, χ, λ and γ. Using Equation (3.1) we get

$$f(\nu, \chi, \lambda, \gamma) = f(\nu/\cos^2\gamma, \chi, \lambda, 0). \tag{3.2}$$

The results of Reference 7 (concerning smectic A structures) and Equation (3.2) form a basis for detailed investigation of equilibrium properties of the system. The obtained phase diagram is shown in Figure 4. One can find a number of qualitatively different phases in this Figure: the nematic (N) phase with reduced free energy (per macromolecule)

$$f = f_{\mathrm{mix}} = \chi\lambda/(1 + \lambda); \tag{3.3}$$

the "weak" smectic A_1 phase (see Figure 2); the "weak" smectic A_2 phase (with doubled period); the "weak" Sm C_1; the "sharp" Sm A_1, A_2 and C_1, C_2.

The structure of the "sharp" C_1 phase is shown in Figure 3a; the reduced free energy and the period of the structure are

$$f = f_{el} + f_{intf} = \lambda \cos^2 \gamma/16\,\nu + (2\nu\chi)^{1/2}/\cos\gamma, \qquad P = L(1+\lambda)\cos\gamma. \quad (3.4)$$

Here the first (elastic) term is due to the stretching of flexible coils, the second (surface) term f_{intf} corresponds to the free energy of interfaces between "rigid" and "flexible" lamellar sheets. A rigid lamellar sheet for the "sharp" Sm C_2 is formed by tilted rods arranged "head to head" (Figure 3b); the corresponding free energy and the period are

$$f \simeq \lambda \cos^2\gamma/4\nu + (\nu\chi/2)^{1/2}/\cos\gamma, \qquad P = 2L(1+\lambda)\cos\gamma. \quad (3.5)$$

For a particular case $\gamma = 0$, "sharp" C_1 and C_2 phases reduce to "sharp" smectics A_1 and A_2.

The characteristics of the "weak" smectic C_1 phase (see Figure 5) are:

$$P = L(1+s)\cos\gamma;$$

$$f = f_{el} + f_{intf} + f_{mix} = s^2\cos^2\gamma/16\nu\lambda + \frac{\pi}{4}(\chi\nu)^{1/2}\frac{1+s}{1+\lambda}\frac{1}{\cos\gamma} + \chi\frac{\lambda - s}{1+\lambda}, \qquad 1 \ll s \ll \lambda. \quad (3.6)$$

Here the first term corresponds to elastic free energy, the second to surface free energy, and the last term is the free energy of mixing (it is nonzero since lamellar sheets containing rigid rods are also partly filled by flexible component). In order to obtain equilibrium characteristics, the free energy f should be minimized as a function of γ (and s).

Let us consider possible phase transitions between different structures (see Figure 4; here solid lines correspond to the first-order transitions, dashed lines to second-

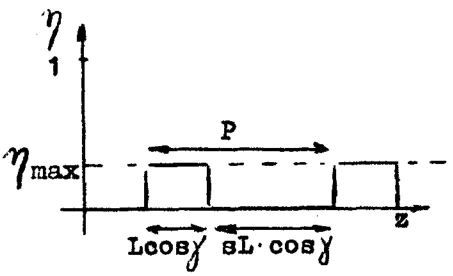

FIGURE 5 The dependence of η on z for a "weak" smectic C_1; $\eta_{max} = (1+s)/(1+\lambda) \ll 1$.

order transitions, and dotted lines to crossover transitions). The transitions N-A_1 (line 1) and A_1-A_2 (line 2) were considered in Section 2. As χ increases, the "weak" A_2 phase (which appeared at line 2) changes to the "sharp" A_2 phase at $\chi \sim \nu/\lambda^2$ (line 3).

Let us pass to the region of larger volume fraction of flexible tails. Smectic ordering here proceeds via the first-order transition $N \rightarrow$ "weak" C_1 (line 4) at

$$\chi_4 \simeq \lambda^{1/3}, \qquad \lambda >> 1; \tag{3.7}$$

the period of this smectic structure is

$$P = L(1 + s)\cos\gamma, \tag{3.8}$$

where

$$s \simeq 16\chi^2/\pi^2, \qquad \cos\gamma \simeq (\pi^2\nu/4\chi)^{1/2}, \qquad \chi_4 << \chi << \lambda^{1/2}. \tag{3.9}$$

As χ is increased in the region $\chi_4 \leqslant \chi \lesssim \lambda^{1/2}$, the "rigid" lamellar sheets become thinner, and the "flexible" sheets (i.e., sheets consisting of flexible component) become thicker. At $\chi = \chi_5 \sim \lambda^{1/2}$ a crossover transition to a "sharp" smectic C_1 occurs; the new structure is characterized by

$$P = L(1 + \lambda)\cos\gamma, \qquad \cos\gamma \simeq 2(2\nu^2\chi/\lambda^2)^{1/6}. \tag{3.10}$$

The tilt angle γ increases with χ in the region $\chi_4 < \chi \lesssim \chi_5$. For $\chi \gtrsim \chi_5$ the angle starts to decrease and reaches zero at

$$\chi_6 \simeq \lambda^2/128\nu^3, \qquad \lambda >> \nu. \tag{3.11}$$

Thus, the second-order transition "sharp" Sm $C_1 \rightarrow$ "sharp" Sm A_1 occurs at $\chi = \chi_6$, the period of the A_1 structure being $P = L(1 + \lambda)$.

The region of stability of A_1-phase is rather narrow:

$$\chi_6 \leqslant \chi \leqslant \chi_7 = \chi_6 + \Delta\chi, \qquad \Delta\chi \sim \lambda/\nu^2 << \chi_6 \quad \text{for} \quad \lambda >> \nu. \tag{3.12}$$

At $\chi = \chi_7$ the "sharp" Sm A_1 turns into the "sharp" Sm C_2 via a first-order phase transition. At the transition point the angle γ changes from $\gamma = 0$ to $\gamma \simeq 60°$; on the other hand, the period of the smectic structure almost does not change in the vicinity of the transition. As γ is further increased, the period P increases and the tilt angle decreases:

$$P = 2L(1 + \lambda)\cos\gamma, \qquad \cos\gamma = (2\chi\nu^3/\lambda^2)^{1/6}, \qquad \chi_7 \leqslant \chi \leqslant \chi_8. \tag{3.13}$$

Finally, at $\chi = \chi_8$,

$$\chi_8 = \lambda^2/2\nu^3, \qquad \lambda >> \nu \tag{3.14}$$

the "sharp" Sm C_2 phase is changed by the "sharp" Sm A_2 structure via second-order phase transition (line 8); the period of the A_2 structure is $P = 2L(1 + \lambda)$.

One more line of phase transitions (line 9) in Figure 4 corresponds to the first-order Sm $A_1 \rightarrow$ Sm C_1 transition at

$$\chi_9 \sim 1/\lambda, \qquad \nu \lesssim \lambda \lesssim 1. \tag{3.15}$$

Both A_1 and C_1 structures near the transition cannot be regarded as "weak" or "sharp": they are "intermediate." The tilt angle changes from $\gamma = 0$ to $\gamma \sim \arccos[(\nu/\lambda)^{1/2}]$, and the period decreases from $P = L(1 + \lambda)$ to $P \sim L(\nu/\lambda)^{1/2}$ at $\chi = \chi_9$. Note that there are two triple points (I: $\lambda \sim \chi \sim 1$ and II: $\lambda \sim \nu$, $\chi \sim 1/\nu$) and one critical point for second-order transitions (III: $\lambda \sim \nu$, $\chi \sim 1/\nu$) in the phase diagram.

4. CONCLUSION

Thus, we have studied smectic ordering in a melt of rod-coil copolymers. Many phase transitions between different smectic structures are predicted. For example, five transitions are expected for $\nu \ll \lambda \ll 1$ (i.e., $a^2d^4/\nu^2 \ll N \ll Ld^2/\nu$) as the parameter of incompatibility is increased (see Figure 4):

$$\text{nematic} \rightarrow \text{Sm } A_1 \rightarrow \text{Sm } C_1 \rightarrow \text{Sm } A_1 \rightarrow \text{Sm } C_2 \rightarrow \text{Sm } A_2.$$

Of course, the diagram in Figure 4 is schematic; nevertheless the method of this paper enables one to calculate all desired equilibrium characteristics of the system for any given set of parameters L, d, N, ν etc.

Diagram of Figure 4 suggests that untilted smectic A structures are expected for large χ or for sufficiently small λ (short flexible tails). For longer flexible tails a tilted smectic (Sm C) is favoured. This last conclusion coincides with that obtained by Halperin,[8,9] for a solution of rod-coil copolymers. As in References 8, 9 this result can be qualitatively understood in terms of the competition between the free energy of the stretching of flexible tails and the free energy of interfaces, F_{intf}. Nevertheless, the dependencies of F_{intf} on γ which were assumed in References 8, 9 and in this work are considerably different. In fact, it was assumed that[8,9]

$$F_{\text{intf}} \text{ (per unit square)} \propto 1 + \tan\gamma. \tag{4.1}$$

This equation corresponds to a regular arrangement of rigid rods in a lamellar sheet (Figure 6a), the energy F_{intf} being due to contacts of rod ends with solvent molecules. Note that Equation (4.1) is correct if the width Δ of the interface layer is much smaller than d. An estimate of Δ for the melt gives

$$\Delta \sim L(a^2d^4/N\nu^2)^{1/2},$$

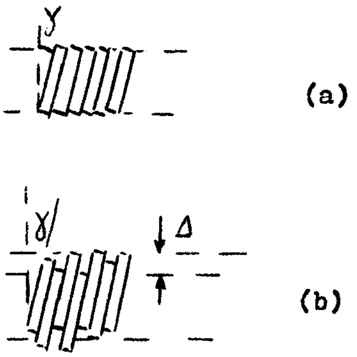

FIGURE 6 A "regular" arrangement of rigid rods in a lamellar sheet; the surface tension corresponding to this arrangement is proportional to $1 + O(\gamma)$ (a); the nonregular arrangement ($\Delta \gtrsim d$), the surface tension $\propto 1 + O(\gamma^2)$ (b).

i.e., Δ is usually greater than d. Therefore, another picture of rod packing (assumed in this work) is more probable (Figure 6b). This picture implies that

$$F_{\text{intf}} \propto 1 + O(\gamma^2). \tag{4.2}$$

Note that Equation (4.2) satisfies the symmetry condition, $F_{\text{intf}}(-\gamma) = F_{\text{intf}}(\gamma)$. Note also that a substitution of Equation (4.1) by Equation (4.2) may result in the conversion of a first-order transition Sm A-Sm C (obtained in References 8, 9) into a second-order transition. It is for this reason that a number of *second-order* Sm A-Sm C phase transitions were predicted in the present work.

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