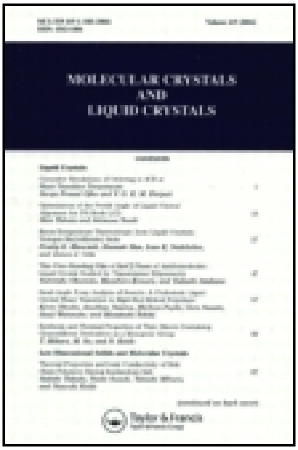

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Correlation of The Elastic Properties and Translational Order of Smectic Liquid Crystals

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Version of record first published: 22 Sep 2006.

To cite this article: I. S. Gersht & V. K. Pershin (1989): Correlation of The Elastic Properties and Translational Order of Smectic Liquid Crystals, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 167:1, 147-166

To link to this article: http://dx.doi.org/10.1080/00268948908037171

Mol. Cryst. Liq. Cryst., 1989, Vol. 167, pp. 147-166
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Printed in the United States of America

Correlation of The Elastic Properties and Translational Order of Smectic Liquid Crystals

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(*Received October 8, 1987; in final form June 23, 1988*)

In terms of the microscopic approach based on the account of the terms nonlinear with respect to the wave vector in frequencies of the translational oscillations of the uniaxial molecules the known smectic phases are investigated and the new ones are predicted. All these phases differ qualitatively by the translational ordering degree in different directions and by elastic properties. The transition between them is followed by a jump of entropy. It is established that the corresponding nonlinear terms lead to the arising of some restoring forces which increase structure ordering significantly if moduli are equal to zero. The account of them allows, in particular, to prove that there exists long range order within the layer of the smectic B even if the "statical" interlayer shear modulus is equal to zero, to describe weak intermolecular correlations within the layer of the smectic A, to interpret the experimental frequency dependence of the elastic moduli of smectics B and A. The new phases occupy the intermediate position between the known ones. The experimental identification of these phases may be fulfilled by means of the x-ray investigation of partial disordering and of the study of the frequency dependence of the shear moduli.

Keywords: microscopic theory, smectic liquid crystals, classification, translational order, dynamical shear moduli, nonlinear effects

1. INTRODUCTION

The smectic liquid crystals (SLC) are mesomorphic phases which are characterized by the difference in the value of translational order in different directions. One of the most known classification techniques of SLC's and the description of phase transitions in them is based on the consideration of groups of "global" symmetry.[1] It allows the solving of these questions in connection with the presence or absence of long range order in the fixed direction. In terms of this technique it is, however, impossible a) to consider phases which have order intermediate between the completely ordered (*i.e.* crystalline) and the disordered (*i.e.* liquid) one in the fixed direction and b) to investigate the effects of local order existing even within the "liquid" layer of the smectic A.[2,3] For example, ordering of layers (*i.e.* in the direction of the normal to the layers) in the smectic A is neither liquid nor crystalline.[4,5] Another example may be intermediate order within the layer in the smectic F.[6,7]

The basic ideas of the approach allowing to solve these problems had been long ago formulated by Landau.[8] This approach is based on the consideration of the temperature fluctuations of particles and leads to the conceptions so as long range, quasi-long-range and short range order. Landau had considered the dependence of the frequencies ω_i of translational oscillations on the wave vector **K** in the investigation of systems with one- or two-dimensional periodicity. He had proposed accounting corresponding second order terms (*i.e.* nonlinear ones with respect to **K**) in the frequencies for the investigation of translational order of the structures where the shear moduli are equal to zero. This idea had been later applied to the interpretation of translational order of the layers in the smectic A[4,5] and of the stacks of SLC formed by disclike molecules (D).[9,10] Second order with respect to **K** is associated with the account of orientational correlations in these papers. Landau had also shown[8] that no long range translational order can exist in low dimensional systems. At present these results are used for the interpretation of experimental data in the investigation of order within the smectic F layer[6] and the stack D.[10]

Thus, the nonlinear and dimensional effects are a matter of principle for understanding of the nature of the mesomorphic substance state. In the present paper the influence of these effects on the elastic properties and translational order of SLC's is studied in terms of the microscopic theory.

2. ELASTIC PROPERTIES

We shall consider a hexagonal layered crystal in terms of the pseudo-harmonic approximation accounting strong anharmonism.[11,12] Let us assume that the molecules of the crystals have a shape of ellipsoids of revolution. Two identical axes of these ellipsoids are parallel to the layer plane and the third one is normal to the layer. These axes are nearly equal in length to the intermolecular distance within the layer and to the distance between the layers, respectively.

Let us write down an expression for the potentional energy of one molecule assuming that it interacts with the first and second neighbors only and not accounting manybody forces in the evident form:

$$\Psi = \frac{1}{2}\sum_{n=1}^{2}\left[\sum_{i=1}^{6}\Psi_{wl}(\mathbf{r}^{ni}) + \sum_{j=7}^{8}\Psi_{il}(\mathbf{r}^{nj})\right]. \tag{1}$$

Here $\mathbf{r}^{ni}$ and $\mathbf{r}^{nj}$ are the molecules coordinates; $n = 1$ corresponds to the first neighbors and $n = 2$—to the second ones; i and j are the molecules numbers within the layer and of the layer, respectively, at the fixed n. The first item in square brackets is the interaction potential of the molecules within the layer, the second one is the effective interlayer potential.

Let us assume that the interaction is non-central

$$\Psi_{wl}(\mathbf{r}^{ni}) \neq \Psi_{wl}(|\mathbf{r}^{ni}|); \quad \Psi_{il}(\mathbf{r}^{nj}) \neq \Psi_{il}(|\mathbf{r}^{nj}|) \tag{2}$$

and anisotropic. Note that the interaction non-centrally allows to account manybody forces in the model manner[13] and its anisotropy is an evident consequence of the shape anisotropy of molecules and of the existence of the preferential orientation direction of their long axes. We choose a system of coordinates so that the axis OZ is perpendicular to layers $l^{17}_{\mu} = \delta_{\mu 3} l_3$ and the axis OX coincides with one of the fundamental translation vectors within the layer $l^{11}_{\mu} = \delta_{\mu 1} l$; $\mathbf{l}^{ni} = \langle \mathbf{r}^{ni} \rangle$; $\mathbf{l}^{nj} = \langle \mathbf{r}^{nj} \rangle$. Here $\langle *** \rangle$ is the statistical mean which is calculated over the equilibrium state of the crystal. Let us investigate the elastic properties of the system assuming the existence of long range crystalline order (we shall consider the essential influence of partial disorder in the third section). In the continual approximation the free energy will be[4,5,9,10,14]

$$F = F_I + \frac{1}{2} K_{11}(u_{3,xx} + u_{3,yy})^2 + \frac{1}{2} K_{33}[(u_{1,zz})^2 + (u_{2,zz})^2]. \tag{3}$$

Here F_I is the energy of the orientationally disordered system. (Let us assume that the absence of orientational correlations is equivalent to the case of spherical molecules). The second and the third items are the corrections connected with the account of the orientational correlations; u_i is the i-component of the displacement from the equilibrium position; $u_{i,zz} = \partial^2 u_i/\partial z^2$, K_{11} and K_{33} are the Frank-constants. By using the standard technique[10,14] it can be shown that the account of these corrections leads to the change of the frequencies ω_i of the translational oscillations

$$\begin{aligned} M(\omega_{1,2})^2 &= M(\omega_{1,2})^2_I + 8(K_{33} l^2/l_3^3)\theta_3^4, \\ M(\omega_3)^2 &= M(\omega_3)^2_I + 16(K_{11} l_3/l^2)\theta^4, \end{aligned} \tag{4}$$

where $(\omega_i)_I$ corresponds to the case of spherical molecules; $\theta_1 = lK_1/2$, $\theta_2 = lK_2/2$, $\theta_3 = l_3K_3/2$, $\theta = \sqrt{\theta_1^2 + \theta_2^2}$, K_i are components of the wave vector; M is the molecule mass. The frequencies $(\omega_i)_I$ can be obtained from the equation[11] of the microscopic theory of atomic crystals

$$\mathrm{Det}\left\| \sum_{p=1}^{8} \sum_{n=1}^{2} \Phi^{\mu\mu'}_{np} \exp(i\mathbf{k}\mathbf{l}^{np}) - M(\omega_i^2)_I \delta_{\mu\mu'} \right\| = 0 \tag{5}$$

where $\Phi^{\mu\mu'}_{np} = \partial^2 \langle \Psi \rangle / \partial l^{np}_{\mu} \partial l^{np}_{\mu'}$ are the force constants. We solve these equations by using the symmetry of force constants.[13] Substituting the solutions into (4) we obtain

$$\begin{aligned} M\omega_1^2 &= 4 \cdot l_3 C_{11} \mathrm{Sin}^2\theta + \frac{4 \cdot l^2}{l_3} C_{1313} \mathrm{Sin}^2\theta_3 + C'_{1313}\theta_3^4, \\ M\omega_2^2 &= 4 \cdot l_3 C_{66} \mathrm{Sin}^2\theta + C'_{66}\theta^4 + 2 \cdot l_3 C_{11}\theta_1^2\theta_2^2 \\ &\quad + \frac{4l^2}{l_3} C_{1313} \mathrm{Sin}^2\theta_3 + C'_{1313}\theta_3^4, \\ M\omega_3^2 &= 4 \cdot l_3 C_{3131} \mathrm{Sin}^2\theta + C'_{3131}\theta^4 + \frac{4l^2}{l_3} C_{33} \mathrm{Sin}^2\theta_3 + C'_{33}\theta_3^4, \end{aligned} \tag{6}$$

C_{ii}, C_{1313}, C_{3131} are combinations of the force constants.

$$C_{11} = 3(3\Phi^{11}_{11} + \Phi^{22}_{11})/8 \cdot l_3; \qquad C_{66} = 3(\Phi^{11}_{11} + 3\Phi^{22}_{11} + 9\Phi^{11}_{21})/8\, l_3;$$

$$C_{1313} = (\Phi^{11}_{17} + 4\Phi^{11}_{27})l_3/l^2; \qquad C_{33} = (\Phi^{33}_{17} + 4\Phi^{33}_{27})l_3/l^2;$$

$$C_{3131} = 3(\Phi^{33}_{11} + 3\Phi^{33}_{21})/2 \cdot l_3.$$

Primed coefficients are connected with the account of the orientational correlations of molecules and of the translational force constants of the second neighbors also: $C'_{66} = -9\Phi^{11}_{21}$; $C'_{33} = -16\Phi^{33}_{27}$; $C'_{1313} = -16\Phi^{11}_{27} + 8K_{33}l^2/l_3^3$; $C'_{3131} = -18\Phi^{33}_{21} + 16K_{11}l_3/l^2$. In particular, it can be shown from the relations (6) that the free energy associated with the molecules oscillations in directions OX and OY has the form

$$F = F(u_{i,x};u_{i,y}) + \frac{1}{2}C_{1313}[(u_{1,z})^2 + (u_{2,z})^2] + \frac{C'_{1313}l_3^3}{16l^2}[(u_{1,zz})^2 + (u_{2,zz})^2] \quad (7)$$

where $i = 1, 2$; $u_{i,z} = \partial u_i/\partial z$.

Note that we had to use the macroscopical theory for the calculation connected with the account of the orientational correlations in the frequencies (6). If, however, the consideration is fulfilled in terms of the standard approximations in accordance with which we may confine ourselves to the investigation of two cases only (1) there exists long range orientational order and 2) there is no orientational order at all) then the macroscopic characteristics—the Frank-constants—can be considered as microscopic parameters also. In terms of such approximations we can assume that the frequencies (6) depend on parameters characterizing the interaction of the first and second neighbors only.

Let us discuss the relations obtained. The interaction of particles is characterized by the force constants in the microscopic theory and—by the elastic moduli in the continual one. For systems possessing long range order there is a connection between these two approaches[13] by using of which in the long wave approximation it can be shown that C_{ii}, C_{1313}, C_{3131} are the elastic moduli of the continual theory; C_{11} characterizes the compression within the layer; C_{66} is the shear within the layer; C_{3131} is the bend of the layers; C_{1313} is the shear of the layers parallel to each other; C_{33} is the compression in the direction of the axis OZ. Let us investigate the influence of the anisotropy of the molecules shape. For spherical molecules the interaction will be isotropic. In this case the force constants are associated by the relation $3\Phi^{33}_{11}/2 \cdot l_3 = l_3\Phi^{11}_{17}/l^2$[15] which, according to (6) indicates

$$(C_{1313})_I = (C_{3131})_I \equiv C_{44} \quad (8)$$

Hence, for the system of anisotropic molecules we have

$$C_{1313} \neq C_{3131} \quad (9)$$

Note that the similar effect—the asymmetry of the elastic moduli $C_{\alpha\beta\mu j} \neq C_{\beta\alpha j\mu}$—is also observed in ferromagnetics and is connected with the invariance breaking due to the magnetization.[16] The primed coefficients in the frequencies (6) depend on the Frank-constants K_{11} and K_{33} and the force constants $\Phi^{\mu\mu}_{2p}$ of the second neighbors. For the case of spherical molecules the Frank-constants are equal to zero. The absolute value of the force constants of the second neighbors decreases quickly with the increase of the distance between these neighbors. The latter indicates that the "stretching" of the molecules along OZ leads to the increase of $\Phi_{21}^{\mu\mu}$ and the decrease of $\Phi_{27}^{\mu\mu}$.

From the analysis shown it is clear that the account of the relation (8) and the fixing $K_{11} = K_{33} = 0$ are necessary for the consideration of the extreme case of spherical molecules. In the extreme case of elongated molecules directed along the axis OZ—*i.e.* $2 \cdot l_3 >> \sqrt{3} \cdot l$ (this case corresponds to the model of the ordinary smectic phase Sm)—we have

$$(C'_{33})_{\mathrm{Sm}} = 0; \quad (C'_{1313})_{\mathrm{Sm}} = 8K_{33}l^2/l_3^3 \tag{10}$$

In the third extreme case corresponding to the model of the discotic mesophase D—when the structure is formed by the disclike molecules possessing large radius and the discs plane perpendicular to OZ, *i.e.* $2 \cdot l_3 << \sqrt{3} \cdot l$—we have

$$(C'_{66})_{\mathrm{D}} = 0; \quad (C'_{3131})_{\mathrm{D}} = 16K_{11}l_3/l^2. \tag{11}$$

It is evident that for real molecules the values of the coefficients considered are to be within the range limited by these three extreme cases.

Let us investigate the conditions at which the shear moduli C_{66}, C_{3131}, C_{1313} are converted into zero. For this purpose we divide the force constants of the first neighbors into two groups: the first one involving the longitudinal constants Φ_{11}^{11}, Φ_{17}^{33} (their designation being $\Phi^{\parallel}$) and the second one—the transversal constants Φ_{11}^{22}, Φ_{17}^{11}, Φ_{11}^{33}—$\Phi^{\perp}$. The intermolecular potential may be represented[17] in the form of the harmonic part and the correction accounting the anharmonism and noncentrality of the interaction. It is obvious from (5) that the force constants can be represented in the similar way

$$\Phi_{1p}^{\mu\mu} = (\Phi_{1p}^{\mu\mu})_{\mathrm{harm}} + (\Phi_{1p}^{\mu\mu})_{\mathrm{an}} \tag{12}$$

Taking into account[13] $(\Phi^{\perp})_{\mathrm{harm}} = 0$ it is not difficult to get[18]

$$\Phi^{\perp} = (\Phi^{\perp})_{\mathrm{an}}; \quad |\Phi^{\perp}| < \Phi^{\parallel} \approx (\Phi^{\parallel})_{\mathrm{harm}}. \tag{13}$$

In particular, it follows from this relation that the corresponding transversal constants can be of negative, positive or zero value. It can be noted that these results are in agreement with experimental data.[13] Putting (13) into (6) we get

$$\begin{gathered} C_{11} \sim 3\Phi_{11}^{11} + (\Phi_{11}^{22})_{\mathrm{an}}; \quad C_{66} \sim \Phi_{11}^{11} + 3(\Phi_{11}^{22})_{\mathrm{an}}; \\ C_{3131} \sim (\Phi_{11}^{33})_{\mathrm{an}}; \quad C_{33} \sim \Phi_{17}^{33}; \quad C_{1313} \sim (\Phi_{17}^{11})_{\mathrm{an}}. \end{gathered} \tag{14}$$

Hence, it appears that there is a principle possibility of the existence of states where the elastic moduli characterizing the compression are nonzero (C_{11}, $C_{33} \neq 0$) and the shear moduli C_{66}, C_{1313}, C_{3131} can become equal to zero independently from each other. (For example, if $C_{66} = 0$ then $C_{11} = \Phi_{11}^{11}/l \neq 0$ and additional conditions are to be introduced in this case for the estimation of the value of the shear moduli C_{1313} and C_{3131}). These states are characterized by the strong influence of the anharmonisms and the non-centrality of the intermolecular interaction. They can not be described at the account of the central forces in the harmonic approximation only.[13,19]

Let us analyze the shear stability of the structure and consider the stability relative to the shear of the layers parallel to each other at first. It is obvious that the system is stable if $C_{1313} \neq 0$. If $C_{1313} = 0$, but $C'_{1313} \neq 0$ then it follows from (6) and (7) that the restoring forces can be caused by the nonlinear deformations ($u_{i,zz} \neq 0$, $i = 1, 2$) only. The external shear stress varying with time must, apparently, lead to the occurrence of such deformations (*i.e.* of the restoring forces). It can be shown by similar considerations that just as in the long wave approximation the zero value of C_{1313}, C_{66}, C_{3131} indicates the existence of the statical shear instability in corresponding directions. In these cases, however, there exists the dynamical shear rigidity associated with the account of second order with respect to **K**. If, for example, the corresponding shear stresses change according to the harmonic law then the dynamical shear moduli are proportional to the frequency ω of the corresponding external stress

$$\begin{aligned} C^d_{1313} &= (l_3\sqrt{MC'_{1313}}/4 \cdot l^2)\omega; \quad C^d_{66} = (\sqrt{MC'_{66}}/4 \cdot l_3)\omega; \\ C^d_{3131} &= (\sqrt{MC'_{3131}}/4 \cdot l_3)\omega. \end{aligned} \tag{15}$$

3. PARTIAL TRANSLATIONAL DISORDER AND ELASTIC STABILITY

Let us write down a relation[11,12] for the correlations of the temperature fluctuations

$$\langle u_\alpha(0, \mathbf{L}^0)u_\alpha(\mathbf{L}, \mathbf{L}^0)\rangle = \sum_{\mathbf{K}j} \{(e^\alpha_j)^2 \exp(i\,\mathbf{K}\,\mathbf{L})cth[\omega_j(\mathbf{K})/2T]\}/2M\omega_j(\mathbf{K}). \tag{16}$$

Here $u_\alpha(\mathbf{L}, \mathbf{L}^0)$ is the α-component of the displacement from the equilibrium position $\mathbf{L} = L\mathbf{i}_1 + L_3\mathbf{i}_3$, $\alpha = 1, 2, 3$. The vector $\mathbf{L}^0 = L^0(\mathbf{i}_1 + \mathbf{i}_2) + L^0_3\mathbf{i}_3$ gives the sample sizes: L^0—within the layer plane and L^0_3—over the normal to the layer. According to, Reference 10, the finiteness of these sizes is accounted in the right side of (16) by means of the limitation by the value of the wave vector $K_i \geq K^0_i$ ($i = 1, 2, 3$), $K^0_1 = K^0_2 = 2\pi/L^0$; $K^0_3 = 2\pi/L^0_3$; e^α_j is the α-component of the polarization vector; T is the temperature.

By going from the summation to the integrating in (16), by calculating e^α_j in the high temperature limit $T >> \omega$ and by using the approximation $C_{11} >> C_{66}$, C_{1313} corresponding to the structures able to form liquid-crystalline phases we get

$$\left\{\frac{x_j(\mathbf{L}, \mathbf{L}^0)}{\langle u^2_j(\mathbf{L}^0)\rangle}\right\} = \frac{32T}{\pi^3}\int_{l/2L^0}^{\pi/2} d\theta_1 d\theta_2 \int_{l_3/2L^0_3}^{\pi/2} \frac{\left\{\dfrac{\mathrm{Sin}^2(\mathbf{K}\,\mathbf{L}/2)}{1/4}\right\}}{M\omega^2_j}\, d\theta_3. \tag{17}$$

Here j is "wl" and "il"; $x_{wl} = x = x_1 + x_2$; $x_{il} = x_3$; $\langle u_{wl}^2 \rangle = \langle u^2 \rangle = 2\langle u_1^2 \rangle = 2\langle u_2^2 \rangle$; $\langle u_{il}^2 \rangle = \langle u_3^2 \rangle$; $x_\alpha(\mathbf{L},\mathbf{L}^0) = \langle [u_\alpha(0,\mathbf{L}^0) - u_\alpha(\mathbf{L},\mathbf{L}^0)]^2 \rangle$ is the mean square of the relative displacements of molecules; $\omega_{wl} = \omega_2$; $\omega_{il} = \omega_3$. The relations (16) and (17) are obtained for crystals. Let us discuss a possibility of their applications to the description of partially ordered systems. In the second section it is shown that the elastic parameters (6) depend on the interaction with the first and second neighbours only. It is obvious that these microscopic parameters can be identified as the local elastic moduli for the infinite sample having short range order at least. It is also evident that the correlation couplings are basically maintained by the interaction with the local surroundings in the real structures (in which the interaction is not a too long range one). The relation (16) describes the dependence between the correlation functions and the local elastic moduli and hence they are applicable to the description of the infinite samples in which there exists order not lower than short range one. It should be, however, remembered that the local (microscopic) and the experimentally measured macroscopic shear moduli can be not coinciding in mesomorphic phases (the connection between them will be investigated below).

For the description of translational order we introduce two parameters.[8,10,19] The first one is

$$\begin{aligned}
&G[\mathbf{L}^0] = G_{wl}[\langle u^2(\mathbf{L}^0)\rangle] \cdot G_{il}[\langle u_3^2(\mathbf{L}^0)\rangle] \sim \langle \rho(\mathbf{r},\mathbf{L}^0)\rangle - \rho_0,\\
&G_{wl}[\langle u^2(\mathbf{L}^0)\rangle] = \exp[-b^2\langle u^2(\mathbf{L}^0)\rangle/2], \qquad (18)\\
&G_{il}[\langle u_3^2(\mathbf{L}^0)\rangle] = \exp[-b_3^2\langle u_3^2(\mathbf{L}^0)\rangle/2],
\end{aligned}$$

where $\mathbf{b} = \Sigma_{\alpha=1}^3 b_\alpha \mathbf{i}_\alpha$ is the reciprocal lattice vector; $b^2 = b_1^2 + b_2^2$; $\rho(\mathbf{r},\mathbf{L}^0)$ is the density in the point $\mathbf{r}$ of the sample of the size $\mathbf{L}^0$; ρ_0 is its mass/volume ratio.

The second one is

$$\begin{aligned}
&\theta(\mathbf{L}) = \theta[x_1(\mathbf{L})] \cdot \theta[x_2(\mathbf{L})] \cdot \theta[x_3(\mathbf{L})] \sim \langle \rho(\mathbf{L})\rho(0)\rangle - \rho_0^2,\\
&\theta[x_\alpha(\mathbf{L})] = \exp[-b_\alpha^2 x_\alpha(\mathbf{L})/2].
\end{aligned} \qquad (19)$$

Here and below the following designations are made: $\rho(\mathbf{L})$ is the density in the point $\mathbf{L}$ of the infinite sample; $\langle u_\alpha^2(L^0)\rangle = \lim_{L_3^0\to\infty} \langle u_\alpha^2(\mathbf{L}^0)\rangle$; $\langle u_\alpha^2(L_3^0)\rangle = \lim_{L^0\to\infty} \langle u_\alpha^2(\mathbf{L}^0)\rangle$; $x_\alpha(\mathbf{L}) = \lim_{L^0, L_3^0\to\infty} x(\mathbf{L},\mathbf{L}^0)$; $x_\alpha(L) = x_\alpha(\mathbf{L})$ where $L_3 = 0$; $x_\alpha(L_3) = x_\alpha(\mathbf{L})$ where $L = 0$.

The parameter $G_{wl}[\langle u^2(L^0)\rangle]$ characterizes translational order within the layer. If $\lim_{L^0\to\infty} G_{wl}[\langle u^2(L^0)\rangle] \neq 0$ then there is long range order within the layer of the infinite sample. Crystalline order may exist otherwise if the layer size is limited $L^0 < L_m^0$. Here L_m^0 is the distance where $G_{wl}[\langle u^2(L^0)\rangle]$ decreases by e times $(G_{wl}[\langle u^2(L_m^0)\rangle] = e^{-1})$. In terms of the clusteric model[20] the parameter $G_{wl}[\langle u^2(L^0)\rangle]$ is applicable to the description of partial order in the infinite sample also. It is supposed in this model that the system consists of non-intercorrelated clusters possessing crystalline order. The more the clusters sizes the more the order value.

These sizes can be apparently identified as the parameter L_m^0 within the layer. The functional dependence $G_{il}[\langle u_3^2(L_3^0)\rangle]$ allows to describe order in the direction to the normal to the layer in similar way.

The parameter $\theta(\mathbf{L})$ may be used for the description of "paracrystalline"[20] partial translational order of the infinite sample. The presence of the "distorted" lattice, i.e. quasi lattice with weakly changing intermolecular distances is supposed in terms of this model. $\theta[x_1(L)]$ and $\theta[x_3(L_3)]$ describe translational order within the layer and along the normal to the layer. $\theta[x_2(L)]$, $\theta[x(L_3)]$ and $\theta[x_3(L)]$ characterize the shear correlations within the layer, of the layers and of the layers bend, respectively. The more the decrease of these functions the more the weakness of the corresponding correlation couplings. A quantitative investigation can be fulfilled by introducing of the correlation radius. The correlation radius is the distance at which the correlation function considered decreases by e times. The corresponding correlation properties at this distance are similar to those of the crystal. Thus, for example, ordering is crystalline at the distance $L_m(\theta[x(L_m)] = e^{-1})$ within the layer.

It can be presumed[8] that order not lower than short range one exists in the system (we would remind that the formalism used in the paper can be valid in this case only) if at least one of the functions $G[\mathbf{L}^0]$ or $\theta(\mathbf{L})$ decreases not more rapidly than in the case of the exponential law. The analysis of (17) can show that so that $\theta[x(L)]$ and $\theta[x_3(L_3)]$ should satisfy this condition it should be enough that $\theta[x(l)] \neq 0$ and $\theta[x_3(l_3)] \neq 0$, respectively.

It should be specified that it is necessary to verify the formalism applicability in the case of short range order, *i.e.* to calculate the dimensions of the ordering region for the structure considered and to show that these dimensions are much greater than the corresponding intermolecular distances. If order is higher than short range one then, apparently, there is no necessity for such a verification.

Note that the parameters (18) and (19) describing though physically different correlation properties are, however, mathematically bound[4,5,8,9] by the asymptotic relations ($l << L = L^0$; $l_3 << L_3 = L_3^0$)

$$\begin{aligned} &x_1(L) \approx x_2(L) \approx 2\langle u^2(L^0)\rangle \quad \text{if} \quad \theta[x(l)] \neq 0, \\ &x_1(L_3) \approx x_2(L_3) \approx 2\langle u^2(L_3^0)\rangle, \\ &x_3(\mathbf{L}) \approx 4\langle u_3^2(\mathbf{L}^0)\rangle \quad \text{if} \quad \theta[x_3(l_3)] \neq 0. \end{aligned} \tag{20}$$

Now we integrate (17) for different values of the elastic parameters (6) using (20) and eliminating the states in which order is lower than short range one. The results we write into the Tables I and II.

Translational order within the layer and the elastic properties characterizing the shear within the layer and of the layers are considered in Table I. The index i in $P_{ij}(i = 1, 2, \ldots 5)$ is numbering different possible types of these properties (in accordance with Table II, j indicates the ordering type in the direction of the normal to the layer and of the elastic properties characterizing the layers bend). Let us consider ordering within the layer. The states P_{1j} and P_{2j} are characterized by the presence of long range order within the layer. There is no such order at $i > 2$. In states $P_{ij}(i > 2)$ we have $\theta[x(l)] \neq 0$ and thus, according to (20), both clusteric and paracrystalline ordering models are equally applicable in them. The simultaneous realization of the conditions $\theta[(l)] = 0$ and $G_{wl}[\langle u^2(L^0)\rangle] \neq 0$ at $L^0 < L^0_m$ in the states P^*_{4j} and P^*_{5j} indicates that partial order corresponds to the clusteric model in this case only.

We ought to discuss the influence of the terms nonlinear with respect to **K** for the characterization of partial order of the states having the shear instability ($C_{1313} = 0$ and/or $C_{66} = 0$). In the long wave approximation (*i.e.* at the account of the terms linear with respect to **K** only) it follows from the condition $C_{66} = 0$, according to (17), that there is actually no short range order in the layer. It is, however, known from the experiment[2,3] that there exists short range order within the layer of the smectic A ($C_{66} = C_{1313} = 0$). For the elimination of this and some other contradictions the account of the nonlinear terms is fulfilled in the paper. If the system possesses the statical shear instability (precisely speaking, C_{66} and/or C_{1313} is equal to zero) then the corresponding nonlinear terms provide the presence of the restoring forces with respect to the dynamical temperature fluctuations of the shear. These forces decrease the integral value (17) significantly, *i.e.* they increase the translational ordering degree. In particular (see Table I), the states characterized by the statical shear instability within the layer ($C_{66} = 0$) may possess local translational order in this direction ($\theta[x_1(l)] \neq 0$).

Now we investigate the elastic properties characterizing the shear of the layers parallel to each other. We modify the results of the second section of the paper by means of the account of partial disorder for the solution of this problem. Let the external shear stress be changed according to the harmonical law. If the radius of the interlayer shear correlations $L_3^{\perp}$ (we remind that $L_3^{\perp}$ is the distance at which $\theta[x(L_3)]$ decreases by e times) is much greater than the length of the excited wave, λ, then the elastic response will be similar to that of the system possessing long range order. It is evident that in this case the macroscopic shear modulus C^{μ}_{1313} coincides with the microscopic one which is investigated in the second section (*i.e.* $C^{\mu}_{1313} = C_{1313}$ if $C_{1313} \neq 0$, $C^{\mu}_{1313} = C^{d}_{1313} \sim \omega$ if $C_{1313} = 0$). The elastic response is, apparently, absent (*i.e.* $C^{\mu}_{1313} = 0$) in the case $\lambda >> L_3^{\perp}$. It is not difficult to understand that the relations mentioned can be re-formulated in following way. If the frequency of the external shear stress is small enough, $\omega << \omega_0 = 2\pi/\tau$ ($\tau = L_3^{\perp}K_3/\omega$ is the time for the transversal wave to pass along the distance which is equal to the correlation radius, *i.e.* the relaxation time) then there is no elastic response (*i.e.* $C^{\mu}_{1313} = 0$). For the opposite case, $\omega >> \omega_0$, the response is the same as in the system possessing long range order.

The possible types of the frequency dependence for the experimentally measured macroscopic interlayer shear modulus C^{μ}_{1313} are shown in the Figure 1. $\omega_0 = 0$ and the micro- and macroscopic shear moduli coincide for any frequency at $i \leq 3$. If $i = 4,5$ then the value of C^{μ}_{1313} is essentially influenced by partial translational disorder and the shear modulus coincides with the microscopic one at the sufficiently high frequencies ($\omega >> \omega_0 \neq 0$) only. The relaxation time does not depend on the external influence frequency and $\omega_0 = 2\pi/\tau = 2\pi\sqrt{l^2 l_3 C_{1313}}/\sqrt{M}\, L_3^{\perp}$ at $i = 4$. If $i = 5$ then $\omega_0 = \pi^2 l_3^2 \sqrt{C'_{1313}}/\sqrt{M}(L_3^{\perp})^2$ and the

TABLE I

Order within the layer $G_{wl}[\langle u^2(L^0)\rangle]$, shear correlations within the layer $\theta[x_2(L)]$ and between the layers $\theta[x_1(L_3) + x_2(L_3)]$

C'_{66}	C_{1313}	C'_{1313}	$G_{wl}[4\langle u^2(L^0)\rangle]$	$\theta[x_1(l)]$	$C^{\mu}_{66}(\omega)$ Fig. 1	order	$\theta[x_1(L_3) + x_2(L_3)]$
–	$\neq 0$	–	$f_1 \exp(\alpha_1 l/L^0)$	$\neq 0$	(*a*)	long-range	$\mu_1(L_3/l_3)^{\beta_1 l_3/L_3}$
–	$=0$	$\neq 0$	$f_2 \exp(\alpha_2\sqrt{l/L^0})$	$\neq 0$	(*a*)	long-range	$\mu_2(L_3/l_3)^{\beta_2 l_3/L_3}$
–	$=0$	$=0$	$f_3(L^0/l)^{-\alpha_3}$	$\neq 0$	(*c*)	quasi-long-range (two-dimensional)	0
$\neq 0$	$\neq 0$	–	$f_4(L^0/l)^{-\alpha_4}$	$\neq 0$	(*d*)	quasi-long-range	$\mu_4(L_3/l_3)^{-\beta_4}$
$=0$	$\neq 0$	–	$f_4^*(L^0/l)^{-\alpha_4^*\ln(L^0/l)}$	$=0$	(*e*)	intermediate (clusteric)	$\mu_4^*(L_3/l_3)^{-\beta_4^*\ln(L_3/l_3)}$
$\neq 0$	$=0$	$\neq 0$	$f_5 \exp(-\alpha_5 L^0/l)$	$\neq 0$	(*d*)	short-range	$\mu_5\exp(-\beta_5 L_3/l_3)$
$=0$	$=0$	$\neq 0$	$f_5^* \exp(-\alpha_5^* L^0/l)$	$=0$	(*e*)	short-range (clusteric)	$\mu_5^*(L_3/l_3)^{-\beta_5^* L_3/l_3}$

$$\text{at } L = L^0 \gg l,\ L_3 = L_3^0 \gg l_3 \qquad \theta[x_1(L)] \approx \theta[x_2(L)] \approx \begin{cases} 0 & \text{at} \quad \theta[x_1(l)] = 0, \\ G_{wl}[2\langle u^2(L^0)\rangle] & \text{at} \quad \theta[x_1(l)] \neq 0, \end{cases}$$

$$\theta[x_1(L_3)] \approx \theta[x_2(L_3)] \approx G_{wl}[2\langle u^2(L_3^0)\rangle],$$

$$\langle u^2(L^0)\rangle \sim T \int_{l/2L^0}^{\pi/2} d\theta_1 d\theta_2 \int_{l_3/2L_3^0}^{\pi/2} \frac{d\theta_3}{4l_3 C_{66}\,\mathrm{Sin}^2\theta + C'_{66}\theta^4 + 2l_3 C_{11}\theta_1^2\theta_2^2 + \dfrac{4l^2}{l_3} C_{1313}\,\mathrm{Sin}^2\theta_3 + C'_{1313}\theta_3^4}.$$

Appendix I (to Table I)

Correlation of the order parameters with the local elastic moduli

$f_1 = \exp(-2\pi^2 T/l^3\sqrt{C_{66}C_{1313}})$,

$f_2 = \exp[-4\pi T/l^2(l_3C_{66})^{3/4}(C'_{1313})^{1/4}]$,

$f_3 = \pi - 8T/l^2l_3C_{66}$

$f_4 = 1$

$f_4^* = \sqrt{\pi}$,

$f_5 = 1$

$f_5^* = 1$,

$\mu_1 = \exp[-2\pi T\ \ln(C_{66}l_3^2/C_{1313}l^2)/l^2l_3C_{66}]$,

$\mu_2 = \exp[-(2\pi T\ \ln(4 \cdot l_3C_{66}/C'_{1313})/l^2l_3C_{66}]$,

$\mu_4 = 1$,

$\mu_4^* = 1$,

$\mu_5 = 1$,

$\mu_5^* = 1$,

$\alpha_1 = 2\pi T/l^3\sqrt{C_{66}C_{1313}}$,

$\alpha_2 = 4\sqrt{\pi}T/l^2(l_3C_{66})^{3/4}(C'_{1313})^{1/4}$,

$\alpha_3 = 8T/l^2l_3C_{66}$,

$\alpha_4 = 4\pi\sqrt{l_3}\ T/l^3\sqrt{C'_{66}C_{1313}}$,

$\alpha_4^* = 8T/l^3\sqrt{C_{11}C_{1313}}$,

$\alpha_5 = 32T/l^2(C'_{1313})^{1/4}(C'_{66})^{3/4}$,

$\alpha_5^* = 60T/l^2l_3^{3/4}(C'_{1313})^{1/4}(C_{11})^{3/4}$,

$\beta_1 = 4T/l^2l_3C_{66}$,

$\beta_2 = 8T/l^2l_3C_{66}$,

$\beta_4 = 4\pi\sqrt{l_3}\ T/l^3\sqrt{C'_{66}C_{1313}}$,

$\beta_4^* = 8T/l^3\sqrt{C_{11}C_{1313}}$,

$\beta_5 = 16\pi T/l^2\sqrt{C'_{66}C'_{1313}}$,

$\beta_5^* = 80T/l^2\sqrt{l_3C_{11}C'_{1313}}$.

relaxation time $\tau = [2(M)^{1/4}L_3^{\frac{1}{2}}/l(C'_{1313})^{1/4}]\omega^{-1/2}$ is a monotonously decreasing frequency function.

We can similarly investigate the macroscopic shear modulus within the layer C_{66}^{μ} and (using Table II) order in the direction of the normal to the layer and the shear modulus C_{3131}^{μ} as well.

We had considered the correlation properties of the system in this section. By analyzing (17) it can be noted that there are following connections between them: firstly, there is a one-to-one correspondence between the properties described in Table I—order within the layer, the correlations characterizing the shear within the layer and of the layers and secondly, the same dependence between order in the direction of the normal to the layer and the correlations of the layers bend considered in Table II. However, the three local shear moduli can be equal to zero for molecules of arbitrary shape independently from each other (see the second section). Thus, there is no connection between the correlation properties described in different Tables for the states where $C_{33} \neq 0$. For example, the change of the order type within the layer is sure to lead to the qualitative change of the shear correlations within the layer and between the layers but it can also not change order types over the normal to the layer and the correlations of the layers bend. Such a differentiation of the correlation properties allow to distinguish $7 \cdot 3 = 21$ (7—Table I; 3—Table II) qualitatively different states. If $C_{33} = 0$ then, according to (14), $C_{1313} = 0$. Therefore we can consider another 8 states where $C_{33} = C_{1313} = 0$. Two from these 29 states are characterized by short range order in all of the

TABLE II

Order over the normal to the layer $G_{wl}[\langle u_3^2(L_3^0)\rangle]$ and the shear correlations associated with the layers bend $\theta[x_3(L)]$

13	C'_{3131}	C_{33}	$G_{il}[4\langle u_3^2(L_3^0)\rangle]$	order	$\theta[x_3(L)]$
0	–	$\neq 0$	$f_{31}(L_3^0/l_3)^{\alpha_{31}l_3/L_3^0}$	long-range	$\mu_{31}\exp(\beta_{31}l/L)$
0	–	$=0$	$f'_{31}(L_3^0/l_3)^{\alpha'_{31}l_3/L_3^0}$	long-range	$\mu'_{31}\exp(\beta'_{31}\sqrt{l/L})$
0	$\neq 0$	$\neq 0$	$f_{32}(L_3^0/l_3)^{-\alpha_{32}}$	quasi-long-range	$\mu_{32}(L/l)^{-\beta_{32}}$
0	$=0$	$\neq 0$	$f_{33}\exp(-\alpha_{33}L_3^0/l_3)$	short-range (one dimensional)	0
0	$\neq 0$	$=0$	$f'_{33}\exp(-\alpha'_{33}L_3^0/l_3)$	short-range	$\mu'_{33}\exp(-\beta_{33}L/l)$

$$\theta[x_3(\mathbf{L})] \approx G_{il}[4\langle u_3^2(\mathbf{L}^0)\rangle] \quad \text{at} \quad L = L^0 >> l,\ L_3 = L_3^0 >> l_3$$

$$\langle u_3^2(\mathbf{L}^0)\rangle \sim T\int_{l/2L^0}^{\pi/2} d\theta_1 d\theta_2 \int_{l_3/2L_3^0}^{\pi/2} \frac{d\theta_3}{4l_3C_{3131}\,\mathrm{Sin}^2\theta + C'_{3131}\theta^4 + \dfrac{4l^2}{l_3}C_{33}\,\mathrm{Sin}^2\theta_3 + C'_{33}\theta_3^4}.$$

Appendix II (to Table II)

Correlation of the order parameters with the local elastic moduli

$$f_{31} = \exp\left[-\frac{16\mathrm{T}}{l^2 l_3 \mathrm{C}_{3131}} \ln \frac{2el_3^2\mathrm{C}_{3131}}{l^2\mathrm{C}_{33}}\right], \qquad \alpha_{31} = 8\mathrm{T}/l^2 l_3 \mathrm{C}_{3131},$$

$$f'_{31} = \exp\left[-\frac{16\mathrm{T}}{l^2 l_3 \mathrm{C}_{3131}} \ln \frac{2el_3\mathrm{C}_{3131}}{\mathrm{C}'_{33}}\right], \qquad \alpha'_{31} = 16\mathrm{T}/l^2 l_3 \mathrm{C}_{3131},$$

$$f_{32} = 1, \qquad \alpha_{32} = 16\pi\mathrm{T}\sqrt{l_3}/l^3\sqrt{\mathrm{C}'_{3131}\mathrm{C}_{33}},$$

$$f_{33} = 1, \qquad \alpha_{33} = 4\pi\mathrm{T}l_3/l^4\mathrm{C}_{33},$$

$$f'_{33} = 1, \qquad \alpha'_{33} = 64\mathrm{T}/l^2\sqrt{\mathrm{C}'_{3131}\mathrm{C}'_{33}},$$

$$\mu_{31} = \exp\left[-\frac{\pi^2\mathrm{T}}{l^3\sqrt{\mathrm{C}_{3131}\mathrm{C}_{33}}}\right], \quad \beta_{31} = \pi^2\mathrm{T}/l^3\sqrt{\mathrm{C}_{3131}\mathrm{C}_{33}},$$

$$\mu'_{31} = \exp\left[-\frac{2\pi^2\mathrm{T}}{l^2(l_3)^{3/4}(\mathrm{C}'_{33})^{1/4}(\mathrm{C}_{3131})^{3/4}}\right],$$

$$\beta'_{31} = 2\pi^2\mathrm{T}/l^2(l_3)^{3/4}(\mathrm{C}'_{33})^{1/4}(\mathrm{C}_{3131})^{3/4},$$

$$\mu_{32} = 1, \qquad \beta_{32} = 4\pi\sqrt{l_3}\mathrm{T}/l^3\sqrt{\mathrm{C}'_{3131}\mathrm{C}_{33}},$$

$$\mu'_{33} = 1, \qquad \beta'_{33} = 4\pi^2\mathrm{T}/l^2(\mathrm{C}'_{33})^{1/4}(\mathrm{C}'_{3131})^{3/4}.$$

directions and are left beyond of our investigation. Three states cannot be described by the extreme cases of rodlike, disc-like and spherical molecules. Thus, 24 states (a crystalline one and 23—smectic ones) differing qualitatively from each other in translational order and elastic properties are considered in the paper (see Table III).

It is necessary to study the frequency dependence of the elastic moduli for the experimental identification of the states investigated. The x-ray analysis of translational order is desirable for the verification of the classification. The investigation of the frequency dependence of the elastic moduli is necessary inasmuch as just such an experimental technique analyzed in accordance to the results obtained in the paper allows to determine the main parameters of the theory—the local elastic moduli. Even the combined investigation of the statical elastic properties and translational order is insufficient for the experimental identification (for example, the two techniques do not allow to distinguish qualitatively between the states P_{3j} and P_{4j}).

Note that the standard classification[1,9,14] allows to distinguish between only two smectic states differing qualitatively by translational order and elastic properties. The first one corresponds to the model "liquid layer"[14] the second one—"liquid column".[9] The extension of the classification is connected in the paper with the consideration of the "intermediate" types of translational ordering in the fixed direction and the specification of the interconnections between different correlation properties.

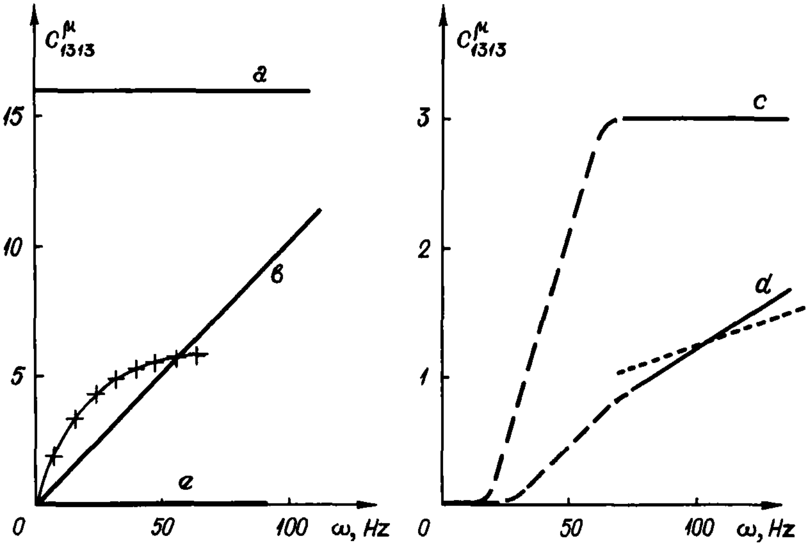

FIGURE 1 Frequency dependence of the interlayer macroscopic shear modulus C^{μ}_{1313}

a) $C^{\mu}_{1313} = C_{1313} = \text{const}$ for the phase P_{1j} (in particular, P_{11}, *i.e.* for a crystal)

b) $C^{\mu}_{1313} = C^{d}_{1313} \sim \omega$ for P_{2j} (in particular, P_{21}, *i.e.* SmB)

c) $C^{\mu}_{1313} = \begin{cases} 0 \text{ at } \omega \ll \omega_0 \\ C_{1313} = \text{constant at } \omega \gg \omega_0 \end{cases}$ for P_{4j} (in particular, P_{41}, *i.e.* SmF_2)

d) $C^{\mu}_{1313} = \begin{cases} 0 \text{ at } \omega \ll \omega_0 \\ C^{d}_{1313} \sim \omega \text{ at } \omega \gg \omega_0 \end{cases}$ for P_{5j} (in particular, P_{52}, *i.e.* SmA_1)

e) $C^{\mu}_{1313} = 0$ at any ω for P_{3j} (in particular, P_{31}, *i.e.* SmF_1)

+ + + + + —experimental curve $C_{1313}(\omega)/C_{1313}(\omega^*)$. ($\omega^* = 0, 1$ Hz) for the smectic B phase of the compound 408; — — — — — —experimental curve of the shear modulus G′ of the non-oriented sample cholesterole-miristate in the smectic A phase.

4. DISCUSSION

24 states differing qualitatively by the elastic properties and translational order are considered in the paper. In accordance with the known thermodynamical definitions[8] we shall demonstrate that different states may be considered different phases. In the high temperature limit $T \gg \omega$ the system entropy has the form[11]

$$S = \sum_{\mathbf{K},j} \ln[T/\omega_j(\mathbf{K})]. \tag{21}$$

Different states are characterized by different values of the local elastic moduli. The jumping discontinuity of these moduli (or of their temperature derivatives) leads to the similar alteration of the frequencies (6) and, hence, of the entropy (21). It is not difficult to notice (Tables I and II) that the entropy increase cor-

TABLE III

Classification of mesomorphic phases according to translational order and elastic properties

P_{1j}	P_{2j}	P_{3j}	P_{4j}	P^*_{4j} (clusteric)	P_{5j}	(cl
Cr (S, I, D)	SmB (S, D)	SmF_1 (S, D)	SmF_2 (S, I)	SmF_3 (S, I, D)	? (S)	(
+	? (D)	? (D)	+	+	+	
? (S, D)	? (S, I, D)	? (S, I, D)	? (S)	? (S, D)	SmA_1 (S, I)	S (S
D_1 (S, D)	D_2 (S, I, D)	? (S, I, D)	? (S)	? (S, D)	+	
+	D_3 (I, D)	? (I, D)	+	+	+	

ystalline, Sm—smectic, D—columnal, ?—the new phases, + —the phases not considered in the paper. In parentheses—the inde
hape of molecules able to form a given state (S)—rodlike, (I)—spherical, (D)—disclike molecules.

responds to the ordering decrease at such a transition. In spite of that not all of the 24 states differ by "global" symmetry the transition between them leads always to the jumping discontinuity of one of the free energy derivatives. Hence, such a transition can be named a phase transition and the different states can be considered the different partially ordered (*i.e.* smectic) phases.

We fulfill the classification (Table III) of the SLC phases in connection with translational order and elastic properties (we shall not repeat the known results[1] allowing to specify this classification by means of the account of orientational order). On this basis we shall apply the results obtained for the description of the known liquid crystals and discuss a possibility of the existence and the experimental identification of the new smectic phases.

It is evident that P_{11} is a crystalline phase. The other 23 phases are smectic phases.

1. P_{21} is an "intermediate" phase. Similar to a crystal it possesses long range order in all directions but is characterized by the instability relatively the slow shear of layers parallel to each other (*i.e.* similar to a liquid crystal this phase is a fluid one). In accordance with the experimental results[21] P_{21} can be identified as the smectic B. It is essential that these experimental results cannot be described in terms of the known theoretical concepts[1,14] since in the long wave approximation long range order within the layer is destroyed at $C_{1313} = 0$ due to the Landau-Peierls divergence.[8] The contradiction indicated can be interpreted by means of the account of second order with respect to the wave vector **K**. It is shown (see Table I) that though order within the layer differs from the ordinary crystalline (P_{11}) one "by the great influence of dimensional effects"[10] ($G_{wl} \sim \exp(\alpha_1 l/L^0)$—for the crystal, $G_{wl} \sim \exp(\alpha_2 \sqrt{l}/\sqrt{L^0})$—for the smectic B) at $C_{1313} = 0$, but $C'_{1313} \neq 0$ but it still is a real long range one. The validity of the theory presented may be also evidenced indirectly by the qualitative correspondence (see Figure 1) of its results for the dynamical shear modulus $C^{\mu}_{1313} \sim \omega$ to the experimental results.[21] For the quantitative estimation of the value C'_{1313} we write down from (6): $C^{d}_{1313} = C'_{1313} l_3^3 K_3^2/16 l^2$. Using the experimental results,[22] $C^{\mu}_{1313} \approx 7 \cdot 10^8$ dyne/cm^2, at $2\pi/K_3 \approx 5145$ Å and putting typical values $l = 5$ Å, $l_3 \approx 30$ Å we get $C'_{1313} \approx 8 \cdot 10^4$ dyne/cm. Hence, it follows according to (6) that $K_{33} \approx 9,6 \cdot 10^{-2}$ dyne. Such a value for K_{33} in the smectic phase is by 4–5 orders higher than the typical values,[23] $K_{33} \sim 10^{-6}$ dyne, in the nematic phase.

Thus, the smectic B possesses long range order in all directions but differs from the ordinary crystal by the great influence of dimensional effects within the layer and by the instability relatively the slow shear of the layers parallel to each other.

2. Phases P_{31}, P_{41} and P^*_{41} are characterized by quasi-long-range order (*i.e.* by intermediate between short and long range ones) within the layers, by the zero value of the statical shear moduli within the layer and between the layers ($C^{\mu}_{66} = C^{\mu}_{1313} = 0$ at $\omega = 0$). In terms of the known notions[6,7] these three phases are not distinctive from each other and identified as the smectic F. In accordance with the Landau-Peierls theorem[8] it can be accepted[6] that long range order is destroyed because of the absence of the interlayer shear correlations in this phase. This interpretation is applicable for the description of P_{31} in the present paper.

The existence of two other phases, P_{41} and P_{41}^*, is bound with the influence of the nonlinear effects (see Tables I and III).

3. P_{52} and P_{52}^* are characterized by short range order within the layer and by quasi-long-range one in the direction to the normal to the layers. In accordance with these properties they can be identified as the smectic A phases. Order along the normal to the layer is completely enough analyzed in the literature.[4,5,14] In addition to the results already known we describe short range order within the layer as well. For this purpose we estimate the value of the correlation radius $L_m = l^3(C'_{1313})^{1/4}(C'_{66})^{3/4}/32T$ (see Table I and Appendix I) of the smectic A (to be precise: P_{52}) at the room temperature $T \approx 4 \cdot 10^{-14}$ erg. It is not difficult to show from the expression for the force constants (5) of the Morse potential[18] that $|\Phi_{21}^{11}| \approx |\Phi_{11}^{11}| \cdot \exp[-g(\sqrt{3} - 1)]$ (g is the parameter of the long range interaction; g decreases at the interaction increase). Whence it follows, according to (6), that $C'_{66} \approx 8 \cdot l_3 C_{11} \exp[-g(\sqrt{3} - 1)]$. Putting $C_{11} = 4 \cdot 10^{10}$ dyne/cm^2, [22] and using the value $C'_{1313} \approx 8 \cdot 10^4$ dyne/cm calculated above we get

$$L_m/l \approx 179 \exp(-0{,}55g) \tag{22}$$

It is clear from this relation that the correlation radius within the layer increases at the increase of the long range interaction. Similar results can be obtained for some other smectic phases by using Tables I and II and Appendixes I and II. We get $L_m/l \approx 7$ for the values $g = 6$ at which the Morse potential corresponds to the Lennard-Jones potential. This result is in good agreement with the experimental data[2] according to which ($L_m/l \approx 5$) and satisfy the main approximation in our paper, $L_m/l >> 1$, as well.

Note that all the shear moduli of this phase have the same form of the frequency dependence. It is evident that the shear modulus of the non-oriented sample must have a dependence of the same type. This result describes (see Figure 1) experimental data[23] qualitatively.

Thus, the existence of short range order within the smectic A layer is provided by the high frequency (described by means of the account of the terms nonlinear with respect to the wave vector) intermolecular correlations. The nonlinear effects allow to interpret the shear rigidity of this phase at the sufficiently high frequencies of the external effects also.

4. $P_{13}(D_1)$ is characterized by short range order along the axis OZ and by long range order in the directions parallel to the plane XOY.

5. $P_{23}(D_2)$ differs from P_{13} by ordering in the plane XOY. Ordering of P_{13} is similar to ordinary crystalline one in these directions and P_{23} possesses the same one as that of the smectic B (*i.e.* P_{23} is characterized by the greater influence of the dimensional effects). P_{13} and P_{23} are experimentally found[24] in columnal systems (the columns are parallel to OZ) formed by disc-like molecules. The theoretical investigation[9,10] fulfilled in terms of the model "liquid column" describes P_{23} quite well but does not admit a possibility of the existence of the phase P_{13}. The interpretation of ordering of P_{13} is fulfilled in the present paper by means of the verification of the limitations connecting the elastic properties and ordering.

In addition to the results concerning the known smectic types new SLC phases are predicted (see Table III) in the paper. These phases occupy the positions intermediate between the known ones due to their elastic properties and translational order. The new phases do not differ from the known ones in terms of the standard notions[1] based on the idea of the "global" symmetry. In correspondence to the known thermodynamic definition,[2] however, the separation of the new phases is necessary since the transition between all the states considered is followed by the discontinuity of one of the free energy derivatives. We remind that the new phases can be experimentally identified by means of the x-ray investigation of translational order and by measuring of the frequency dependence of the shear moduli (Tables I and II).

Let us discuss a possibility of the existence of translational order typical for smectic phases in the systems formed by spherical molecules or atoms. It is evident from the conditions $C_{1313} = C_{44} = (\Phi^{11}_{17} + 4\Phi^{11}_{27})l_3/l^2$ (see (6), (8)) and $\Phi^{11}_{27} < 0$ that the conversion of C_{44} into zero is followed by the decrease of Φ^{11}_{17} and the increase of the absolute value $|\Phi^{11}_{27}|$. $|\Phi^{11}_{27}| \sim |\Phi^{11}_{17}| \cdot \exp(-g)$ in th crystalline phase and thus, it follows from (6) that $C'_{1313}(P_{52})$ and $C_{44}(P_{11})$ satisfy the estimation $C'_{1313}(P_{52})l_3/16\, l^2C_{44}(P_{11}) > \exp(-g)$. Substituting this estimation into the expression for L_m considered above for the smectic A we get

$$L_m/l \geq \mu \exp(-0,8g) \tag{23}$$

where $\mu \approx 0,3\sqrt{l^5 l_3}\,(C_{44})^{1/4}(C_{11})^{3/4}/T$. It follows from this relation that $L_m/l \gtrsim 7$ at $g < g_0(L_m/l \sim 7$ corresponds to the experimental data mentioned above and to their theoretical interpretation for Sm A). In particular, we have $g_0 \approx 5,5$ and $\mu \approx 573$ for Ru and $g_0 \approx 4,3$ and $\mu \approx 222$ for Zn.[13] Such g_0 correspond to the range of the reasonable values ($2 < g < 10$) of this parameter. By means of analogous considerations it may be shown that the correlations over the normal to the layers are not weaker than those in the smectic A at $g < g_0$.

Thus, in the orientationally non-correlated systems the phases may exist in which translational order and elastic properties are similar to those of the smectics.

5. CONCLUSION

Twenty-three smectic phases differing by translational order, elastic properties and transforming into each other by means of phase transitions are considered in the paper in terms of the microscopic approach on the basis of the account of the second order with respect to the wave vector **K**. The known smectic phases are studied. The existence of new SLC's is proved in connection with the investigation allowing a) to characterize intermediate (between the long and short range ones) translational order in the fixed direction, and b) to verify the limitations connecting the elastic properties and ordering. A technique of the experimental identification of the new phases is described.

Let us formulate the most interesting results:

1. It is shown that the anharmonism and non-centrality of the intermolecular interaction are to be accounted in the microscopic description of the elastic and correlation properties of the phases possessing the statical shear instability.

2. The existence of the dynamical shear rigidity at the high frequencies ($\omega >> \omega_0$) and its absence at the low ones ($\omega << \omega_0$) is connected with the availability of local translational order. The increase of the shear moduli observed in some phases (for example, in smectics A and B) at the frequency increase is interpreted by means of the account of the second order with respect to the wave vector.

3. It is established that translational order and elastic properties are similarly influenced by the orientational correlations of the long axes of molecules and by their translational transversal correlations with the second neighbours. It is proved on this basis that the phases not ordered orientationally but possessing translational order and elastic properties typical for smctic phases can exist at the sufficiently high long range intermolecular interaction.

4. It is shown that the smectic B possesses long range order in all directions but differs from the ordinary crystal by the great influence of dimensional effects within the layer and by the instability with respect to the slow shear of the layers parallel to each other (*i.e.* $C^{\mu}_{1313} = 0$ at $\omega = 0$).

5. It is found that local translational order within the layer of the smectic A and the dynamical rigidity of this phase at the sufficiently high frequencies are maintained by the restoring forces connected to the terms nonlinear with respect to $\mathbf{K}$.

6. It is demonstrated that the phase transitions (*i.e.* the discontinuity of one of the free energy derivatives) can be not followed by the change of the "global" symmetry of the system.

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