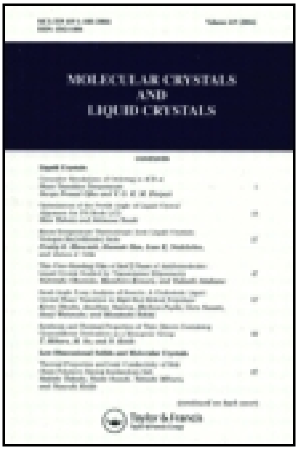

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006.

To cite this article: V. P. Romanov & S. V. Ul'yanov (1996): Ultrasound in the Isotropic Phase of Cholesteric Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 281:1, 187-204

To link to this article: http://dx.doi.org/10.1080/10587259608042244

Mol. Cryst. Liq. Cryst., 1996, Vol. 281, pp. 187–204
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Ultrasound in the Isotropic Phase of Cholesteric Liquid Crystals

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(Received January 23, 1994; Revised February 16, 1995; in revised form August 1, 1995)

The acoustical properties of cholesteric liquid crystals in the isotropic phase including the vicinity of the phase transition point to the ordered phase are investigated. An interaction of fluctuating field of the tensor order parameter with the sound wave is considered. In Gaussian approximation the contribution of fluctuating modes to the sound velocity dispersion and attenuation is calculated. The obtained formulae are compared with ones for nematics in isotropic phase. It was found that the difference between these results rises in the vicinity of the phase transition point. This difference is connected, on the one hand, with the specific fluctuating spectrum and on the other hand with the closing of the instability temperatures of some fluctuating modes to the phase transition temperature T_c. The results are illustrated by the numerical calculations.

Keywords: Ultrasound, cholesteric liquid crystals, tensor order parameter, isotropic phase.

1. INTRODUCTION

The ultrasonic velocity and the attenuation of sound in the isotropic phase of nematic liquid crystals are studied in detail both theoretically and experimentally.[1–3] Theoretical descriptions of these phenomena are based on the calculation of the sound wave interaction with the fluctuation field of the tensor order parameter. A numerical comparison of the theory with the experiment shows that the experimental data for the frequency and temperature dependencies of the ultrasonic velocity and attenuation are in close agreement with the theoretical predictions.[3] It is important to note that the theoretical formulae do not contain any fitting parameters. It means that acoustical methods are essential for obtaining of liquid crystal parameters which are difficult to determine by other experimental methods.

A similar problem exists for the isotropic phase of cholesteric liquid crystals since the traditional method such as light scattering is not effective in this phase. The cholesteric isotropic phase is of particular interest owing to existence of the intermediate blue phase which is currently studied very intensively. Here the acoustical methods are important for a study of the vicinity of the isotropic-ordered phase transition point.

One of the characteristic feature of cholesteric isotropic phase is the unusual form of the thermal fluctuations spectrum of the tensor order parameter. Fluctuations of several modes are maximal for zero wave number whereas the fluctuations of some other modes are maximal for the wave number equals to the cholesteric pitch. In contrast to nematics these modes have three different temperatures of instability which are similar to the temperature T^* for nematics.

Recently the ultrasonic absorption measurements in the ordered and isotropic phases of cholestryl valerate were completed by Muralidhar *et al.*[4] Here it was shown that frequency and temperature dependencies for the sound attenuation are qualitatively similar to the ones in the vicinity of the isotropic- nematic phase transition point. The theoretical calculations presented in[4] are based on the simplified form of the fluctuation spectrum of the tensor order parameter. This approach is similar to the Imura and Okano theory[1] but with the strong dependence on the cut-off parameter.

In this work we study the critical behavior of the ultrasonic velocity and attenuation arising due to the sound waves interaction with all fluctuating modes of the order parameter in the isotropic phase of cholesterics. The results are illustrated by the numerical calculations. The sound velocity dispersion and the attenuation coefficient are found to be different from those for the isotropic phase of nematics in the vicinity of the phase transition point.

2. FLUCTUATIONS OF THE ORDER PARAMETER NEAR T_c

A detailed description of the behavior of the cholesterics in the region of the phase transition requires the approximation of the free energy by the power-series expansion over the tensor order parameter $\hat{Q}$. In the Gaussian approximation it can be written as[5]

$$F\{\hat{Q}\} = F_0 + \frac{1}{2}\int d\vec{r}\left[a\,Sp\hat{Q}^2 + b\frac{\partial Q_{\gamma\delta}(\vec{r})}{\partial r_\alpha}\cdot\frac{\partial Q_{\gamma\delta}(\vec{r})}{\partial r_\alpha} + c\frac{\partial Q_{\alpha\gamma}(\vec{r})}{\partial r_\alpha}\cdot\frac{\partial Q_{\beta\gamma}(\vec{r})}{\partial r_\beta}\right.$$
$$\left. + 2de_{\alpha\beta\gamma}Q_{\alpha\delta}(\vec{r})\frac{\partial Q_{\beta\delta}(\vec{r})}{\partial r_\gamma}\right], \qquad (1)$$

where $\hat{Q}$ is the symmetric tensor with $Sp\hat{Q} = 0$. The coefficient a is assumed to vary linearly with temperature

$$a = a_0(T - T^*).$$

The other parameters a_0, b, c, d are temperature independent, $e_{\alpha\beta\gamma}$ is the unit antisymmetric tensor of the third rank. Coefficient d is pseudoscalar. It is related to the value of the cholesteric pitch p. It follows from a comparison of the free energy expansion (1) with the formula for the distortion energy of the ordered cholesteric[6]

$$F = F_0 + \frac{1}{2}\{K_{11}(\mathrm{div}\vec{n})^2 + K_{22}(\vec{n}\cdot\mathrm{rot}\vec{n} + q_0)^2 + K_{33}[\vec{n}\times\mathrm{rot}\vec{n}]^2\}, \qquad (2)$$

where K_{11}, K_{22}, K_{33} are the elastic Frank constants, $\mathbf{n}$ is the director, $|q_0| = 2\pi/p$.

Supposing that a variation of the order parameter results from a variation of the director $\mathbf{n}$ only, we may write $Q_{\alpha\beta} = Q(n_\alpha n_\beta - \delta_{\alpha\beta}/3)$, where Q is constant. Substituting this expression into Equation (1) and comparing with Equation (2) we get the following expression

$$p = \left| \frac{2\pi K_{22}}{dQ^2} \right|,$$

or

$$p = \left| \frac{4\pi b}{d} \right|,$$

where we used the relation between the Frank modulus and the coefficients in the expansion (1) which is valid in the Gaussian approximation over the order parameter.[7]

It should be noted that the sign of the coefficient d depends on a type of the cholesteric spiral (right or left). The case $d = 0$ relates to the nematic liquid crystals. The final results are independent of a sign of the coefficient d. We consider $d > 0$. Further we study an isotropic phase of the cholesteric liquid crystal where a mean value of the order parameter equals zero $\langle Q_{\alpha\beta} \rangle = 0$. In this case Equation (1) may be used for calculation of the order parameter fluctuations in the Gaussian approximation.[8]

Using the Fourier transformation

$$\hat{Q}_{\vec{q}} = \frac{1}{\sqrt{V}} \int d\vec{r}\, \hat{Q}(\vec{r}) e^{-i\vec{q}\vec{r}},$$

$$\hat{Q}(\vec{r}) = \frac{1}{\sqrt{V}} \sum_{\vec{q}} \hat{Q}_{\vec{q}} e^{i\vec{q}\vec{r}},$$

we can write the free energy (1) in the following form

$$F\{\hat{Q}\} = F_0 + \frac{1}{2} \sum_{\vec{q}} [(a + bq^2) Q_{\alpha\beta,\vec{q}} Q_{\alpha\beta,-\vec{q}} + c q_\alpha q_\beta Q_{\alpha\gamma,\vec{q}} Q_{\beta\gamma,-\vec{q}} + 2id e_{\alpha\beta\gamma} q_\gamma Q_{\alpha\delta,-\vec{q}} Q_{\beta\delta,\vec{q}}]. \tag{4}$$

In order to calculate fluctuations of the tensor order parameter it is convenient to reduce Equation (4) to the diagonal form. The tensor $\hat{Q}_q$ has five independent modes. They may be parametrized as follows:

$$\hat{Q}_{\vec{q}} = \sum_{l=-2}^{2} \xi_{\vec{q}}^{(l)} \sigma^{(l)}(\vec{e}_3), \tag{5}$$

where $\mathbf{e}_3 = \mathbf{q}/q, \hat{\sigma}\ (l)(\mathbf{e}_3)$ are the symmetrical tensors. These tensors form a basis in the space of symmetric traceless tensors of the second rank. These tensors are constructed in the Cartesian coordinate system $(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$ where $\mathbf{e}_3 = [\mathbf{e}_1 \times \mathbf{e}_2]$. For convenience we introduce the complex vector $\mathbf{m}(\mathbf{e}_3)$

$$\vec{m}(\vec{e}_3) = \frac{1}{\sqrt{2}} (\vec{e}_1 + i\vec{e}_2), \tag{6}$$

with the evident property $\mathbf{m}(\mathbf{e}_3) = \mathbf{m}^*(-\mathbf{e}_3)$. The basis $\hat{\sigma}^{(l)}(\mathbf{e}_3)$ has the form

$$\sigma^{(2)}_{\alpha\beta} = m_\alpha m_\beta, \quad \sigma^{(-2)}_{\alpha\beta} = m^*_\alpha m^*_\beta,$$

$$\sigma^{(1)}_{\alpha\beta} = \frac{i}{\sqrt{2}}(m_\alpha e_{3\beta} + m_\beta e_{3\alpha}), \quad \sigma^{(-1)}_{\alpha\beta} = \frac{i}{\sqrt{2}}(m^*_\alpha e_{3\beta} + m^*_\beta e_{3\alpha}),$$

$$\sigma^{(0)}_{\alpha\beta} = \sqrt{\frac{3}{2}}\left(e_{3\alpha} e_{3\beta} - \frac{1}{3}\delta_{\alpha\beta}\right). \tag{7}$$

It follows from Eqs. (6) and (7) that

$$m_\alpha m_\alpha = 0, \quad m_\alpha m^*_\alpha = 1,$$

$$m_\alpha m^*_\beta = \frac{1}{2}(-ie_{\alpha\beta\gamma}e_{3\gamma} + \delta_{\alpha\beta} - e_{3\alpha}e_{3\beta}),$$

$$\hat{\sigma}^{(l)}(\vec{e}_3) = (-1)^l \hat{\sigma}^{(-l)}(-\vec{e}_3),$$

$$\hat{\sigma}^{(l)}(\vec{e}_3) = \hat{\sigma}^{(l)*}(-\vec{e}_3). \tag{8}$$

The system of tensors $\hat{\sigma}^{(l)}$ forms the orthogonal basis normalised in five-dimensional space of the symmetric traceless tensors. The scalar product in this space is defined as

$$(\hat{\chi}, \hat{\eta}) = S_p(\hat{\chi}\hat{\eta}^*).$$

For tensors $\hat{\sigma}^{(l)}$ the following relations are valid

$$\sigma^{(i)}_{\alpha\beta}\sigma^{(j)}_{\beta\alpha} = \delta_{ij},$$

$$\sum_{l=-2}^{2} \sigma^{(l)}_{\alpha\beta}(\vec{e}_3)\sigma^{(l)*}_{\gamma\delta}(\vec{e}_3) = I_{\alpha\beta\gamma\delta}, \tag{9}$$

where $I_{\alpha\beta\gamma\delta}$ is the unit symmetric tensor of the fourth rank

$$I_{\alpha\beta\gamma\delta} = \frac{1}{2}\left[\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma} - \frac{2}{3}\delta_{\alpha\beta}\delta_{\gamma\delta}\right].$$

The separate terms of the order parameter expansion (5) describe the various types of the spontaneously arising structures, i.e, the mode with $l = 0$ means the ordering of the nematic type. Modes with $l = \pm 2$ mean the structure of two cholesteric spirals rotating in opposite directions and modes with $l = \pm 1$ describe the structure of the opposite rotating conical spirals.[8]

With the aid of relations (5)–(9) we can rewrite the expression for free energy (4) in a diagonal form

$$F\{\xi\} = F_0 + \frac{1}{2}\sum_{\vec{q}}\sum_{l=-2}^{2} G_{\vec{q}}^{(l)}|\xi_{\vec{q}}^{(l)}|^2, \tag{10}$$

where

$$\begin{aligned} G_{\vec{q}}^{(l)} &= a + ldq + \left[b + \frac{c}{6}(4 - l^2)\right]q^2 \\ &= g_l + \Delta_l(q - q_l)^2, \quad l = 0, \pm 1, \pm 2, \end{aligned} \tag{11}$$

and

$$\Delta_l = b + \frac{c}{6}(4 - l^2),$$

$$g_l = a - \frac{d^2 l^2}{4\Delta_l}, \quad q_l = -\frac{dl}{2\Delta_l}.$$

From Equation (10) we obtain the following expression for the fluctuation modes[8]

$$\langle|\xi_{\vec{q}}^{(l)}|^2\rangle = \frac{kT}{G_{\vec{q}}^{(l)}} = \frac{kT}{a_0(T - T_l^*) + \Delta_l(q - q_l)^2}, \quad l = 0, \pm 1, \pm 2. \tag{12}$$

It follows from the relations (11), (12) that there exist three different temperatures of instability T_l^* for five fluctuating modes.

It is easy to obtain the expression for T_l^*

$$T_l^* = T^* + \frac{d^2 l^2}{4a_0\Delta_l}. \tag{13}$$

For cholesterics the condition $\Delta_l \geqslant 0$ is valid and the following inequalities take place

$$T^* = T_0^* < T_{\pm 1}^* < T_{\pm 2}^* < T_c$$

Here T_c is the temperature of the first order phase transition. It follows from expression (13) that the temperatures $T_{\pm 2}^*$ are closest to T_c and consequently in the vicinity of T_c the modes $l = \pm 2$ are the most important. Considering the dependence of fluctuations on the wave number q it could easily be seen that the modes with $l = 0, 1, 2$ are maximal at $q = 0$ while the modes with $l = -1, -2$ have maximal values for $q_l = -ld/(2\Delta_l)$.

The relaxation equation for $\xi^{(l)}$ is

$$\dot{\xi}_q^{(l)} = -\Gamma\left(\frac{\delta(F-F_0)}{\delta\xi^{(l)}}\right)_q, \tag{14}$$

where Γ is the kinetic coefficient. From Equation (14) we can find the damping fluctuation law

$$\xi_q^{(l)}(t) = \xi_q^{(l)}(0)\exp\left(-\frac{t}{t_q^{(l)}}\right), \tag{15}$$

where

$$t_q^{(l)} = (\Gamma G_q^{(l)})^{-1} = \{\Gamma[a_0(T-T_l^*) + \Delta_l(q-q_l)^2]\}^{-1}. \tag{16}$$

3. SOUND ATTENUATION AND VELOCITY DISPERSION NEAR T_c

In order to calculate the velocity dispersion and the sound attenuation result from the relaxation of the order parameter fluctuations several methods are used. Among them are the calculation of the dynamic heat capacity,[1,9] the calculation of the fluctuation contribution to the complex bulk viscosity coefficient,[3,10,11] a consideration of the fluctuation field interaction with the sound wave[12,13] and other methods. All these methods lead to similar results in the lowest approximation over the fluctuation parameter. The analysis of viscosity coefficients shows that the variation of acoustic properties is essentially determined by the bulk viscosities in the vicinity of phase transition points of liquid crystals.[13-15] It is due to the drastic increase of these coefficients in critical regions in contrast with shear viscosities. Therefore we calculate the fluctuation contribution to the complex coefficient of the bulk viscosity only.

We start from the statistical expression for the bulk viscosity coefficient (see e.g.[16,17])

$$\tilde{\eta}_v(\omega) = \frac{1}{kT}\int_0^\infty dt\, e^{i\omega t}\langle(\delta p_{q=0} - \delta p_{q=0}^{(1)})(\delta p_{q=0}(t) - \delta p_{q=0}^{(1)}(t))\rangle, \tag{17}$$

where δp is the fluctuation of pressure and $\delta p^{(1)}$ is its thermodynamic part. The value $\tilde{\eta}_v(\omega)$ is complex. Its real and imaginary parts determine the absorption coefficient

$$\alpha = \frac{\omega^2}{2\rho C^3}\mathrm{Re}\,\tilde{\eta}_v(\omega), \tag{18}$$

and sound velocity dispersion

$$C(\omega) - C = \frac{\omega}{2\rho C}\,\mathrm{Im}\,\tilde{\eta}_v(\omega), \tag{19}$$

where C is the velocity at zero frequency, ρ is the mass density.

Equation (17) gives the possibility of extracting the input of various fluctuations to the bulk viscosity coefficient. The general approach is based on the projection of the pressure nonthermodynamic part $(\delta p_{q=0} - \delta p^{(1)}_{q=0})$ on the set of variables $\{a\}$ describing the local equilibrium. The set of variables $\{a\}$ includes the collective variables such as the number density, the energy density, the momentum density and additional variables. In our case these additional variables are the Fourier-components $\xi^{(l)}_q$ describing the tensor order parameter. In Gaussian approximation this projection $P_{\{a\}}(\delta p_{q=0} - \delta p^{(1)}_{q=0})$ has the form[18]

$$P_{\{a\}}(\delta p_{q=0} - \delta p^{(1)}_{q=0}) = \langle(\delta p_{q=0} - \delta p^{(1)}_{q=0})a\rangle\langle aa\rangle^{-1}a(t)$$

$$+\frac{1}{2}\langle(\delta p_{q=0} - \delta p^{(1)}_{q=0})aa\rangle\langle aa\rangle^{-1}a(t)\langle aa\rangle^{-1}a(t). \tag{20}$$

The expression (20) requires the knowledge of correlation functions

$$\langle\delta p_{q=0}a\rangle,\quad \langle\delta p^{(1)}_{q=0}a\rangle,\quad \langle\delta p_{q=0}aa\rangle,\quad \langle\delta p^{(1)}_{q=0}aa\rangle.$$

The thermodynamic fluctuation theory[6] gives the possibility of calculating the correlator $\langle\delta p^{(1)}_{q=0}Y\rangle$, where Y is an arbitrary microscopic value. The Fourier component $\delta p^{(1)}_{q=0}$ is connected with the fluctuation of the pressure thermodynamic part $\delta p^{(1)}(\mathbf{r})$ averaged over the system volume

$$\delta p^{(1)}_{q=0} = \frac{1}{\sqrt{V}}\int d\vec{r}\,\delta p^{(1)}(\vec{r}) = \sqrt{V}\delta p^{(1)}. \tag{21}$$

The correlator $\langle\delta p^{(1)}Y\rangle$ may be presented in the form

$$\langle\delta p^{(1)}Y\rangle = \left(\frac{\partial\langle Y\rangle}{\partial\rho}\right)_S\langle\delta p^{(1)}\delta\rho\rangle + \left(\frac{\partial\langle Y\rangle}{\partial S}\right)_\rho\langle\delta p^{(1)}\delta S\rangle$$

$$= \frac{kT\rho}{V}\left(\frac{\partial\langle Y\rangle}{\partial\rho}\right)_S, \tag{22}$$

where the identities[6]

$$\langle\delta p^{(1)}\delta\rho\rangle = \frac{KT\rho}{V},\quad \langle\delta p^{(1)}\delta S\rangle = 0,$$

are used.

From Equations (21) and (22) we get

$$\langle\delta p^{(1)}_{q=0}Y\rangle = \frac{KT}{\sqrt{V}}\rho\left(\frac{\partial\langle Y\rangle}{\partial\rho}\right)_S. \tag{23}$$

In the vicinity of a phase transition point the fluctuations of the tensor order parameter increase critically. Therefore we take into account only the Fourier-components $\xi_q^{(l)}$ in the set of variables $\{a\}$. The correlator $\langle \delta p_{q=0} \xi_q^{(l)} \rangle$ is not considered since it contains the noncritical input to the bulk viscosity only. Its value may be estimated in the same way as in[17] where it was shown that the correlator $\langle \delta p_{q=0} \ \xi_{q=0}^{(l)} \rangle$ is proportionate to $(\partial \langle \xi_{q=0}^{(l)} \rangle / \partial \rho)_T$. Note that the correlators $\langle \delta p_{q=0}^{(1)} \xi_{q=0}^{(l)} \rangle$ and $\langle \delta p_{q=0} \xi_{q=0}^{(l)} \rangle$ are equal to zero since $\langle \xi_q^{(l)} \rangle = 0$ in the isotropic phase. Therefore the first term in expression (20) turns to zero and we have

$$\tilde{\eta}_v(\omega) = \frac{1}{2kT} \sum_{l=-2}^{2} \sum_{\vec{q}} \int_0^\infty dt\, e^{(i\omega - 2\Gamma G_{\vec{q}}^{(l)})t} \times \langle \delta p_{q=0}^{(1)} | \xi_{\vec{q}}^{(l)} |^2 \rangle^2 \langle | \xi_{\vec{q}}^{(l)} |^2 \rangle^{-2}. \tag{24}$$

where the fluctuation temporal dependencies (15) are taken into account. Using Equation (23) after integrating over time we have

$$\tilde{\eta}_v(\omega) = \frac{kT}{2V} \sum_{l=-2}^{2} \sum_{\vec{q}} \frac{\rho^2 \left(\dfrac{\partial \langle | \xi_{\vec{q}}^{(l)} |^2 \rangle}{\partial \rho} \right)_S^2}{\langle | \xi_{\vec{q}}^{(l)} |^2 \rangle^2 (-i\omega + 2\Gamma G_{\vec{q}}^{(l)})}. \tag{25}$$

Replacing the summation by integrating over wave vectors $\Sigma_q \rightarrow V/(2\pi)^3 \int d\mathbf{q}$ in Equation (25) we get

$$\tilde{\eta}_v(\omega) = \frac{kT\rho^2}{4\pi^2} \sum_{l=-2}^{2} \int_0^\infty q^2 dq \frac{\left(\dfrac{\partial \langle | \xi_{\vec{q}}^{(l)} |^2 \rangle}{\partial \rho} \right)_S^2}{\langle | \xi_{\vec{q}}^{(l)} |^2 \rangle^2 (-i\omega + 2\Gamma G_{\vec{q}}^{(l)})}. \tag{26}$$

Due to Equations (11) and (12) we may write

$$\left(\frac{\partial \langle | \xi_{\vec{q}}^{(l)} |^2 \rangle}{\partial \rho} \right)_S = -\frac{kTa_0}{[G_{\vec{q}}^{(l)}]^2} \left(\frac{\partial (T - T^*)}{\partial \rho} \right)_S. \tag{27}$$

Substituting Equation (27) into Equation (26) we obtain

$$\tilde{\eta}_v(\omega) = \frac{kTa_0^2}{4\pi^2} \rho^2 \left(\frac{\partial (T - T^*)}{\partial \rho} \right)_S^2 \times \sum_{l=-2}^{2} \int_0^\infty \frac{q^2 dq}{[G_{\vec{q}}^{(l)}]^2 (-i\omega + 2\Gamma G_{\vec{q}}^{(l)})}. \tag{28}$$

Let us transform the thermodynamic derivative in Equation (28). Firstly, we connect the derivatives $(\partial Y / \partial \rho)_S$ and $(\partial Y / \partial T)_p$ of an arbitrary function depending on the difference $T - T^*$, i.e. $Y = Y(T - T^*)$. Using the Jacobian properties[6] we get

$$\left(\frac{\partial Y}{\partial \rho} \right)_S = \frac{\partial (Y, S)}{\partial (T, p)} \Big/ \frac{\partial (\rho, S)}{\partial (T, p)} = -\frac{\dfrac{\alpha_T}{\rho} \left(\dfrac{\partial Y}{\partial T} \right)_p + \dfrac{C_p}{T} \left(\dfrac{\partial Y}{\partial p} \right)_T}{\alpha_T^2 - \dfrac{C_p^2}{TC_vC^2}}, \tag{29}$$

where C_p and C_v are the heat capacities per unit mass, $\alpha_T = 1/V(\partial V/\partial T)_p$ is the thermal bulk expansion coefficient, $C = \sqrt{(\partial p/\partial \rho)_S}$ is the sound velocity at zero frequency. Since the temperature T^* is the function of pressure, $T^* = T^*(p)$,[19] the derivative $(\partial Y/\partial p)_T$ may be presented in the form

$$\left(\frac{\partial Y}{\partial p}\right)_T = -\left(\frac{\partial Y}{\partial T}\right)_p \frac{dT^*}{dp}. \tag{30}$$

Using the thermodynamic identity[6]

$$C_p - C_v = \frac{T\alpha_T^2 C^2}{\gamma}, \tag{31}$$

where $\gamma = C_p/C_v$, and Equations (29) and (30) we may write the value $(\partial Y/\partial \rho)_S^2$ as follows

$$\left(\frac{\partial Y}{\partial \rho}\right)_S^2 = \left(\frac{\partial Y}{\partial T}\right)_p^2 \frac{T(\gamma - 1)C^2}{\rho^2 C_p}\left(1 - \frac{\rho C_p}{T\alpha_T}\frac{dT^*}{dp}\right)^2. \tag{32}$$

This identity gives the possibility to present the value $\rho^2(\partial(T - T^*)/\partial\rho)_S^2$ in the form

$$\rho^2\left(\frac{\partial(T - T^*)}{\partial \rho}\right)_S^2 = \frac{T(\gamma_0 - 1)C^2}{C_{p^\circ}}\left(1 - \frac{\rho C_{p^\circ}}{T\alpha_T}\frac{dT^*}{dp}\right)^2, \tag{33}$$

where C_{p0}, C_{v0} are the nonsingular parts of the heat capacities and $\gamma_0 = C_{p0}/C_{v0}$. In the used Gaussian approximation the singular heat capacity parts had to be omitted.

We introduce the dimensionless variables

$$x_l = \frac{\omega}{\omega_l}, \tag{34}$$

where

$$\omega_l = 2\Gamma a_0(T - T_l^*), \tag{35}$$

and

$$\tilde{q}_l = \sqrt{\frac{\Delta_l}{a_0(T - T_l^*)}}\, q_l, \tag{36}$$

instead of ω and q_l. With these variables the integral in Equation (28) has the form

$$\int_0^\infty \frac{q^2\,dq}{[G_q^{(l)}]^2(-i\omega + 2\Gamma G_q^{(l)})} = \frac{1}{2\Gamma(\Delta_l a_0(T - T_l^*))^{3/2}} \int_0^\infty \frac{\tilde{q}^2\,d\tilde{q}}{[1 + (\tilde{q} - \tilde{q}_i)^2]^2(1 - ix_l + (\tilde{q} - \tilde{q}_l)^2]}. \tag{37}$$

The expression (28) may be rewritten as

$$\tilde{\eta}_v(\omega)=\frac{kT^2}{8\pi^2}\frac{(\gamma_0-1)}{\gamma_0}\frac{a_0^{1/2}C^2}{C_{p0}}\left(1-\frac{\rho C_{p^\circ}}{T\alpha_T}\frac{dT^*}{dp}\right)^2\times\sum_{l=-2}^{2}\frac{J_l}{[\Delta_l(T-T_l^*)]^{3/2}}, \tag{38}$$

where the integral

$$J_l=\int_0^\infty\frac{\tilde{q}^2\,d\tilde{q}}{[1+(\tilde{q}-\tilde{q}_l)^2]^2[1-ix_l+(\tilde{q}-\tilde{q}_l)^2]}, \tag{39}$$

is calculated in the Appendix. Each of the five modes have their own characteristic time $\tau_l=[\Gamma a_0(T-T_l^*)]^{-1}, l=0, \pm 1, \pm 2$ where T_l^* are given by Equation (13). The largest characteristic times have the modes $l=\pm 2$.

Therefore, the complex coefficient of the bulk viscosity has the form

$$\tilde{\eta}_v(\omega)=\frac{kT^2(\gamma_0-1)a_0^{3/2}}{16\pi C_{p0}\omega}C^2\left(1-\frac{\rho C_p}{T\alpha_T}\frac{dT^*}{dp}\right)^2$$
$$\times\sum_{l=-2}^{2}\frac{F_1(x_l)+\tilde{q}_l^2E_1(x_l)+i(F_2(x_l)+\tilde{q}_l^2E_2(x_l))}{\Delta_l^{3/2}(T-T_l^*)^{1/2}}, \tag{40}$$

where

$$\begin{aligned}F_1(x)&=\frac{\sqrt{2}}{x}\sqrt{\sqrt{1+x^2}+1}-\frac{2}{x},\\E_1(x)&=\frac{2}{x}-\frac{\sqrt{2}}{x}\sqrt{\frac{\sqrt{1+x^2}+1}{1+x^2}},\\F_2(x)&=1-\frac{\sqrt{2}}{x}\sqrt{\sqrt{1+x^2}-1},\\E_2(x)&=1-\frac{\sqrt{2}}{x}\sqrt{\frac{\sqrt{1+x^2}-1}{1+x^2}}.\end{aligned} \tag{41}$$

Equations (18), (19), (40) and (41) give the possibility of calculating the sound absorption coefficient and the sound velocity dispersion in the cholesteric isotropic phase in the vicinity of phase transition. Note that these expressions are free from fitting parameters. All values in these equations may be measured experimentally.

4. DISCUSSION

Equation (40) describing the critical input to the bulk viscosity coefficient has a quite complicated form. Therefore it needs special analysis to clarify the sense of the obtained expressions. Firstly, we compare the Equation (40) with the results for the isotropic nematic phase transition. If in the free energy expansion (4) the coefficient d vanishes and one correlation length approximation ($c = 0$) is used, Equation (40) transforms into

$$\tilde{\eta}_v^N(\omega) = \frac{5kT^2 a_0^{3/2}(\gamma_0 - 1)C^2}{16\pi\Delta_0^{3/2}C_{p0}(T - T^*)^{1/2}\omega} \times \left(1 - \frac{\rho C_{p0}}{T\alpha_T}\frac{dT^*}{dp}\right)^2 (F_1(x_0) + iF_2(x_0)). \tag{42}$$

This expression describes the bulk viscosity coefficient in the isotropic phase of a nematic. It turns to the Imura and Okano relation[1] for $dT^*/dp = 0$. But T^* dependence on the pressure p is important and the term $\rho C_{p0}/T_{\alpha_T} \times dT^*/dp$ is of the order of $2 \div 4$.

Let us analyse and compare the temperature and frequency dependencies of nematic and cholesteric acoustical parameters in the isotropic phase. For low frequencies ($\omega \to 0$, $x_l \to 0$) Equations (41) give

$$\begin{aligned} F_1(x) &\sim \frac{x}{4}, \quad E_1(x) \sim \frac{3x}{4}, \\ F_2(x) &\sim \frac{x^2}{8}, \quad E_2(x) \sim \frac{5x^2}{8}. \end{aligned} \tag{43}$$

For high frequencies ($\omega \to \infty$, $x_l \to \infty$) we have

$$\begin{aligned} F_1(x) &\sim \sqrt{\frac{2}{x}}, \quad E_1(x) \sim \frac{2}{x}, \\ F_2(x) &\sim 1, \quad E_2(x) \sim 1. \end{aligned} \tag{44}$$

The expressions (43) and (44) make it possible to estimate the asymptotic behaviour of the acoustic parameters near the phase transition point. By eliminating the difference between T_l^*, $l = 0, \pm 1, \pm 2$ we have:

for $\omega \to 0 (\omega \ll \omega_0)$

I-N transition

$$\begin{aligned} \alpha(\omega) &\sim \omega^2 (T - T^*)^{-3/2}, \\ C(\omega) - C &\sim \omega^2 (T - T^*)^{-5/2}, \end{aligned} \tag{45}$$

I-Ch transition

$$\begin{aligned} \alpha(\omega) &\sim \omega^2 (T - T^*)^{-5/2}, \\ C(\omega) - C &\sim \omega^2 (T - T^*)^{-7/2}, \end{aligned} \tag{46}$$

and for $\omega \to \infty (\omega \gg \omega_0)$.

I-N transition

$$\begin{aligned}\alpha(\omega) &\sim \omega^{1/2},\\ C(\omega)-C &\sim (T-T^*)^{-1/2},\end{aligned}\tag{47}$$

I-Ch transition

$$\begin{aligned}\alpha(\omega) &\sim (T-T^*)^{-1/2},\\ C(\omega)-C &\sim (T-T^*)^{-3/2}.\end{aligned}\tag{48}$$

Comparing these relations we conclude that frequency dependencies of acoustical parameters at low frequencies for nematics and cholesterics are similar. At high frequencies the sound absorption coefficient for cholesterics is frequency independent while it increases as $\omega^{1/2}$ for nematics.

As to the temperature dependencies of the sound absorption and the velocity dispersion one can see that the acoustical parameters near the phase transition point increase more rapidly for cholesterics than for nematics. It is interesting for experimental studies that at high frequencies $\alpha \sim (T-T^*)^{-1/2}$ and independent of frequency for cholesterics while $\alpha \sim \omega^{1/2}$ and independent of temperature for nematics.

In order to illustrate the numerical values of the results obtained we compare the ultrasonic velocity dispersion and the attenuation coefficient in the nematic and cholesteric isotropic phases.

The calculations were completed for system with the parameters of CE_2 cholesteric.[20] In this case

$$a_0 = 0.96 \times 10^6\,\mathrm{erg/cm^3K}, \quad b = 6.2 \times 10^{-7}\,\mathrm{erg/cm}, \quad c = 0, \quad d = 0.78\,\mathrm{erg/cm^2}$$

For the remaining parameters we used the typical values which are well known for nematics. We take the numerical data for MBBA:[19, 21, 22]

$$T_c - T^* = 1.4\mathrm{K}, \quad \rho = 1.04\,\mathrm{g/cm^3}, \quad \Gamma = 0.4\,\mathrm{cm^3/erg\,s}, \quad \alpha_T = 7.8 \times 10^{-4}\,\mathrm{K^{-1}}$$

$$dT^*/dp \approx dT_c/dp = 3.9 \times 10^{-8}\,\mathrm{K\,cm^2/din}.$$

The temperature dependence of C_{p0} in MBBA in the isotropic phase was used from:[23]

$$C_{p0} \simeq \frac{R}{M}\left(55.6 + 31.9\left(\frac{T-T_c}{T_c}\right)\right),$$

where R is the universal gas constant, M is the molecular weight. The temperature dependence of C_{v0} was found using the Equation (31). We calculate the coefficient of the sound attenuation α/f^2 and the sound velocity dispersion $C(\omega) - C$ from Equations (18), (19), (40) and (42).

Figures 1 and 2 show the results of calculations in the vicinity of I-Ch and I-N phase transition points for frequencies $f_1 = 1$ MHz and $f_2 = 10$ MHz. These frequencies are typical for acoustical experiments. For our set of parameters the value $f_2 > \omega_0/(2\pi)$ belongs to the high frequency region whereas f_1 is the intermediate frequency, $f_1 \sim \omega_0/(2\pi)$. It is seen from Figures 1 and 2 that the sound velocity dispersion and the attenuation coefficient increase more rapidly for cholesteric than for nematic as $T \rightarrow T_c$. This behaviour is in accordance with the asymptotics (45)–(48), i.e. the variation of acoustical parameters much more visible for the low frequency than for the high one. It follows from Equation (47) that for nematic the sound absorption coefficient has to be independent of temperature at high frequencies, $f \gg \omega_0/(2\pi)$. For our case, $f_2 > \omega_0/(2\pi)$, one can see the tendency toward this behaviour. The dashed parts of the lines correspond to the deviation from the scaling laws (45)–(46) due to the difference between the instability temperatures T_l^* for various modes, e.g. $T^*_{\pm 2} - T^*_0 \sim 1$ K.

For the systems with a large pitch it is convenient to use the power series expansion on the parameter d, or $1/p$, for the ultrasonic attenuation and the sound velocity dispersion. From Equations (18), (19), (40) and (42) we obtain in the lowest order on

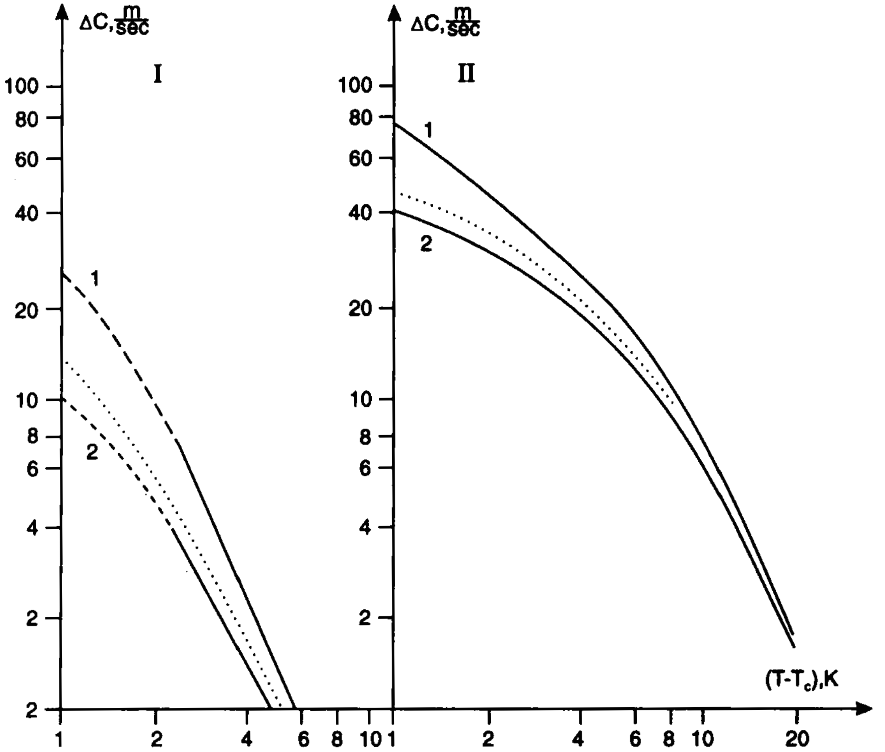

FIGURE 1 Temperature dependence of sound velocity dispersion $\Delta C = C(\omega) - C$ for cholesteric (1) and nematic (2) for various frequencies: I. $f = 1$ MHz, II. $f = 10$ MHz. The dotted lines are calculated with the help of Eq. (50).

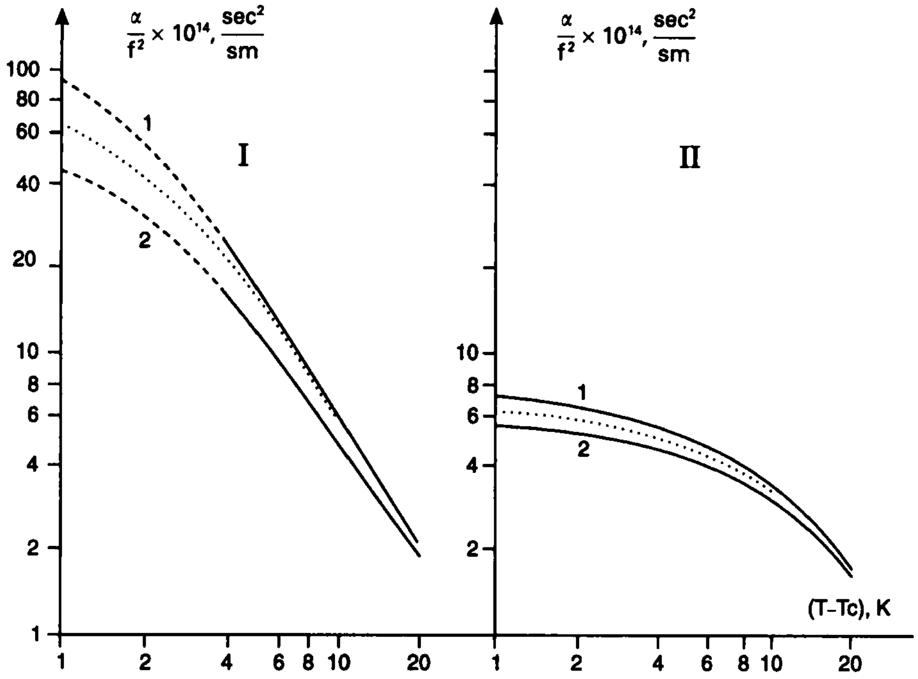

FIGURE 2 Temperature dependence of α/f^2 for cholesteric (1) and nematic (2) for various frequencies: I. $f = 1$ MHz, II. $f = 10$ MHz. The dotted lines are calculated with the help of Eq. (49).

dimensionless parameter $2\pi r_c/p$

$$\frac{\alpha}{f^2} \approx \left[\frac{\alpha}{f^2}\right]_{p\to\infty} + A(T,\omega)\left(\frac{2\pi r_c}{p}\right)^2, \tag{49}$$

$$C(\omega) - C \approx [C(\omega) - C]_{p\to\infty} + B(T,\omega)\left(\frac{2\pi r_c}{p}\right)^2, \tag{50}$$

where we introduce the correlation length $r_c = \{b/[a_0(T - T^*)]\}^{1/2}$.

The first terms in the right hand side of Equations (49) and (50) correspond to nematic. The coefficients $A(T,\omega)$ and $B(T,\omega)$ are

$$A(T,\omega) = \frac{\pi D(T)}{C^2\omega}\left[\frac{1}{\sqrt{1+x_0^2}}\left(\frac{x_0}{\nu_0} - 4\frac{\nu_0}{x_0}\right) - 2\left(\frac{\nu_0}{x_0} - \frac{3}{x_0}\right)\right], \tag{51}$$

$$B(T,\omega) = \frac{D(T)}{4\pi}\left(1 + 2\frac{\mu_0}{x_0} - \frac{1}{\sqrt{1+x_0^2}}\frac{x_0}{\mu_0}\right), \tag{52}$$

where

$$D(T)=\frac{5kT^2a_0^2(\gamma_0-1)Cr_c}{8\rho C_{p0}b^2}\left(1-\frac{\rho C_{p0}}{T\alpha_T}\frac{dT^*}{dp}\right)^2,$$

μ_0, ν_0, x_0 are given by Equations (A.4) and (34).

Note that Equations (49) and (50) contain even powers of parameters $(2\pi r_c)/p$ only. For cholesteric CE_2 the results of calculation by Equations (49) and (50) are shown in Figures 1 and 2 by dotted lines. One can see that for our set of parameters which corresponds to the system with a small pitch the exact equations must be used. For systems with a large pitch Equations (49) and (50) are suitable.

The results obtained in this work may be used for quantitative analysis of the acoustical experimental data and deriving information about cholesteric parameters from the experiments of this type.

APPENDIX

For calculating the integral (24) it is convenient to introduce the contour integral

$$\oint_C f(z)\ln z\,dz,$$

where the contour C is shown in Figure 3. The function $f(z)$ decreases quite rapidly as $|z|\to\infty$ and has no singularity at the zero point. This integral contains contribution on the upper and the lower side of the cut only and it equals the sum of the residues. Thus we have

$$\int_0^\infty f(z)dz=-\sum_{\mathrm{Res}}\mathrm{Res}[f(z)\ln z]. \tag{A1}$$

For our integral we can write

$$J_l=-\sum_{\mathrm{Res}}\mathrm{Res}\frac{z^2\ln z}{[1+(z-\tilde{q}_l)^2]^2[1-ix_l+(z-\tilde{q}_l)^2]}. \tag{A2}$$

In this case there are four poles

$$z_{1,2}=\tilde{q}_l\pm i,\quad z_{3,4}=\tilde{q}_l\pm(\mu_l+i\nu_l), \tag{A3}$$

where

$$\mu_l=\left[\frac{\sqrt{1+x_l^2}-1}{2}\right]^{\frac{1}{2}},\quad \nu_l=\left[\frac{\sqrt{1+x_l^2}+1}{2}\right]^{\frac{1}{2}}.$$

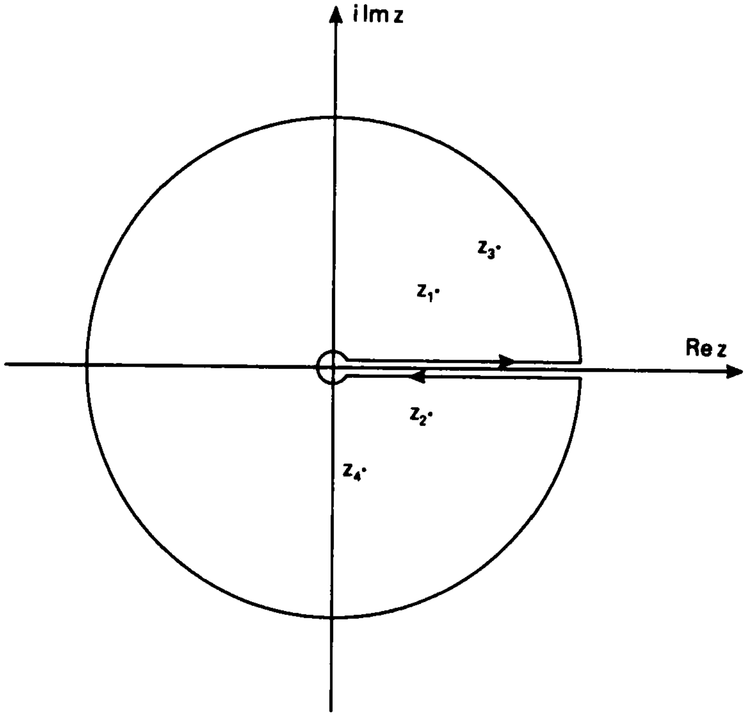

FIGURE 3 The integrating contour C.

So we have

$$J_l=\frac{1}{4x_l}\{(\tilde{q}_l+i)\ln(\tilde{q}_l+i)\left[i\left(1+\frac{2\tilde{q}_l}{x_l}\right)-\tilde{q}_l\left(1+\frac{2}{\tilde{q}_l x_l}\right)\right]$$

$$+2i\tilde{q}_l+(\tilde{q}_l-i)\ln(\tilde{q}_l-i)\left[i\left(1-\frac{2\tilde{q}_l}{x_l}\right)+\tilde{q}_l\left(1-\frac{2}{\tilde{q}_l x_l}\right)\right]\Bigg\}$$

$$+\frac{1}{2x_l^2(\mu_l+i\nu_l)}\Big[(\tilde{q}_l+\mu_l+i\nu_l)^2\ln(\tilde{q}_e+\mu_l+i\nu_l)$$

$$-(\tilde{q}_l-\mu_l-i\nu_l)^2\ln(\tilde{q}_l-\mu_l-i\nu_l)\Big]. \qquad \text{(A5)}$$

After a simple calculation we come to

$$J_l=\operatorname{Re}J_l+i\operatorname{Im}J_l, \qquad \text{(A6)}$$

where

$$\operatorname{Re} J_l = \frac{1}{2x_l^2}\left\{(\tilde{q}_l^2 - 1)(\pi + \operatorname{arctg}\tilde{q}_l) + \tilde{q}_l \ln\left[1 + \frac{x_l^2}{(1+\tilde{q}_l^2)^2}\right]\right.$$

$$+ \frac{\mu_l(\sqrt{1+x_l^2} + \tilde{q}_l^2)}{2\sqrt{1+x_l^2}} \ln \frac{\tilde{q}_l^2 + 2\tilde{q}_l\mu_l + \sqrt{1+x_l^2}}{\tilde{q}_l^2 - 2\tilde{q}_l\mu_l + \sqrt{1+x_l^2}}$$

$$\left. + \frac{\nu_l(\sqrt{1+x_l^2} - \tilde{q}_l^2)}{\sqrt{1+x_l^2}}\left[\pi + \operatorname{arctg}\left(\frac{\tilde{q}_l - \mu_l}{\nu_l}\right) + \operatorname{arctg}\left(\frac{\tilde{q}_l - \mu_l}{\nu_l}\right)\right]\right\}, \quad \text{(A7)}$$

$$\operatorname{Im} J_l = \frac{1}{2x_l^2}\left\{x_l\left[\tilde{q}_l + (1+\tilde{q}_l^2)\left(\operatorname{arctg}\tilde{q}_l + \frac{\pi}{2}\right)\right] - \tilde{q}_l\left[\pi - 2\operatorname{arctg}\frac{1+\tilde{q}_l^2}{x_l}\right]\right.$$

$$+ \frac{\nu_l(\sqrt{1+x_l^2} - \tilde{q}_l^2)}{2\sqrt{1+x_l^2}} \ln \frac{\tilde{q}_l^2 + 2\tilde{q}_l\mu_l + \sqrt{1+x_l^2}}{\tilde{q}_l^2 - 2\tilde{q}_l\mu_l + \sqrt{1+x_l^2}}$$

$$\left. - \frac{\mu_l(\sqrt{1+x_l^2} + \tilde{q}_l^2)}{\sqrt{1+x_l^2}}\left[\pi + \operatorname{arctg}\left(\frac{\tilde{q}_l - \mu_l}{\nu_l}\right) + \operatorname{arctg}\left(\frac{\tilde{q}_l + \mu_l}{\nu_l}\right)\right]\right\}. \quad \text{(A8)}$$

In the expressions (A7) and (A8) the odd parameter $\tilde{q}_l$ functions vanish after summing over the modes l in Equation (38). Therefore it is necessary to take into account in Equations (A7) and (A8) the even part of the functions $\operatorname{Re} J_l$ and $\operatorname{Im} J_l$ only. Thus, we have

$$\operatorname{Re} \bar{J}_l = \frac{\pi}{2x_l^2}\left[\nu_l - 1 + \left(1 - \frac{\nu_l}{\sqrt{1+x_l^2}}\right)\tilde{q}_l^2\right], \quad \text{(A9)}$$

$$\operatorname{Im} \bar{J}_l = \frac{\pi}{2x_l^2}\left[\frac{x_l}{2} - \mu_l + \left(\frac{x_l}{2} - \frac{\mu_l}{\sqrt{1+x_l^2}}\right)\tilde{q}_l^2\right]. \quad \text{(A10)}$$

After substitution Equations (A 9) and (A 10) into Equation (38) we get Equation (40).

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