Smectic layer displacement fluctuations in solid substrate supported smectic-*A* films

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In this paper we present results of calculations of static and dynamic characteristics of smectic layer displacement fluctuations in solid substrate supported smectic-*A* films with due regard for asymmetric profiles of the bending elastic constant *K* and the smectic layer compressibility *B*. We also take into account difference in properties of boundary surfaces of the film, namely, the surface tension of the free surface is taken to be finite whereas that of a film-substrate interface is assumed to be infinitely large. Profiles of the smectic layer displacement fluctuations and correlations between them are calculated for films formed of liquid crystalline compounds with the bulk smectic-*A* to nematic phase transition. The calculations are performed at temperatures much lower than that of the bulk phase transition and at maximum temperatures of existence of films of given thickness. The time dependent displacement-displacement correlation functions for thermal smectic layer displacement fluctuations and time dependent intensity-intensity correlation functions for diffuse x-ray scattering from the films are also calculated. It is shown that unlike free-standing smectic-*A* films, an effect of the temperature on dynamics of smectic layer displacement fluctuations in solid substrate supported smectic-*A* films can be observed in experiments on coherent x-ray dynamic scattering from not very thick films ($N \sim 20$) and at significantly smaller wave vector transfer component in the film plane.

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I. INTRODUCTION

Smectic liquid crystals possess a one-dimensional layering [1] due to which they have an ability to form free-standing films with a macroscopic surface area ($\sim$cm^2) [2] and thickness which can be varied from thousands of molecular layers down to two and even one smectic layer [3,4]. These unique properties make them the most suitable model systems for studying the crossover from three-dimensional (3D) to 2D behavior. In addition, the surface-induced ordering combines with finite-size effects in free-standing smectic films (FSSFs), and this combination gives rise to the appearance of phenomena that are not observed in bulk liquid crystal (LC) samples [5–9]. Therefore, during the last 20 to 25 years FSSFs have been the objects of intensive experimental and theoretical investigations.

At present, a significant interest is focused on solid substrate supported smectic films [10–15]. Similar to FSSFs, the most complete information on the structure of these films can be obtained from experiments on specular and diffuse x-ray scattering. These experiments provide us with information on both equilibrium properties of the films (number of film layers, the layer spacing, the local layer structure) as well as the thermal fluctuation in them. In addition, experiments on diffuse x-ray scattering [10–12,15] yield information on the substrate roughness which induces distortions in the smectic film. In Ref. [16] it has been shown that displacement-displacement correlation functions for such films, which determine intensity of the diffuse x-ray scattering, consist of two parts, one of which is due to intrinsic thermal smectic layer displacement fluctuations and the second part is due to substrate roughness replication in the film. Thus, an information on intrinsic thermal smectic layer fluctuations and the substrate roughness cannot be extracted separately from data of experiments on the diffuse x-ray scattering without an adequate theoretical description of the smectic layer displacement fluctuations in the solid substrate supported smectic films.

Theoretical description of the thermal layer displacement fluctuations in solid substrate supported smectic-*A* (Sm-*A*) films has been developed in Refs. [16,17]. In these papers such fluctuations are described in the framework of well known discrete Holyst's model [18–20] earlier proposed for description of the layer displacement fluctuations in FSSAFs. In this model the solid substrate supported smectic-*A* film is assumed to be spatially homogeneous and characterized with only the number of the smectic layers *N*, the surface tension γ its boundary free surface (in Ref. [16] the surface tension of a film-substrate interface is assumed to be infinitely large, and in Ref. [17], the film layer adjacent to the substrate surface is assumed to be rigidly fixed), and the elastic constants *K* and *B* for bending and compression of the smectic layers, respectively. The latter constants are assumed to be similar for all film layers and equal to those for the bulk Sm-*A* phase. In Refs. [21–23] it has been pointed out that, even for FSSAFs, this assumption is physically justified only for temperatures significantly lower than the bulk Sm-*A*–nematic (Sm-*A*–*N*) or Sm-*A*–isotropic (Sm-*A*–*I*) transition temperatures. In this case the Sm-*A* structure is well developed in whole volume of the film, and both orientational and translational molecular ordering in internal film layers should be similar to those near the boundary free surfaces. Since the bending elastic constant *K* is proportional to p^2, and the smectic layer compressibility *B* is proportional to s^2 [1], where *p* and *s* are the orientational and translational order parameters, respectively, the elastic constants *K* and *B* should also be almost equal for all film layers. However, thin smectic films of some LCs can exist at temperatures much higher than the bulk Sm-*A*–*I* or Sm-*A*–*N* transition temperatures [5–9]. The microscopic model proposed in Refs. [24–27], which describes many features of behavior of the FSSAFs at these temperatures, predicts that well above the bulk

Sm-A–I or Sm-A–N transition points the internal film layers can be significantly less ordered than the outermost ones. This theoretical result has been experimentally confirmed by experiments on a visible light transmission through FSSAFs [28] and x-ray scattering from smectic-A films [9] heated above the bulk Sm-A–N transition temperature. Therefore, in such films both the bending elastic constant K and the smectic layer compressibility B should decrease with distance from the boundary free surface and reach minimum values in the interior of the film. In the Holist's model [18–20] such profiles of the elastic constants K and B are not taken into account, and, consequently, above the bulk Sm-A–I or Sm-A–N transition temperatures this model should not give correct values of the smectic layer displacement fluctuations and correlations between them. An effect of spatial inhomogeneity of FSSAF on the thermal layer displacement fluctuations has been theoretically investigated in Refs. [21–23]. It has been found that taking into account this inhomogeneity, for maximum temperatures of existence of FSSAFs, one can obtain results significantly different from predictions of the Holyst's model. It should be, however, noticed that an assumption of spatial homogeneity of the solid substrate supported smectic-A films can be invalid even for lower temperatures. The point is that their boundary surfaces (the free surface and the film-substrate interface) are not similar, and, hence, these surfaces could have different orienting action on the LC molecules. As a result, such films are not symmetrical with respect to their central layer that is not consistent with the assumption of their spatial homogeneity. Therefore, the theoretical description of the smectic layer displacement fluctuations proposed in Refs. [16,17] cannot be considered as adequate.

As for dynamics of the thermal layer displacement fluctuations in FSSAFs, it has been under experimental and theoretical investigations since only the last few years. For its experimental study, the dynamic soft x-ray scattering [29] and the dynamic hard x-ray scattering [30] techniques have been developed, and theoretical description of the experimental results has been presented in Refs. [31–34]. This description is based on linearized equations of the smectic-A hydrodynamics and the above mentioned Holyst's model [18–20] for the free energy excess associated with the layer displacement fluctuations in FSSAFs. The models [31–34] allow to determine the dynamic correlation functions for these fluctuations and calculate time dependent intensity-intensity correlations for x-ray scattering from FSSAF. Their predictions are in a qualitative agreement with results of the experiments [29,30] on the dynamic x-ray scattering from FSSAFs of various thickness. As for dynamics of the thermal layer displacement fluctuations in the solid substrate supported smectic-A films, it is not experimentally investigated up to now. Nevertheless, its theoretical investigation has been already performed [17] in the framework of the Holyst's model [18–20], neglecting the spatial inhomogeneity of the films. As a result, such an approach yields temperature independent dynamics of these fluctuations.

An effect of both the bending elastic modulus K and the smectic layer compressibility B profiles, and, consequently, the temperature, on the dynamics of the thermal layer displacement fluctuations in FSSAFs has been theoretically investigated in our previous paper [35]. It has been shown that this effect can be observed in experiments on the dynamic x-ray scattering from sufficiently thick films ($N \geqslant 100$) and for large enough ($\geqslant 10^6$ cm^{-1}) wave vector transfer component in the film plane. In thinner films and for not so large wave vector transfer component in the film plane, the major role in the dynamics of the thermal layer displacement fluctuations in FSSAFs belongs to the so called acoustic mode [31,32] with practically temperature independent relaxation time

$$\tau^{(1)} = N d \eta_3 / 2\gamma, \tag{1}$$

where d is the smectic layer spacing, and η_3 is the layer sliding viscosity. This mode corresponds to such motion of the film when an interlayer spacing is constant, and, hence, any dependence on the elastic moduli K and B profiles is absent. However, for the solid substrate supported smectic-A films, the acoustic mode of its motion vanishes [17]. Thus, the thermal layer displacement fluctuations always give rise to change in the interlayer spacing. Therefore, dynamic characteristics of these fluctuations should depend on the elastic moduli K and B profiles, and, hence, on the temperature, not only in very thick films and for not so large wave vector transfer component in the film plane. In other words, an effect of spatial inhomogeneity of the solid substrate supported smectic-A films on their thermal layer displacement fluctuations should be stronger than analogous effect in FSSAFs.

In this paper we present results of calculations of both static and dynamic characteristics of the layer displacement fluctuations in the solid substrate supported smectic-A films with due regard for the bending elastic modulus K and the smectic layer compressibility B profiles. These calculations are analogous to those for the layer displacement fluctuations in FSSAFs presented in Refs. [21–23] and [35], but here we take also into account that the boundary surfaces of the film are not similar (the surface tension of the boundary free surface is taken to be finite, whereas that of the film-substrate interface is assumed to be infinitely large), and that the elastic moduli profiles are not symmetrical with respect to the film center. These profiles are determined from the microscopic model [24–27] for FSSAFs, taking into account the difference in orienting actions of the boundary surfaces on molecules of the film.

In the following section we present results of calculations of the smectic layer displacement fluctuation profiles and correlations between them for the films formed by liquid crystalline compounds with the bulk Sm-A–N phase transition. The calculations have been performed for both the temperatures well below the bulk phase transition temperature and the maximum temperatures of existence of the films of given thickness. It has been shown that, well below the temperature at which the smectic order in the bulk LC disappears, taking into account the profiles of the elastic moduli K and B does not produce noticeable differences from the results of Refs. [16,17] obtained in the framework of the Holyst's model. However, at maximum temperatures of existence of the films, our results are considerably different from the predictions of this model, especially when an orienting action of the film-solid substrate interface on the LC molecules is much weaker than the orienting action of the free surface of the film.

In Sec. III the results of calculations of the time dependent displacement-displacement correlation functions and intensity-intensity correlations for diffuse x-ray scattering from the solid substrate supported smectic-A films are presented. It has been shown that, unlike FSSAFs, an effect of temperature on the dynamics of the layer displacement fluctuations in such films can be observed in experiments on the dynamic x-ray scattering from not very thick films ($N\sim 20$) and for significantly smaller values ($\leqslant 10^5\ \mathrm{cm}^{-1}$) of the wave vector transfer component in the film plane.

II. THE SMECTIC LAYER DISPLACEMENT FLUCTUATIONS AND CORRELATIONS BETWEEN THEM IN THE SOLID SUBSTRATE SUPPORTED SMECTIC-*A* FILMS

In Refs. [16,17] it has been shown that the thermal smectic layer displacement fluctuations in the solid substrate supported smectic-A films can be described in a framework of discrete model similar to that proposed by Holyst [18–20] for description of these fluctuations in FSSAFs. Let us consider the N layer solid substrate supported smectic-A film. In this film the smectic layer displacements $u_n(x,y)$ from equilibrium positions $z_n=(n-1)d$ along z axis normal to the film layers, where n is the layer index and d is the smectic layer spacing, give rise to the free energy excess F consisting of a bulk contribution F_B determined by Eqs. (2) and (3) in Ref. [21], and a surface contribution F_S which according to Ref. [16] is given by

$$F_S=\frac{1}{2}\int [\gamma_1|\nabla_\perp u_1(\vec{R})|^2+\gamma_N|\nabla_\perp u_N(\vec{R})|^2]d\vec{R}, \qquad (2)$$

where γ_1 is the surface tension of the free surface of the film, γ_N is the surface tension of the film-substrate interface, $\vec{R}$ is the radius vector in the plane of the film ($R^2=x^2+y^2$), $\nabla_\perp$ is the projection of the $\vec{\nabla}$ operator on the (x,y) plane.

Using the Fourier transformation

$$u_n(\vec{R})=(2\pi)^{-2}\int u_n(\vec{q}_\perp)\exp(i\vec{q}_\perp\cdot\vec{R})d\vec{q}_\perp, \qquad (3)$$

one can obtain the following simple and compact expression for the free energy excess F:

$$F=\frac{1}{2}\sum_{k,n=1}^{N}\int u_k(\vec{q}_\perp)M_{kn}u_n(-\vec{q}_\perp)d\vec{q}_\perp, \qquad (4)$$

where M_{kn} are the elements of ribbonlike matrix. The nonzero elements of this matrix are determined as

$$M_{11}=\gamma_1 q_\perp^2+K_1 d q_\perp^4+(B_1+B_2)/2d=b_1, \qquad (5)$$

$$M_{NN}=\gamma_N q_\perp^2+K_N d q_\perp^4+(B_{N-1}+B_N)/2d=b_N, \qquad (6)$$

$$M_{nn}=K_n d q_\perp^4+(B_{n-1}+2B_n+B_{n+1})/2d=b_n, n=2,N-1, \qquad (7)$$

$$M_{n+1n}=M_{nn+1}=-(B_n+B_{n+1})/2d=c_n, n=1,N-1, \qquad (8)$$

where K_n is the elastic modulus for bending of the nth smectic layer, and B_n is the compressibility of this layer. If we know the magnitudes of elastic moduli K and B for the bulk Sm-A phase of a given LC at a certain temperature T_0 [$K(T_0)\equiv K_0$, $B(T_0)\equiv B_0$] much lower the bulk Sm-A–I or Sm-A–N transition temperature, we can determine values of the elastic moduli K_n, B_n for any film of this LC at any temperature T within an interval of its existence via the microscopic model [24–27] for a thin LC layer with two boundary surfaces. The algorithm of determination of these elastic moduli is described in detail in our previous papers [21,23]. Further, one can find the elements $(M^{-1})_{kn}$ of inverse matrix, and, using these elements, calculate the average film layer displacement fluctuations $\sigma_n=\langle u_n^2(0)\rangle^{1/2}$ and the displacement-displacement correlations $g_{k,n}(R)=\langle u_k(\vec{R})u_n(0)\rangle/(\sigma_k\sigma_n)$. According to Refs. [18,19],

$$\sigma_n^2=\langle u_n^2(0)\rangle=\frac{k_BT}{(2\pi)^2}\int (M^{-1})_{nn}d\vec{q}_\perp, \qquad (9)$$

$$\langle u_k(\vec{R})u_n(0)\rangle=\frac{k_BT}{(2\pi)^2}\int (M^{-1})_{kn}\exp(i\vec{q}_\perp\cdot\vec{R})d\vec{q}_\perp. \qquad (10)$$

In right-hand sides of Eqs. (9) and (10), the lower limit of integration is determined by the transverse film size L, whereas the upper limit is determined by the molecular diameter a ($2\pi/L\leqslant|q_\perp|\leqslant 2\pi/a$). If the film has a macroscopic transverse size $L\sim$cm, then one can set the lower limits of integration in Eqs. (9) and (10) to be equal to zero.

Numerical calculations of the smectic layer displacement fluctuations σ_n and correlations $g_{k,n}(R)$ have been carried out for the solid substrate supported smectic-A film consisting of $N=24$ layers. The film is assumed to be made of a LC having a "weak" first order Sm-A–N phase transition. According to the well known McMillan theory [36] for the bulk Sm-A phase and the microscopic model [24–27] for a thin LC layer with two boundary surfaces, in this case the model parameter $\alpha=2\exp[-(\pi r_0/d)^2]$ used in the theory must be $\alpha\leqslant 0.98$ where r_0 is a characteristic radius of the model pair potential proposed by McMillan. As in Refs. [21–23], our calculations have been performed for $\alpha=0.871$. The smectic layer displacement fluctuations and correlations between them have been calculated for two temperatures. The first temperature T_1 is well below the bulk Sm-A–N transition temperature and the second temperature T_2 is just below the maximum temperature of existence of the film of a given thickness. According to Refs. [24–27], above the maximum temperature, the smectic order completely disappears in volume of the film ($s\rightarrow 0$). As in Refs. [21–23], we take $T_1=0.204(V_0/k_B)$ [according to Ref. [36], for $\alpha=0.871$, the bulk Sm-A–N phase transition temperature is equal to $T_{AN}=0.2091(V_0/k_B)$], where V_0 is the intermolecular interaction constant in the McMillan theory. In the framework of the model proposed in Refs. [24–27], a value of the temperature T_2 is determined by the orienting actions of the boundary surfaces of the film on the LC molecules. These actions are simulated by effective short-range external fields, the strength of which is proportional to interaction constants W_1 and W_N corresponding to the free surface of the film and the film-substrate interface, respectively. As in our previous papers [21–23], we set $W_1/V_0=1.6$. As for the constant W_N, we considered three cases. In the first case we set $W_N=W_1$ (orienting actions of two boundary surfaces are equal to each other). In the second case we take $W_N=5W_1$ (the orienting action of the film-substrate interface is much stronger than that of its free surface). Finally, in the third case we set $W_N=W_1/5$ that corresponds to a very weak orienting action of the film-substrate interface. Then, in the first case, as in Refs. [21–23], we obtain $T_2=0.210\,35(V_0/k_B)$, in the second case $T_2=0.210\,39(V_0/k_B)$, and in the third case $T_2=0.2093(V_0/k_B)$.

The bending elastic constant K_0 and the smectic layer compressibility B_0 for the bulk Sm-*A* phase at the temperature T_0 well below the bulk Sm-*A*–*N* phase transition temperature T_{AN} are assumed, as in Refs. [21–23], to be equal to $K_0=10^{-6}$ dyn and $B_0=10^8$ dyn/cm^2 (typical value for most LCs [1]). A value of the surface tension $\gamma_1=25$ dyn/cm for the free surface of the film has been taken from Ref. [9], and the surface tension γ_N of the film-substrate interface is assumed, as in Ref. [16], to be infinitely large (in numerical calculations we set $\gamma_N=1000\gamma_1$). The film layer spacing d is assumed to be temperature independent and equal to $d=30A$, and we set the molecular diameter $a=4A$ (typical values for the LC molecules [1]).

First of all, using the model [24–27], we have calculated the bending elastic constant K and the smectic layer compressibility B profiles for three above mentioned relations between orienting actions of two boundary surfaces of the film. As expected, in the first case ($W_N=W_1$), the profiles obtained are completely similar to those presented in our previous papers on the thermal layer displacement fluctuations in FSSAFs (see Figs. 1 and 2 in Refs. [21,23]). In the second case ($W_N=5W_1$), the profiles obtained are also very similar to those in Refs. [21,23], though values of K/K_0 and B/B_0 for the Nth layer are slightly larger than analogous values for the first layer. In the third case ($W_N=W_1/5$), however, the profiles obtained are significantly different from those presented in Refs. [21,23]. First, as expected, these profiles are not symmetrical with respect to the center of the film. Second, the elastic moduli, especially the compressibility B, have their minimum values not in the central part of the film, but in the layer adjacent to the solid substrate. It should be also noticed that, for the lower temperature T_1 (see curves 1 in Figs. 1 and 2 and Figs. 1 and 2 in Refs. [21,23]), in all above mentioned cases, the elastic moduli K and B profiles have a large plateau in the central part of the film, on which these moduli are nearly constant and very close to the bulk values K_0 and B_0, respectively. On the contrary, for the maximum temperature T_2 of existence of the film, this plateau is absent (see curves 2 in these figures). Consequently, for the temperature T_1, a significant part of the solid substrate supported smectic-*A* film is really spatially homogeneous, or almost homogeneous, and the Holyst's model [18–20] used in Refs. [16,17] should give results not very different from ours. However, close to the maximum temperature of existence of the film of given thickness ($T=T_2$), in all above mentioned cases, the film is already not spatially homogeneous (see curves 2 in Figs. 1 and 2 and

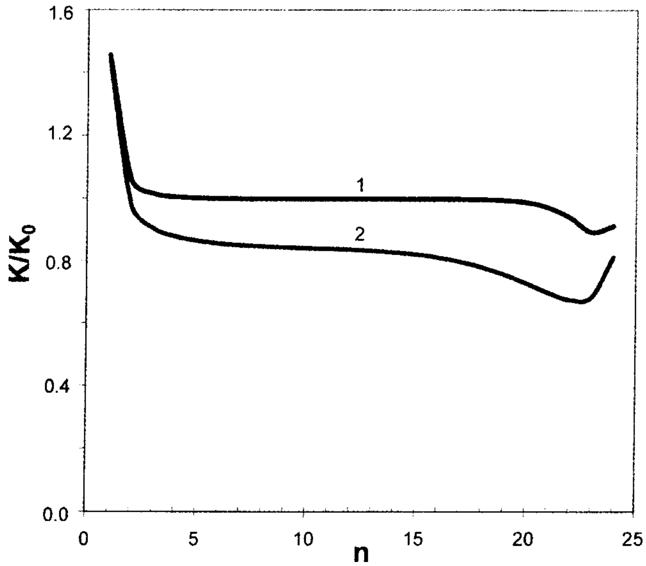

FIG. 1. The bending elastic constant K profiles in the solid substrate supported smectic-*A* film well below the bulk Sm-*A*–*N* transition temperature and near the maximum temperature of its existence. $N=24$; $\alpha=0.871$; $W_1/V_0=1.6$, $W_N=W_1/5$. Curve 1, $T=T_1=0.204(V_0/k_B)$; curve 2, $T=T_2=0.2093(V_0/k_B)$.

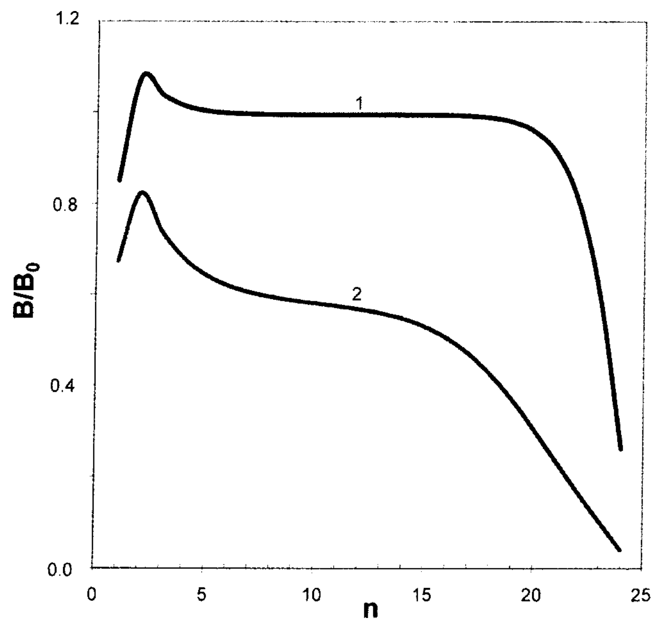

FIG. 2. The smectic layer compressibility B profiles in the solid substrate supported smectic-*A* film under the same conditions as in Fig. 1. Curve 1, $T=T_1=0.204(V_0/k_B)$; curve 2, $T=T_2=0.2093(V_0/k_B)$.

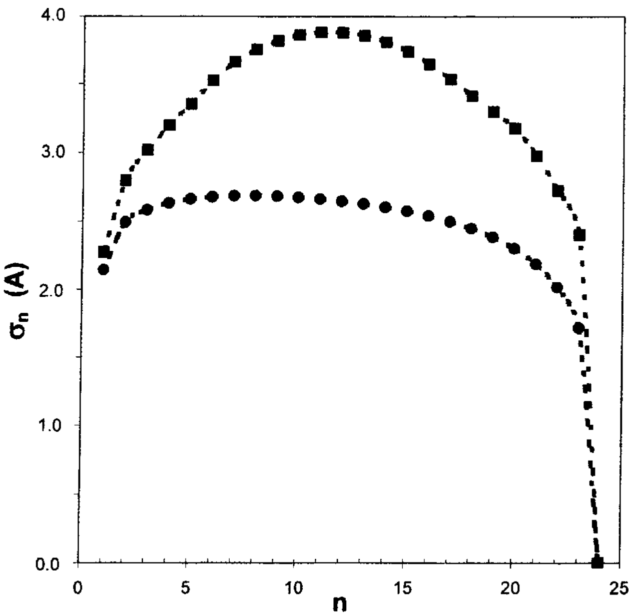

FIG. 3. The smectic layer displacement fluctuation profiles in the solid substrate supported smectic-A film. $W_1/V_0=1.6$, $W_N=W_1$, $K_0=10^{-6}$ dyn; $B_0=10^8$ dyn/cm^2; $\gamma_1=25$ dyn/cm. Solid circles, $T=T_1=0.204(V_0/k_B)$; solid squares, $T=T_2=0.210\,35(V_0/k_B)$; dashed line, the results of the Holyst's model [18–20].

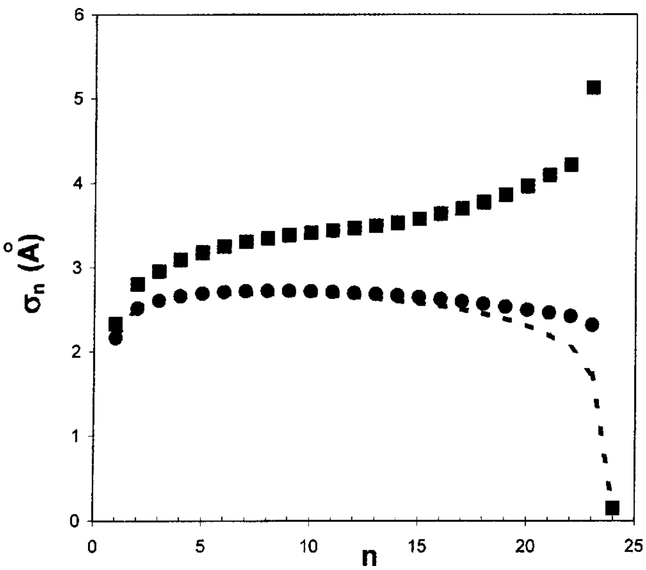

FIG. 4. Analogous profiles for $W_N=W_1/5$. Other parameters are the same as in Fig. 3. Solid circles, $T=T_1=0.204(V_0/k_B)$; solid squares, $T=T_2=0.2093(V_0/k_B)$; dashed line, the results of the Holyst's model.

Figs. 1 and 2 in Refs. [21,23]). In addition, in the third case, the film is strongly asymmetrical with respect to its center, and, in the layers adjacent to the substrate, the elastic moduli K and B are much weaker than those close to the free surface of the film. Consequently, just in this case, a difference between results obtained in Refs. [16,17] in the framework of the Holyst's model and our results should be most noticeable.

Further, the elastic moduli K and B profiles obtained above have been used in calculations of the layer displacement fluctuation profiles σ_n in the 24-layer solid substrate supported smectic-A film for both the lower temperature T_1 and maximum temperature T_2 of its existence. The results of these calculations for the first ($W_N=W_1$) and the third ($W_N=W_1/5$) cases are shown in Fig. 3 and Fig. 4, respectively (the σ_n profile for the second case is slightly different from analogous curves in Fig. 3). In the same figures, using the dashed curves, the thermal fluctuation profiles obtained in the framework of the Holyst's model [18–20] are also shown. As expected, in both cases, for $T=T_1$ our results are very similar to those given by this model. However, close to the maximum temperatures of existence of the films ($T=T_2$), taking into account the elastic moduli K and B profiles gives rise to a considerable deviation from the Holyst's model [18–20] predictions. So, in the first case (see Fig. 3), a maximum value of the layer displacement fluctuations the σ_n calculated at the temperature $T_2=0.210\,35(V_0/k_B)$ is about 1.5 times larger than that calculated at the temperature T_1. In addition, the maximum of the σ_n profile is shifted to the center of the film, where the elastic moduli K and B have minimum values. At the same time, according to calculations performed in the framework of the Holyst's model, such growth of temperature of the film gives rise to very weak change in the σ_n profile. In the third case, heating the film from the lower temperature T_1 to the maximum temperature $T_2=0.2093(V_0/k_B)$ of existence of the film gives rise to even more radical change in the σ_n profile (see Fig. 4). For $T=T_1$, we have a very weak dependence of σ_n on the layer index n, excepting the sharp decay of σ_n to zero at $n=24$, whereas, for the maximum temperature T_2 of existence of the film, we see a significant growth of σ_n with increasing n up to the last but one film layer followed by the sharp decay to zero at $n=24$. So, the maximum value of σ_n is shifted to the solid substrate surface, where the elastic moduli K and B have minimum values (see Figs. 1 and 2). In other words, in all cases under consideration, maximum values of the thermal smectic layer displacement fluctuations are observed where the layering structure of the film is weakest, and a position of these maxima is determined by orienting actions of the boundary surfaces of the film on the LC molecules.

We have also calculated the displacement-displacement correlations $g_{k,n}(R)$ for different layers in the solid substrate supported smectic-A films. The results of these calculations for correlations between the layer displacement fluctuations of the central film layer ($k=12$) and other layers ($n=1,24,\vec{R}=0$) for the case of $W_N=W_1$ are shown in Fig. 5. Well below the bulk Sm-A–N transition temperature ($T=T_1$), our results (curve 1 in Fig. 5) are very similar to those obtained in the framework of the Holyst's model [18–20] (dashed curve in this figure). One can see a significant decrease of the correlation $g_{12,n}(0)$ with increasing absolute value of difference $12-n$. However, as expected, the curves obtained are not symmetrical with respect to the center of the film, and decay of this correlation with approaching the solid substrate surface is much faster than that with approaching the free surface of the film. So, near the free surface ($n=1$), the correlation $g_{12,n}(0)$ exceeds 0.2, whereas for the

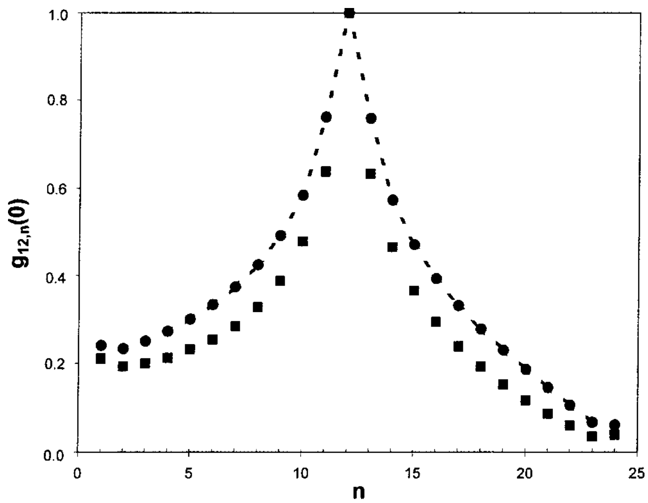

FIG. 5. The correlations $g_{12,n}(0)$ between the displacement fluctuations of the 12th and other smectic layers ($n=1,24$) in the solid substrate supported smectic-A film. The parameters N, α, W_1, W_N, K_0, B_0, γ_1 are the same as in Fig. 3. Solid circles, $T=T_1=0.204(V_0/k_B)$; solid squares, $T=T_2=0.210\,35(V_0/k_B)$. The dashed curve represents the results of the Holyst's model.

last but one film layer ($n=23$), this correlation is close to zero. Such difference between magnitudes of these correlations is due to the fact that the smectic layers disposed near the free surface of the film can fluctuate "in unison" with the central film layers. At the same time, the smectic layers situated close to the last film layer, which is rigidly fixed at the solid substrate surface, have no such opportunity because of very large energy excess associated with their stretch or compression.

Our calculations show also that heating the solid substrate supported smectic-A films up to the maximum temperatures T_2 of their existence gives rise to changes in values of correlations $g_{,n}(0)$ much weaker than the changes in the profiles of fluctuations σ_n (see Fig. 5). In addition, the thermally controlled changes in values of $g_{,n}(0)$ are determined by the orienting actions of the boundary surfaces of the film on the LC molecules. If the orienting action of the film-substrate interface is equal to the orienting action of the free surface of the film ($W_N=W_1$) or exceeds it ($W_N=5W_1$), then heating the film gives rise, as in the case of FSSAFs, to decrease in values of the correlations $g_{12,n}(0)$ (see Fig. 5). On the contrary, when the orienting action of the film-substrate interface is weaker than that of the free surface of the film ($W_N=W_1/5$), a growth in the temperature gives rise to an enhancement of these correlations. These results can be physically interpreted as follows. In the first two cases ($W_N=W_1$ and $W_N=5W_1$), heating the solid substrate supported smectic-A film to the maximum temperature T_2 of its existence gives rise to a significant decrease in values of the elastic moduli K and B in the center of the film, whereas these moduli in its interfacial layers practically do not change. As said above, in these cases, the elastic moduli K and B profiles are very similar to those in FSSAFs (see Figs. 1 and 2 in Refs. [21,23]). Since the displacement fluctuations of the central film layers are transmitted to other layers through the layers adjacent to central ones, a significant decrease of their elasticity should give rise to weakness of the correlations $g_{12,n}(0)$ between the displacement fluctuations of the central layers and those of other film layers. In the third case ($W_N=W_1/5$), however, heating the film to the maximum temperature T_2 of its existence not only gives rise to decrease in elasticity of its central layers, but also to a more considerable extent decreases elasticity of the smectic layers adjacent to the substrate surface (see Figs. 1 and 2 of the present paper). As said above, a rigid fixation of these layers hinders other film layers from fluctuating "in unison." So, in this case, heating the film eliminates an obstacle for such "synchronous" fluctuations, and, hence, enhances the correlations between them.

III. DYNAMICS OF THE SMECTIC LAYER DISPLACEMENT FLUCTUATIONS IN THE SOLID SUBSTRATE SUPPORTED SMECTIC-*A* FILMS

According to the model proposed in Refs. [31,32], a time dependence of the smectic layer displacement fluctuations $u_n(x,y)$ from equilibrium positions in the smectic-A film is determined by the following equations of motion:

$$\rho_0 \frac{\partial^2 u_n}{\partial t^2} = -\eta_3 \Delta_\perp \frac{\partial u_n}{\partial t} - \frac{1}{d}\,\delta F/\delta u_n, \tag{11}$$

where ρ_0 is an average density of LC, t is the time, and F is the above mentioned free energy excess associated with thermal smectic layer displacement fluctuations in the film. From Eqs. (11), using the Fourier transformation (3) and introducing dimensionless variables $t'=[(K_0B_0)^{1/2}/(d\eta_3)]t$ and $q'=q_\perp/q_0$, $q_0^2=[B_0/(K_0d^2)]^{1/2}$, one can obtain a set of equations which can be written in the following compact matrix form:

$$(\rho_0 K_0/\eta_3^2)\frac{\partial^2 u_n}{\partial t'^2} = -q'^2 \frac{\partial u_n}{\partial t'} - M'_{nm} u_m, \tag{12}$$

where M'_{nm} are elements of a ribbonlike matrix analogous to the above defined matrix M_{nm}. In the case of the solid substrate supported smectic-A film, nonzero elements of this matrix are given by Eqs. (11)–(15) in our previous paper [35] devoted to dynamics of the layer displacement fluctuations in FSSAFs if the dimensionless surface tension $\bar{\gamma}=\gamma(K_0B_0)^{-1/2}$ in Eqs. (11) and (12) in this paper is replaced by $\bar{\gamma}_1=\gamma_1(K_0B_0)^{-1/2}$ and $\bar{\gamma}_N=\gamma_N(K_0B_0)^{-1/2}$, respectively. As in Refs. [31,32,35], the solution $u_n(q',t')$ of Eqs. (12) can be expressed in terms of eigenvectors $v_n^{(k)}(q')$ of the matrix $M'_{mn}(q')$ as follows:

$$u_n(q',t') = \sum_{k=1}^{N} u_n^{(k)}(q',t')\,v_n^{(k)}(q'), \tag{13}$$

and the time dependence of the normal modes $u_n^{(k)}(q',t')$ in this expansion is determined by the equation

$$u_n^{(k)}(q',t') = u_{n+}^{(k)}(q')\exp[\beta_+^{(k)}(q')t'] + u_{n-}^{(k)}(q')\exp[\beta_-^{(k)}(q')t']. \tag{14}$$

By using Eqs. (18)–(21) in Ref. [35], the exponents $\beta_\pm^{(k)}(q')$ can be expressed in terms of relaxation times $\tau_\pm^{(k)}(q')$ and frequencies $\omega^{(k)}(q')$. A knowledge of the time dependences of the normal modes $u_n^{(k)}(q',t')$ enables us to calculate the time dependent displacement-displacement correlations which in the Fourier representation are determined [31,32] by

$$C_{m,n}(q',t') = \langle u_m(q',t')u_n(-q',0)\rangle. \tag{15}$$

Finally, using Eqs. (27) and (28) in Ref. [35], one can express the time dependent intensity-intensity correlation $\langle I(q,t)I(q,0)\rangle$ for the diffuse x-ray scattering from the film in terms of the correlation functions $C_{m,n}(q',t')$.

Numerical calculations of the time dependent displacement-displacement $C_{m,n}(q_\perp,t)$ and intensity-intensity $\langle I(q,t)I(q,0)\rangle$ correlations have been performed for the 24-layer solid substrate supported smectic-*A* films at values of the model parameters similar to those used in Sec. II in calculations of the smectic layer displacement fluctuation profiles and correlations between these fluctuations. The layer sliding viscosity η_3 was assumed to be equal to $\eta_3 = 0.4$ g/(cm s) that is a typical value for smectic-*A* LCs. The calculations have been performed for the three above mentioned relations between interaction constants W_1 and W_N at both temperatures T_1 and T_2.

First of all, we have investigated an effect of the temperature of the film on the behavior of the time dependent displacement-displacement correlation functions $C_{m,n}(q_\perp,t)$. In our previous paper [35] it has been shown that, for FSSAFs, this effect can be observed in sufficiently thin films ($N \geqslant 100$) and at large enough ($\geqslant 10^6$ cm^{-1}) values of the wave vector transfer component in the film plane (see Figs. 3 and 4 in Ref. [35]). However, in our case of the solid substrate supported smectic-*A* films, this effect is noticeable for thinner films and at significantly smaller values of this wave vector transfer component. This fact can be illustrated by Fig. 6 demonstrating the time dependence of the displacement-displacement correlation function $C_{12,12}$ calculated for the 24-layer film at $q_\perp = 10^5$ cm^{-1}, $W_N = W_1$, and for the temperatures T_1 (curve 1) and T_2 (curve 2). One can see that, for maximum temperature T_2 of existence of the film, an absolute value of the function $C_{12,12}$ at $t=0$ is about two times larger than that for the lower temperature T_1, and, for $T=T_2$, a decay of this correlation function with time is significantly slower than analogous decay for $T=T_1$. Other time dependent displacement-displacement correlation functions ($C_{1,1}$, $C_{1,12}$, etc.) demonstrate a similar behavior. In the case of FSSAFs, for the same values of N and $q_\perp$, these correlation functions are absolutely temperature insensitive. Such difference in behavior of the solid substrate supported smectic-*A* films and FSSAFs can be qualitatively explained as follows. In not very thick ($N \leqslant 100$) FSSAFs and for $q_\perp \leqslant 10^6$ cm^{-1}, a major role in dynamics of the layer displacement fluctuations belongs to the so-called acoustic mode [31,32], which corresponds to such motion of the film that does not change interlayer spacing. Therefore, no dependence of the relaxation times on the elastic moduli *K* and *B* profiles should be observed in such motion. In the solid substrate supported smectic-*A* film, however, the layer adjacent to the substrate surface is rigidly fixed, and the acoustic mode does not occur in its motion [17]. Therefore, the layer displacement fluctuations in such films always give rise to change in the interlayer spacings, and, hence, the relaxation times $\tau_\pm^{(k)}(q')$, which determine the time dependences of the displacement-displacement correlation functions, should depend on the elastic moduli *K* and *B* profiles, and, consequently, the temperature, even for not very thick ($N \leqslant 100$) films and not very large $q_\perp$. It should be noticed that, for the substrate surfaces supported smectic-*A* films, the temperature dependence of these correlation functions can be observed even for more smaller values of the wave vector

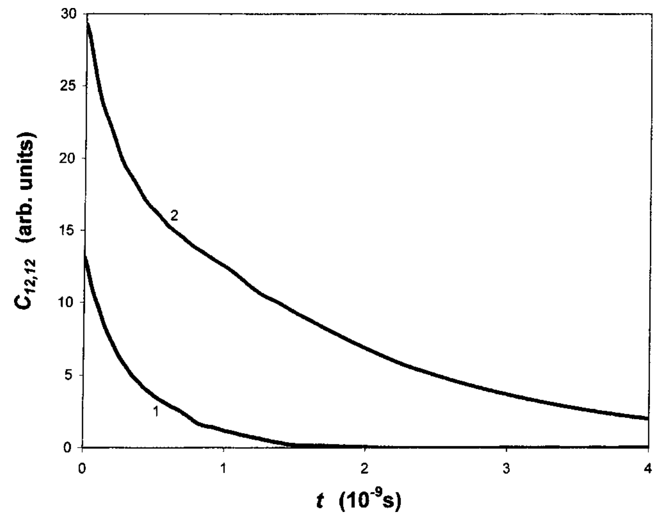

FIG. 6. Time dependences of the displacement-displacement correlation function $C_{12,12}$. $W_N = W_1$, $q_\perp = 10^5$ cm^{-1}. Curve 1, $T = T_1 = 0.204(V_0/k_B)$; curve 2, $T = T_2 = 0.210\,35(V_0/k_B)$.

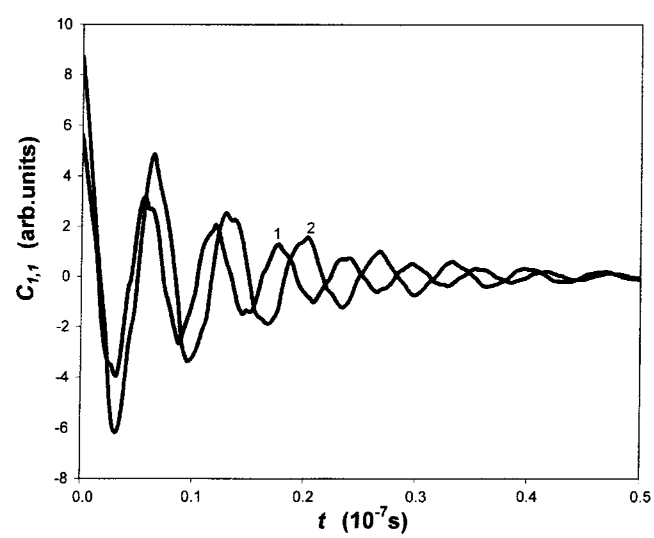

FIG. 7. Analogous dependences for $C_{1,1}$ at $q_\perp = 2\times 10^4$ cm^{-1}.

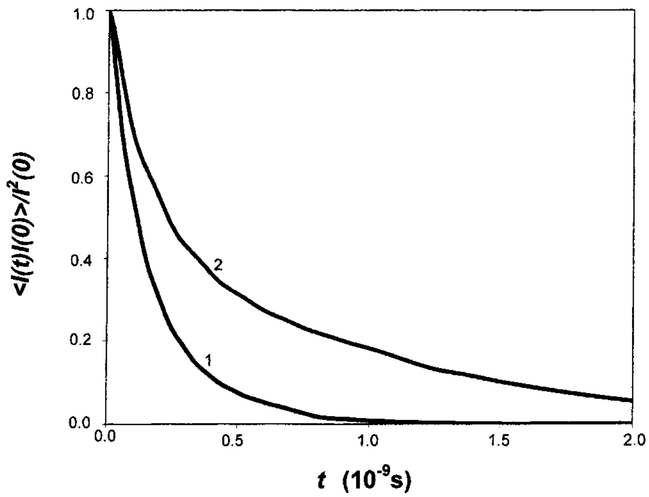

FIG. 8. Time dependences of the intensity-intensity correlation function $\langle I(q,t)I(q,0)\rangle$. $W_N=W_1$, $q_\perp=10^5$ cm^{-1}. Curve 1, $T=T_1=0.204(V_0/k_B)$; curve 2, $T=T_2=0.210\,35(V_0/k_B)$.

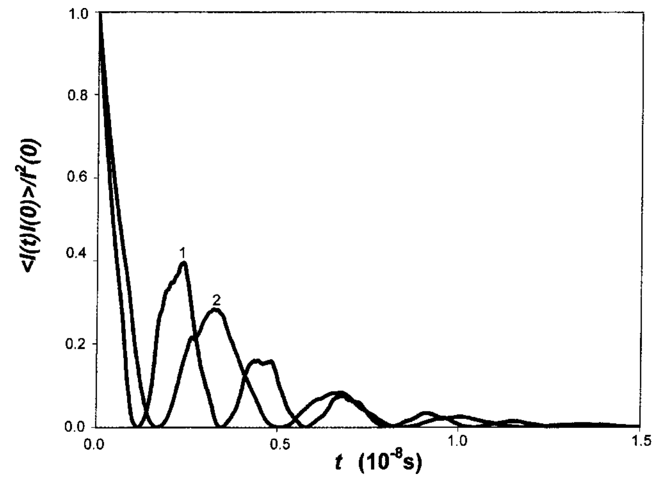

FIG. 9. The same dependences as in Fig. 8 but for $W_N=W_1/5$ and $q_\perp=3\times10^4$ cm^{-1}. Curve 1, $T=T_1=0.204(V_0/k_B)$; curve 2, $T=T_2=0.2093(V_0/k_B)$.

transfer component in the film plane. This fact is illustrated in Fig. 7, demonstrating the time dependences of the displacement-displacement correlation function $C_{1,1}$ for $q_\perp=2\times10^4$ cm^{-1} at both $T=T_1$ (curve 1) and $T=T_2$ (curve 2). For such a not very large value of $q_\perp$, both dependences demonstrate oscillations, but these oscillations are noticeably different from each other.

Then we have calculated the time dependent intensity-intensity correlations $\langle I(q,t)I(q,0)\rangle$ for the 24-layer solid substrate supported smectic-*A* film. The results of these calculations for the diffuse x-ray scattering from the film in the vicinity of the first Bragg peak ($q_z=2\pi/d$) at the wave vector transfer component in the film plane $q_\perp=10^5$ cm^{-1}, and for $W_N=W_1$, are shown in Fig. 8. Curve 1 corresponds to the temperature T_1 well below the bulk Sm-*A*–*N* phase transition temperature, and curve 2 corresponds to results of calculation at the temperature T_2 just below the maximum temperature of existence of the film. One can see that heating the film to the temperature T_2 noticeably decelerates the decay of the intensity-intensity correlation function $\langle I(q,t)I(q,0)\rangle$ with the time *t*, and observation of this phenomenon is most convenient for $t\sim10^{-9}$ s. It should be also noticed that when the orienting action of the film-substrate interface is very strong ($W_N=5W_1$), the results of calculations are very similar to those shown in Fig. 8. On the contrary, when the orienting action of this interface is much weaker than that of the free surface of the film ($W_N=W_1/5$), the decay of the intensity-intensity correlation function $\langle I(q,t)I(q,0)\rangle$ at the maximum temperature T_2 of existence of the film becomes even more slower. Finally, our calculations show that, for the 24-layer solid substrate supported smectic-*A* film, an effect of the temperature on the time dependence of the intensity-intensity correlation $\langle I(q,t)I(q,0)\rangle$ is observable for even more smaller values, for example, $q_\perp=3\times10^4$ cm^{-1}, of the wave transfer component in the film plane, when this dependence demonstrate noticeable oscillations (see Fig. 9). In FSSAFs, for such values of $q_\perp$, this correlation function is absolutely temperature independent.

Thus, the results obtained show that the dynamics of the layer displacement fluctuations in the solid substrate supported smectic-*A* films is much more sensitive to change in internal structure caused by its heating, and an experimental study of this dynamics can be a sufficiently effective tool for investigation of this structure.

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