Anisotropy of electrostatic interaction in free-standing smectic-C^* films

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The correlation function of the director fluctuations in a free-standing smectic ferroelectric film is calculated theoretically. In the functional of free energy, the anisotropy of the Coulomb interaction of polarization charges is taken into account. The results of calculations were used to obtain the angular dependences of scattered light intensity. It has been shown that for relatively thick films, the anisotropy of the Coulomb interaction of polarization charges can change significantly the scattered light intensity.

I. INTRODUCTION

Liquid crystals, known as smectic-C^* or Sm-C^* liquid crystals, continue to attract interest, primarily due to their unique material properties and possible applications in engineering [1–4]. For this type of liquid crystal, the centers of mass of the molecules in the equilibrium state are arranged in equidistant plane-parallel layers. The molecules exhibit an elongated shape and the angle θ between principal axes of molecules and normal **N** to a layer is temperature-dependent. Within each layer, the molecules form a sort of two-dimensional liquid. The unit vector director **n** indicates the average direction of the long axes of the molecules at a given point. The projection of the director **n** on the plane of the smectic layer, normalized to unity, forms a two-dimensional vector **c**-director. All of these properties are characteristic of Sm-C, while Sm-C^* additionally possesses spontaneous polarization **P** directed perpendicular to both the **c**-director and the normal **N**. In bulk Sm-C^* samples the polarization vector **P** rotates through a certain angle while passing from one layer to another. For various types of Sm-C^*, a complete turn of vector **P** occurs through a different number of layers, from a few layers to thousands of them [2–4].

Thermal spatial fluctuations of spontaneous polarization **P** will produce a polarization charge with density $\rho = -\operatorname{div} \mathbf{P}$. Usually the interaction of these polarization charges are neglected, assuming them to be screened by charges of impurities [1]. The short-range interaction of the screened polarization charges was described in Ref. [5]. It was shown that the charges effectively increase the bending elastic modulus in the two-dimensional systems. It turns out to be consistent with the experimental data on the texture of islands found in the same work and with experimental results of Ref. [6] for periodic stripe patterns in free-standing Sm-C^* films. The interaction of impurity ions with the polarization charges was accounted for in Ref. [7], describing the dynamics of the orientation field. It was anticipated that this interaction should manifest itself in experiments on light scattering from free-standing Sm-C^* films. In Ref. [8] it was shown that the interaction of the impurity ions with polarization charges also leads to the increase of orientational viscosity.

The long-range interaction of unscreened polarization charges in Sm-C^* films was studied experimentally and theoretically in Refs. [9–12]. It has been found that the contribution of the interaction of polarization charges to the free energy is clearly visible in the light scattering measurements performed for thin Sm-C^* films. A theoretical description of the interaction of unscreened polarization charges in the plane Sm-C^* cell with bookshelf geometry was proposed in Ref. [13]. For the free-standing smectic-C^* films the inhomogeneity of the director fluctuations in the volume of the film was taken into account in Ref. [14].

Usually, the anisotropy of the permittivity tensor is ignored when describing the contribution of the interaction of polarization charges to the free energy of the ferroelectric smectics. However, there remains a significant difference between the principal values of the dielectric permittivity tensor [15,16]. So the question arises whether this difference manifests itself in optical experiments performed in not very thin films. The theoretical description of **c**-director fluctuations was obtained in Ref. [17], accounting for the anisotropy of the Coulomb interaction between polarization charges. It was shown that for a bulk Sm-C^* pattern this anisotropy can change the scattered light intensity by about 10% .

In this article the correlation function of **c**-director fluctuations is calculated for the free-standing Sm-C^* film of finite thickness, taking account of the anisotropy of the Coulomb interaction of polarization charges. The obtained correlation function is used for calculation of the angular dependences for the scattered light intensity.

II. DISTORTION FREE ENERGY

We consider a free-standing film of the ferroelectric Sm-C^*, in a constant external electric field **E** directed parallel to the film surface. We assume that the helix of the director **n** rotation is unwound and that the temperature is fixed. In this case the director tilt angle θ remains a constant value. The external field is assumed to be sufficiently weak so that only the linear term of the interaction between the field **E** and the spontaneous polarization **P** in the expression for the free energy can be taken into account. In this case the distortion free energy can be presented in the form

$$F = F_{\mathrm{Fr}} + F_P + F_C. \tag{2.1}$$

Here F_{Fr} is the elastic part of the free energy of the film. For the unwound Sm-C^* it can be presented in the following

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form:

$$F_{\text{Fr}} = \frac{1}{2} \int d\mathbf{r} [K_{11}(\text{div}\,\mathbf{n})^2 + K_{22}(\mathbf{n} \cdot \text{rot}\,\mathbf{n})^2$$
$$+ K_{33}(\mathbf{n} \times \text{rot}\,\mathbf{n})^2]. \tag{2.2}$$

Here K_{ii}, $i = 1,2,3$, are Frank elastic constants. The term F_P in Eq. (2.1) arises from the interaction of spontaneous polarization $\mathbf{P}$ with the external electric field:

$$F_P = -\int d\mathbf{r}(\mathbf{P} \cdot \mathbf{E}). \tag{2.3}$$

The last term in Eq. (2.1) describes the Coulomb interaction between the polarization charges that arise with the charge density $\rho = -\text{div}\,\mathbf{P}$ due to thermal spatial fluctuations of spontaneous polarization. As we know, the impurity ions are present in all films and they can screen the polarization charges. As was shown in Refs. [12,18], the diffusion times associated with ionic motions are by a factor of 1000 longer than the relaxation time of the **c**-director fluctuations for the wave numbers corresponding to the light scattering experiments. Therefore, ions of impurities do not have time to screen the polarization charges arising from rapid fluctuations of the **c**-director and in what follows we neglect the screening. Taking into account the anisotropy of the permittivity tensor $\hat{\varepsilon}$ in Sm-C^*, we can write the Coulomb interaction term in the form [17]

$$F_C = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\text{div}\,\mathbf{P}(\mathbf{r})\,\text{div}'\,\mathbf{P}(\mathbf{r}')}{\sqrt{\det\hat{\varepsilon}\,\varepsilon_{ik}^{-1}(\mathbf{r}-\mathbf{r}')_i(\mathbf{r}-\mathbf{r}')_k}}, \tag{2.4}$$

where ε_{ik}^{-1} is the permittivity tensor inverse.

Here we consider the free-standing film of thickness L. In the equilibrium state the film consists of planar smectic layers, with the director oriented perpendicular to the external field $\mathbf{E}$. In what follows we neglect deviations of the smectic layers from the given flat state, as it is usually assumed [5,8–12]. Actually, we are interested in director fluctuations that are mainly associated with the free rotation of the director $\mathbf{n}$ around the normal to the smectic layer.

The calculations are performed in the Cartesian coordinate system shown in Fig. 1. The film occupies the region $-L/2 \leqslant z \leqslant L/2$ with smectic layers parallel to the xy plane. The y axis is directed along the external field $\mathbf{E}$. The polarization vector $\mathbf{P}$ can be expressed via the **c**-director and the normal $\mathbf{N}$: $\mathbf{P} = P[\mathbf{N} \times \mathbf{c}]$, where P is the spontaneous polarization.

Taking into account the anisotropy of the Coulomb interaction of polarization charges, we parametrize the permittivity tensor using its principal values ε_1, ε_2, and ε_3:

$$\varepsilon_{ik} = \varepsilon_1\delta_{ik} + (\varepsilon_3 - \varepsilon_1)n_{0i}n_{0k} + (\varepsilon_2 - \varepsilon_1)p_{0i}p_{0k}, \tag{2.5}$$

where

$$\mathbf{n_0} = (\sin\theta, 0, \cos\theta),$$
$$\mathbf{c_0} = (1,0,0),$$
$$\mathbf{p_0} = [\mathbf{N} \times \mathbf{c_0}] = (0,1,0). \tag{2.6}$$
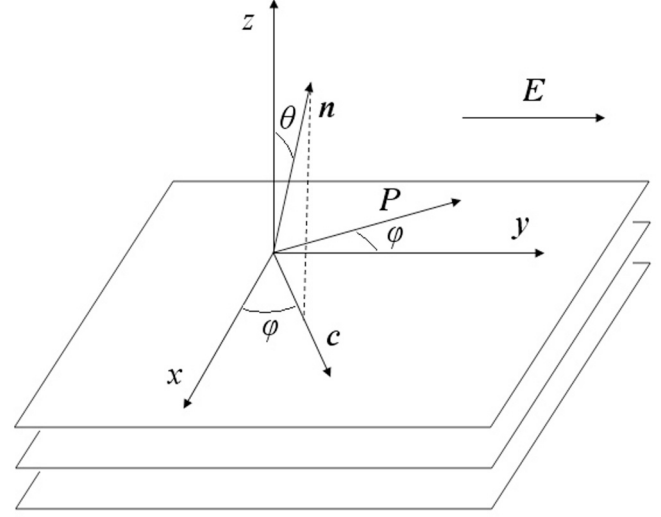

FIG. 1. Vectors $\mathbf{P}$, $\mathbf{n}$, and $\mathbf{c}$ in Sm-C^* film.

In the equilibrium $\varphi = 0$, though due to thermal fluctuations $\varphi \neq 0$ and thus for the vectors $\mathbf{P}$, $\mathbf{n}$, and $\mathbf{c}$, we have

$$\mathbf{P} = P(-\sin\varphi, \cos\varphi, 0),$$
$$\mathbf{n} = (\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta),$$
$$\mathbf{c} = (\cos\varphi, \sin\varphi, 0). \tag{2.7}$$

Assuming angular fluctuations φ to be small, we obtain, for vectors $\mathbf{P}$, $\mathbf{n}$, and $\mathbf{c}$,

$$\mathbf{P} \approx P\left(-\varphi, 1 - \frac{\varphi^2}{2}, 0\right),$$
$$\mathbf{n} \approx \left[\left(1 - \frac{\varphi^2}{2}\right)\sin\theta, \varphi\sin\theta, \cos\theta\right], \tag{2.8}$$
$$\mathbf{c} \approx \left(1 - \frac{\varphi^2}{2}, \varphi, 0\right).$$

We can see that in the considered approximation only one value, namely, the angle φ, fluctuates independently. Thus the contribution of the **c**-director fluctuations to the free energy takes the form, up to the second-order terms,

$$\delta F = \frac{1}{2}\int d\mathbf{r}\left[B_1\left(\frac{\partial\varphi}{\partial x}\right)^2 + B_2\left(\frac{\partial\varphi}{\partial y}\right)^2 + B_3\left(\frac{\partial\varphi}{\partial z}\right)^2\right.$$
$$+ 2B_{13}\left(\frac{\partial\varphi}{\partial x}\right)\left(\frac{\partial\varphi}{\partial z}\right) + PE\varphi^2$$
$$\left.+ P^2\int d\mathbf{r}' \frac{\frac{\partial\varphi(\mathbf{r}')}{\partial x'}\frac{\partial\varphi(\mathbf{r})}{\partial x}}{\sqrt{\det\hat{\varepsilon}(\hat{\varepsilon}^{-1})_{ik}(\mathbf{r}-\mathbf{r}')_i(\mathbf{r}-\mathbf{r}')_k}}\right]. \tag{2.9}$$

Here

$$B_1 = K_{22}\sin^2\theta\cos^2\theta + K_{33}\sin^4\theta,$$
$$B_2 = K_{11}\sin^2\theta,$$
$$B_3 = K_{22}\sin^4\theta + K_{33}\sin^2\theta\cos^2\theta,$$
$$B_{13} = \sin^2\theta\cos\theta(K_{33} - K_{22}). \tag{2.10}$$

Now we discuss the approximations used in Eqs. (2.8) and (2.9). As it was predicted theoretically in Ref. [19] and shown

experimentally in Refs. [20,21], the angular φ fluctuations can be large in thin films. Thus the free energy described by Eq. (2.9) is not valid for very thin films. In accord with Refs. [19–21], we estimate the **c**-director fluctuations in the framework of the one-constant approximation $K_{11} = K_{22} = K_{33} = K$:

$$\langle \varphi^2 \rangle \approx \frac{k_B T}{\pi K L} \ln \frac{d}{a}. \tag{2.11}$$

Here k_B is the Boltzmann constant, T is the temperature, d is the linear size of the film, and a is a spatial parameter of the order of the length of the molecule. Performing estimations, we use the typical set of parameters $k_B T = 4 \times 10^{-21}$ J, $K = 10^{-11}$ N, $d = 1$ mm, and $a = 3$ nm. Thus we obtain, from Eq. (2.11),

$$\langle \varphi^2 \rangle \approx 0.75 \quad \text{for } L = 2 \text{ nm},$$
$$\langle \varphi^2 \rangle \approx 0.075 \quad \text{for } L = 20 \text{ nm},$$
$$\langle \varphi^2 \rangle \approx 0.0015 \quad \text{for } L = 1 \ \mu\text{m}. \tag{2.12}$$

Terms of fourth order φ^4 are omitted in Eq. (2.9); therefore, this expression cannot be applied for very thin films.

On the other hand, very thin films are effectively uniform in the z direction. This supposition is correct if the film thickness is much smaller than the correlation length along the layer normal. Thus it is important to obtain the dependence of the correlation function of the angle φ fluctuations on the distance in the z direction. We can estimate this dependence in the bulk sample in the framework of the one-constant approximation. If we neglect the Coulomb interaction for simplicity we can obtain the fluctuating part of the free energy in the following form:

$$\delta F = \frac{1}{2} \int d\mathbf{r}[B(\nabla\varphi)^2 + PE\varphi^2]. \tag{2.13}$$

In this case correlation function is well known [22]:

$$\langle \varphi(\mathbf{r})\varphi(\mathbf{r}') \rangle = \frac{k_B T}{4\pi B r} \exp\left(-\sqrt{\frac{PE}{B}}\,r\right), \tag{2.14}$$

where $r = |\mathbf{r} - \mathbf{r}'|$ and $B = K \sin^2\theta$. It is necessary to note that this expression cannot be used in the case $r = 0$ because Eq. (2.13) is valid for long-range fluctuations only. If the distance along the layer normal is much larger than the width of layer Eq. (2.14) can be used to estimate the dependence of the correlation function $\langle \varphi(\mathbf{r}_\perp,z)\varphi(\mathbf{r}_\perp,z') \rangle$ on $|z - z'|$. In estimations we use the same set of parameters as before and $E = 10$ V/cm, $P = 20$ stC/cm$^2 = 6.67$ nC/cm^2, and $\theta = 15°$. Thus we obtain, from Eq. (2.14),

$$\langle \varphi(\mathbf{r}_\perp,z)\varphi(\mathbf{r}_\perp,z') \rangle \approx 0.024 \quad \text{for } |z - z'| = 20 \text{ nm},$$
$$\langle \varphi(\mathbf{r}_\perp,z)\varphi(\mathbf{r}_\perp,z') \rangle \approx 0.00035 \quad \text{for } |z - z'| = 1 \ \mu\text{m}. \tag{2.15}$$

Comparing the estimations (2.15) and (2.12), we conclude that in relatively thick films fluctuations of orientation can significantly change along the layer normal. Therefore, we will consider the anisotropic three-dimensional Coulomb interaction of polarization charges. In what follows we will perform numerical calculations for films with thicknesses $L = 20$ nm and $L = 1 \ \mu$m.

We assume that the size of the film in the plane of the smectic layers is much larger than the film thickness L. In this case it is convenient to use a Fourier two-dimensional representation for coordinates (x,y):

$$\varphi_{\mathbf{q}_\perp}(z) = \int d\mathbf{r}_\perp e^{-i\mathbf{q}_\perp \cdot \mathbf{r}_\perp} \varphi(\mathbf{r}_\perp,z),$$
$$\varphi(\mathbf{r}_\perp,z) = \frac{1}{(2\pi)^2} \int d\mathbf{q}_\perp e^{i\mathbf{q}_\perp \cdot \mathbf{r}_\perp} \varphi_{\mathbf{q}_\perp}(z). \tag{2.16}$$

Integrating by parts the terms with coefficients B_3 and B_{13} in Eq. (2.9) we obtain

$$\delta F = \frac{1}{2(2\pi)^2} \int d\mathbf{q}_\perp \left[\int_{-L/2}^{L/2} dz\, \varphi_{\mathbf{q}_\perp}^*(z) \left(B_1 q_x^2 + B_2 q_y^2 + PE - B_3 \frac{\partial^2}{\partial z^2} - 2B_{13} i q_x \frac{\partial}{\partial z} \right) \varphi_{\mathbf{q}_\perp}(z) \right.$$
$$\left. + \frac{2\pi P^2 q_x^2}{\bar\varepsilon Q(\mathbf{q}_\perp)} \int_{-L/2}^{L/2} dz \int_{-L/2}^{L/2} dz' e^{[iAq_x(z-z') - Q(\mathbf{q}_\perp)|z-z'|]} \varphi_{\mathbf{q}_\perp}^*(z')\varphi_{\mathbf{q}_\perp}(z) + \left(B_3 \varphi_{\mathbf{q}_\perp}^*(z) \frac{\partial \varphi_{\mathbf{q}_\perp}(z)}{\partial z} + 2B_{13} i q_x \varphi_{\mathbf{q}_\perp}(z)\varphi_{\mathbf{q}_\perp}^*(z) \right)\Big|_{-L/2}^{L/2} \right]. \tag{2.17}$$

Here

$$A = \frac{\varepsilon_3 - \varepsilon_1}{\bar\varepsilon} \sin\theta \cos\theta,$$
$$Q(\mathbf{q}_\perp) = \sqrt{\frac{\varepsilon_1 \varepsilon_3}{\bar\varepsilon^2} q_x^2 + \frac{\varepsilon_2}{\bar\varepsilon} q_y^2},$$
$$\bar\varepsilon = \varepsilon_1 \sin^2\theta + \varepsilon_3 \cos^2\theta. \tag{2.18}$$

The first term in the second line in Eq. (2.17) describes the input of the Coulomb interaction of polarization charges, which is derived in the Appendix.

III. CORRELATION FUNCTION

The fluctuations of the **c**-director are shown to be completely determined by the fluctuations of the angle φ, within the approximations considered. Thus we determine the angular correlation function

$$g_{\mathbf{q}_\perp}(z,z') = \int d\mathbf{r}_\perp e^{-i\mathbf{q}_\perp \cdot \mathbf{r}_\perp} \langle \varphi(\mathbf{r}_\perp,z)\varphi(\mathbf{0},z') \rangle, \tag{3.1}$$

where the angular brackets denote statistical averaging. In order to calculate the correlation function $g_{\mathbf{q}_\perp}(z,z')$ it is convenient to represent the distortion free energy (2.17) in

a quadratic form

$$\delta F = \tfrac{1}{2}(\varphi, \hat{M}\varphi),\qquad(3.2)$$

or, explicitly,

$$\delta F = \frac{1}{2(2\pi)^2}\int d\mathbf{q}_\perp \int_{-L/2}^{L/2} dz\, \varphi^*_{\mathbf{q}_\perp}(z)\int_{-L/2}^{L/2} dz' \left\{\delta(z-z')\left(B_1 q_x^2 + B_2 q_y^2 + PE - B_3\frac{\partial^2}{\partial z^2} - 2B_{13} i q_x \frac{\partial}{\partial z}\right)\right.$$
$$\left. + \frac{2\pi P^2 q_x^2}{\bar{\varepsilon} Q(\mathbf{q}_\perp)}\exp\left(i A q_x(z-z') - Q(\mathbf{q}_\perp)|z-z'|\right) + 4\delta(z-z')\left[\delta\left(z'-\frac{L}{2}\right) - \delta\left(z'+\frac{L}{2}\right)\right]\left(B_3\frac{\partial}{\partial z'} + 2B_{13}iq_x\right)\right\}\varphi_{\mathbf{q}_\perp}(z').$$
$$(3.3)$$

Here the expression in large curly brackets is the kernel of the operator $\hat{M}$. The correlation function $g_{\mathbf{q}_\perp}(z,z')$ is the kernel of the inverse operator $\hat{M}^{-1}$ multiplied by $k_B T$. So the correlation function should obey the equation

$$\hat{M}g = k_B T \delta(z-z'),\qquad(3.4)$$

or in explicit form

$$\left(B_1 q_x^2 + B_2 q_y^2 + PE - B_3\frac{\partial^2}{\partial z^2} - 2B_{13}iq_x\frac{\partial}{\partial z}\right)g_{\mathbf{q}_\perp}(z,z') + \frac{2\pi P^2 q_x^2}{\bar{\varepsilon}Q(\mathbf{q}_\perp)}\int_{-L/2}^{L/2} dz''\, e^{[iAq_x(z-z'')-Q(\mathbf{q}_\perp)|z-z''|]}g_{\mathbf{q}_\perp}(z'',z')$$
$$+4\left[\delta\left(z-\frac{L}{2}\right) - \delta\left(z+\frac{L}{2}\right)\right]\left(B_3\frac{\partial}{\partial z} + 2B_{13}iq_x\right)g_{\mathbf{q}_\perp}(z,z') = k_B T\delta(z-z').\qquad(3.5)$$

The solution of this equation can be obtained in a way similar to that used in Refs. [13,14]. We divide the search for a solution of Eq. (3.5) into several stages. In the first stage we replace this integro-differential equation by a set of differential equations with boundary conditions. For this purpose we introduce the following auxiliary function:

$$v_{\mathbf{q}_\perp}(z,z') = Q(\mathbf{q}_\perp)\int_{-L/2}^{L/2} dz''\, e^{[iAq_x(z-z'')-Q(\mathbf{q}_\perp)|z-z''|]}g_{\mathbf{q}_\perp}(z'',z').\qquad(3.6)$$

Thus, instead of Eq. (3.5), we are to solve the following system of differential equations:

$$\left(-\partial_z^2 - 2b_{13}iq_x\partial_z + b_1 q_x^2 + b_2 q_y^2 + \frac{PE}{B_3}\right)g_{\mathbf{q}_\perp}(z,z') + \frac{2\pi}{B_3\bar{\varepsilon}}\left(\frac{Pq_x}{Q(\mathbf{q}_\perp)}\right)^2 v_{\mathbf{q}_\perp}(z,z') = \frac{k_B T}{B_3}\delta(z-z'),$$
$$\left[\partial_z^2 - 2iAq_x\partial_z - Q^2(\mathbf{q}_\perp) - A^2 q_x^2\right]v_{\mathbf{q}_\perp}(z,z) + 2Q^2(\mathbf{q}_\perp)g_{\mathbf{q}_\perp}(z,z) = 0.\qquad(3.7)$$

Here we used the notation

$$\partial_z = \frac{\partial}{\partial z},\quad \partial_z^2 = \frac{\partial^2}{\partial z^2},\quad b_1 = \frac{B_1}{B_3},\quad b_2 = \frac{B_2}{B_3},\quad b_{13} = \frac{B_{13}}{B_3}.\qquad(3.8)$$

Inside the film $-L/2 < z < L/2$ the first of Eqs. (3.7) coincides with Eq. (3.5) and the second is obtained by differentiating the auxiliary function (3.6).

Boundary conditions for Eq. (3.7) take the form

$$\partial_z g_{\mathbf{q}_\perp}\left(z=\pm\frac{L}{2},z'\right) + 2iq_x b_{13}g_{\mathbf{q}_\perp}\left(z=\pm\frac{L}{2},z'\right) = 0,$$
$$\partial_z v_{\mathbf{q}_\perp}\left(z=\pm\frac{L}{2},z'\right) + [\pm Q(\mathbf{q}_\perp) - iAq_x]v_{\mathbf{q}_\perp}\left(z=\pm\frac{L}{2},z'\right) = 0.\qquad(3.9)$$

The first boundary condition allows us to remove the δ-function term from the left-hand side of Eq. (3.5). The second condition in Eq. (3.9) appears as a result of differentiation of the auxiliary function (3.6) at the film boundaries.

In the second stage we rewrite the system (3.7) with boundary conditions (3.9) in a vector form as it was done in Refs. [13,14]. Introducing a four-dimensional vector

$$\mathbf{W} = [g,v,\partial_z g,(\partial_z - 2iAq_x)v]^t\qquad(3.10)$$

and the vector

$$\mathbf{D} = \frac{k_B T}{B_3}(0,0,1,0)^t,\qquad(3.11)$$

where t denotes the transposition, we can rewrite the system (3.7) as

$$(\partial_z - \hat{H})\mathbf{W} = -\mathbf{D}\delta(z-z').\qquad(3.12)$$

Here the matrix $\hat{H}$ is

$$\hat{H} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & h_{22} & 0 & 1 \\ h_{31} & h_{32} & h_{33} & 0 \\ h_{41} & h_{42} & 0 & 0 \end{pmatrix},\qquad(3.13)$$

with the matrix elements

$$h_{22} = 2iAq_x, \quad h_{31} = b_1 q_x^2 + b_2 q_y^2 + \frac{PE}{B_3},$$

$$h_{32} = \frac{2\pi}{B_3 \bar{\varepsilon}} \left(\frac{Pq_x}{Q(\mathbf{q}_\perp)} \right)^2, \quad h_{33} = -2ib_{13}q_x,$$

$$h_{41} = -2Q^2(\mathbf{q}_\perp), \quad h_{42} = Q^2(\mathbf{q}_\perp) + A^2 q_x^2. \quad (3.14)$$

The boundary conditions (3.9) are rewritten as

$$\hat{\Gamma}_\sigma \mathbf{W}\left(z = \sigma \frac{L}{2}, z' \right) = 0, \quad (3.15)$$

where $\sigma = \pm$ corresponds to $z = \pm L/2$ and

$$\hat{\Gamma}_\sigma = \begin{pmatrix} 2iq_x b_{13} & 0 & 1 & 0 \\ 0 & \sigma Q(\mathbf{q}_\perp) + iAq_x & 0 & 1 \end{pmatrix}. \quad (3.16)$$

In the third stage we solve Eq. (3.12) with boundary conditions (3.16). Obviously, the linearly independent vectors

$$\mathbf{w}_1^{(\sigma)} = (-1, 0, 2ib_{13}q_x, 0)^t,$$

$$\mathbf{w}_2^{(\sigma)} = [0, -1, 0, \sigma Q(\mathbf{q}_\perp) + iAq_x]^t \quad (3.17)$$

satisfy these boundary conditions. Now the solution of Eq. (3.12) with the boundary conditions (3.16) can be written as follows:

$$\mathbf{W}_{\mathbf{q}_\perp}(z, z') = \begin{cases} \mathbf{W}_{\mathbf{q}_\perp}^{(+)}(z, z') & \text{for } z > z' \\ \mathbf{W}_{\mathbf{q}_\perp}^{(-)}(z, z') & \text{for } z < z', \end{cases} \quad (3.18)$$

where

$$\mathbf{W}_{\mathbf{q}_\perp}^{(\sigma)}(z, z') = e^{[z - \sigma(L/2)]\hat{H}} \left[\mathbf{w}_1^{(\sigma)} C_1^{(\sigma)}(z') + \mathbf{w}_2^{(\sigma)} C_2^{(\sigma)}(z') \right]. \quad (3.19)$$

In order to find the unknown functions $C_1^{(\sigma)}(z')$ and $C_2^{(\sigma)}(z')$ we insert Eq. (3.19) into Eq. (3.12) and integrate over z the resulting equation in the infinitely small region: $[z' - \varepsilon, z' + \varepsilon]$, $\varepsilon \to +0$. As a result we obtain the linear algebraic equation for functions $C_1^{(\sigma)}(z')$ and $C_2^{(\sigma)}(z')$:

$$C_1^{(+)}(z')\mathbf{w}_1^{(+)} + C_2^{(+)}(z')\mathbf{w}_2^{(+)} - C_1^{(-)}(z')e^{L\hat{H}}\mathbf{w}_1^{(-)}$$

$$- C_2^{(-)}(z')e^{L\hat{H}}\mathbf{w}_2^{(-)} = -e^{[(L/2)-z']\hat{H}}\mathbf{D}. \quad (3.20)$$

Suggesting that the determinant of the system is nonzero $\det \hat{S} \neq 0$, where the matrix $\hat{S}$ is composed of the vectors $\mathbf{w}_1^{(+)}, \mathbf{w}_2^{(+)}, -e^{L\hat{H}}\mathbf{w}_1^{(-)}$, and $-e^{L\hat{H}}\mathbf{w}_2^{(-)}$, i.e.,

$$\hat{S} = (\mathbf{w}_1^{(+)}, \mathbf{w}_2^{(+)}, -e^{L\hat{H}}\mathbf{w}_1^{(-)}, -e^{L\hat{H}}\mathbf{w}_2^{(-)}), \quad (3.21)$$

we obtain

$$\begin{pmatrix} C_1^{(+)}(z') \\ C_2^{(+)}(z') \\ C_1^{(-)}(z') \\ C_2^{(-)}(z') \end{pmatrix} = -\hat{S}^{-1} e^{[(L/2)-z']\hat{H}} \mathbf{D}. \quad (3.22)$$

Substituting Eq. (3.22) into (3.18) and (3.19), we obtain the vector $\mathbf{W}_{\mathbf{q}_\perp}(z, z')$; its first component presents the correlation function $g_{\mathbf{q}_\perp}(z, z')$. The obtained correlation function permits us to calculate the angular dependence of the light scattering intensity.

IV. LIGHT SCATTERING

Now we analyze the effect of the Coulomb interaction anisotropy upon the light scattering from the free-standing Sm-C^* film. In this system the scattering is caused by the permittivity tensor fluctuations and consequently is due to the fluctuations of the **c**-director. So in lowest approximation with respect to the angle φ we can write

$$\delta \tilde{\varepsilon}_{\alpha\beta} = \left[\Delta\tilde{\varepsilon} \left(\frac{\partial n_\alpha}{\partial \varphi} n_\beta + n_\alpha \frac{\partial n_\beta}{\partial \varphi} \right)_{\varphi=0} \right.$$

$$\left. + \delta\tilde{\varepsilon} \left(\frac{\partial p_\alpha}{\partial \varphi} p_\beta + p_\alpha \frac{\partial p_\beta}{\partial \varphi} \right)_{\varphi=0} \right] \varphi. \quad (4.1)$$

Here we used the notation $\tilde{\varepsilon}_{\alpha\beta}$ (instead of $\varepsilon_{\alpha\beta}$) as long as $\tilde{\varepsilon}_{\alpha\beta}$ is the permittivity tensor at the optical frequency. In contrast, in the description of the Coulomb interaction of the polarization charges we must use the low-frequency permittivity tensor, because the characteristic time of the **c**-director fluctuations is much larger than the period of light oscillations. In Eq. (4.1) we used also $\Delta\tilde{\varepsilon} = \tilde{\varepsilon}_3 - \tilde{\varepsilon}_1$ and $\delta\tilde{\varepsilon} = \tilde{\varepsilon}_2 - \tilde{\varepsilon}_1$.

To understand how the anisotropy of the Coulomb interaction contributes to the light scattering measurements, we perform calculations within the first Born approximation, neglecting therewith the difference between ordinary and extraordinary beams. In this case the scattered intensity I can be presented as follows [23–25]:

$$I = \frac{VI_0 k^4}{(4\pi R)^2} e_\alpha^{(s)} e_\beta^{(s)} W_{\alpha\nu\beta\mu}(\mathbf{q}_{sc}) e_\nu^{(i)} e_\mu^{(i)}. \quad (4.2)$$

Here V is the scattering volume, I_0 is the intensity of the incident beam, k is the wave number of incident radiation, R is the distance between the scattering volume and the point of observation, $\mathbf{e}^{(i)}$ and $\mathbf{e}^{(s)}$ are the unit polarization vectors of incident and scattered waves, respectively, and $\mathbf{q}_{sc} = \mathbf{k}_s - \mathbf{k}_i$ is the scattering vector. Vectors $\mathbf{k}_i$ and $\mathbf{k}_s$ are the wave vectors of the incident and the scattered beams, respectively, and $W_{\alpha\nu\beta\mu}(\mathbf{q}_{sc})$ is the Fourier image of the permittivity correlation function at the optical frequency, i.e.,

$$W_{\alpha\nu\beta\mu}(\mathbf{q}_{sc}) = \frac{1}{L} \int_{-L/2}^{L/2} dz \int_{-L/2}^{L/2} dz' e^{-iq_z(z-z')}$$

$$\times \int d\mathbf{r}_\perp e^{-i\mathbf{q}_\perp \cdot \mathbf{r}_\perp} \langle \delta\tilde{\varepsilon}_{\alpha\nu}(\mathbf{r}_\perp, z) \delta\tilde{\varepsilon}_{\beta\mu}(\mathbf{0}, z') \rangle, \quad (4.3)$$

where the transversal and longitudinal components of the scattering vector are introduced explicitly $\mathbf{q}_{sc} = (\mathbf{q}_\perp, q_z)$. Combining Eqs. (4.1)–(4.3) with Eq. (3.1), we obtain

$$I \sim \left\{ e_\alpha^{(s)} \left[\Delta\tilde{\varepsilon} \left(\frac{\partial n_\alpha}{\partial \varphi} n_\beta + n_\alpha \frac{\partial n_\beta}{\partial \varphi} \right)_{\varphi=0} \right. \right.$$

$$\left. \left. + \delta\tilde{\varepsilon} \left(\frac{\partial p_\alpha}{\partial \varphi} p_\beta + p_\alpha \frac{\partial p_\beta}{\partial \varphi} \right)_{\varphi=0} \right] e_\beta^{(i)} \right\}^2 G_{\mathbf{q}_{sc}}, \quad (4.4)$$

where

$$G_{\mathbf{q}_{sc}} = \frac{1}{L} \int_{-L/2}^{L/2} dz \int_{-L/2}^{L/2} dz' e^{-iq_z(z-z')} g_{\mathbf{q}_\perp}(z, z'). \quad (4.5)$$
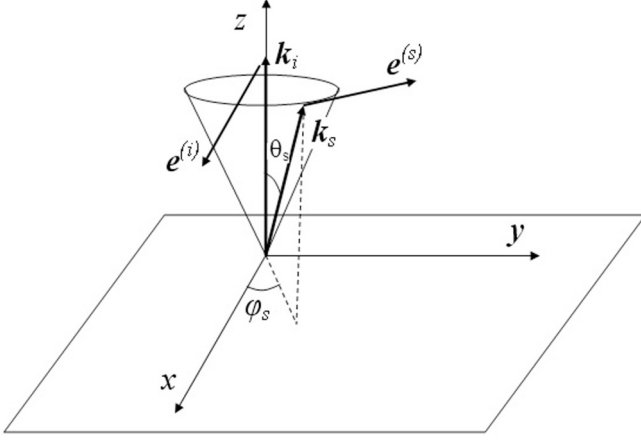
FIG. 2. Geometry of the light scattering experiment. The external electric field **E** is directed along the y axis.

In the numerical calculations we put the incident beam being normal to the film surface, $\mathbf{k}_i = (0,0,k)^t$, with the polarization $\mathbf{e}^{(i)} = (1,0,0)^t$. The polarization of the scattered beam can be written as $\mathbf{e}^{(s)} = (-\sin\varphi_s, \cos\varphi_s, 0)^t$ and the wave vector as $\mathbf{k}_s = (k\sin\theta_s\cos\varphi_s, k\sin\theta_s\sin\varphi_s, k\cos\theta_s)^t$, where θ_s and φ_s are the polar and azimuthal angles of the scattered radiation, as shown in Fig. 2.

For such a geometry the light scattering intensity can be written as

$$I \sim (\Delta\tilde{\varepsilon}\sin^2\theta - \delta\tilde{\varepsilon})^2 \cos^2\varphi_s G_{\mathbf{q}_{sc}}. \tag{4.6}$$

It should be noted that the angular dependence of scattering intensity is completely determined by the last two factors in Eq. (4.6), while the first factor is determined by the material constants, i.e.,

$$I \sim \cos^2\varphi_s G_{\mathbf{q}_{sc}}. \tag{4.7}$$

The obtained results are shown in Figs. 3 and 4. The calculations are carried out with the following set of parameters: $k_B T = 4 \times 10^{-21}$ J, $E = 10$ V/cm $= 3.34 \times 10^{-2}$ stV/cm, $k = 10^5$ cm^{-1}, $K_{11} = 0.7 \times 10^{-11}$ N, $K_{22} = 0.43 \times 10^{-11}$ N, and $K_{33} = 1.7 \times 10^{-11}$ N. We take relatively small values of spontaneous polarization. In Fig. 3 the plots are derived for the films with different combinations of the principal values of the permittivity tensor, but with the same average value of permittivity equal to 5. The angular dependence of light scattering intensity in the plane of the normal **N** and equilibrium **c**-director is shown in Figs. 3(a) and 3(b). In the experimental geometry shown in Fig. 2, the light scattering intensity is strongly dependent on the orientation of the plane of scattering. In particular, in the plane perpendicular to the **c**-director the scattered intensity will be zero for all $\theta_s > 0$. This is a consequence of the presence of the polarization factor $\cos^2\varphi_s$ in Eq. (4.7). In Fig. 4 the curves are obtained for a relatively thick film with $L = 1$ μm and $\theta_s = 10°$.

The most interesting results can be obtained in thick films in the case $\varepsilon_2 > \varepsilon_1\varepsilon_3/\bar{\varepsilon}$, as in Ref. [15]. The function $Q(\mathbf{q}_\perp)$ can be rewritten as

$$Q = \frac{k\sin\theta_s}{\bar{\varepsilon}}\sqrt{\varepsilon_1\varepsilon_3 + (\varepsilon_2\bar{\varepsilon} - \varepsilon_1\varepsilon_3)\sin^2\varphi_s}. \tag{4.8}$$
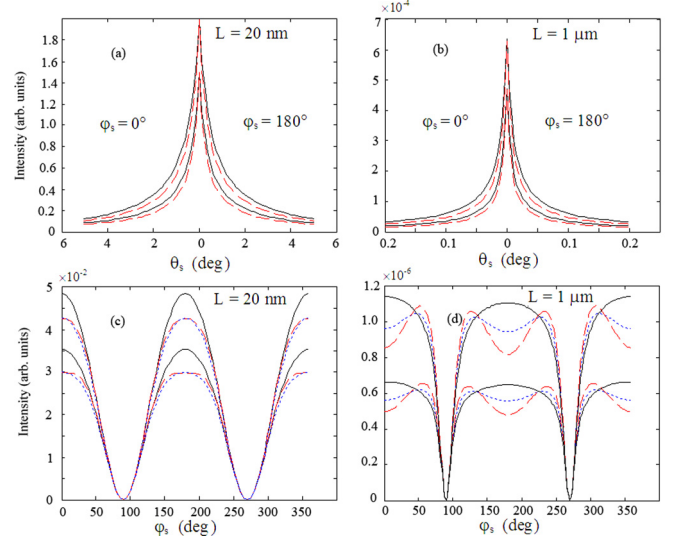

FIG. 3. Light scattering from free-standing films of various thicknesses for the geometry shown in Fig. 2. (a) and (b) Light scattering intensity against the polar angle θ_s in the xz plane. For the two upper curves $P = 15$ stC/cm$^2 = 5$ nC/cm^2 and for the two bottom curves $P = 20$ stC/cm$^2 = 6.67$ nC/cm^2. The solid black lines correspond to $\varepsilon_1 = \varepsilon_2 = \varepsilon_3 = 5$; the dashed red lines are for the biaxial system with $\varepsilon_1 = 3$, $\varepsilon_2 = 7$, and $\varepsilon_3 = 5$ and for the biaxial system with $\varepsilon_1 = 5$, $\varepsilon_2 = 7$, and $\varepsilon_3 = 3$. (c) and (d) Dependence of the scattered light intensity on the azimuth angle φ_s for the fixed polar angle $\theta_s = 10°$; $P = 15$ stC/cm$^2 = 5$ nC/cm^2 for three upper curves and $P = 20$ stC/cm$^2 = 6.67$ nC/cm^2 for three bottom curves. The solid black lines correspond to $\varepsilon_1 = \varepsilon_2 = \varepsilon_3 = 5$; the dashed red lines are for the biaxial system with $\varepsilon_1 = 3$, $\varepsilon_2 = 7$, and $\varepsilon_3 = 5$; and the dotted blue lines are for the biaxial system with $\varepsilon_1 = 5$, $\varepsilon_2 = 7$, and $\varepsilon_3 = 3$.

At a constant value of the angle θ_s an increase in the angle φ_s from zero leads to an increase of the function Q. In this case, the correlation function $G_{\mathbf{q}_{sc}}$ also increases. At the same time, the geometric multiplier $\cos^2\varphi_s$ in Eq. (4.7) is decreasing. Thus, in the case $\varepsilon_2 > \varepsilon_1\varepsilon_3/\bar{\varepsilon}$ the dependence of the scattered light intensity on the angle φ_s is nonmonotonic on the interval $0 \leqslant \varphi_s \leqslant \pi/2$. Explicitly, these dependences are shown in Figs. 3(d), 4(c), and 4(d). In the case $\varepsilon_2 \leqslant \varepsilon_1\varepsilon_3/\bar{\varepsilon}$ the dependence of the scattered light intensity on the angle φ_s is monotonic for $0 \leqslant \varphi_s \leqslant \pi/2$. As we can see from Figs. 4(a) and 4(b), the angular dependences of the correlation function $G_{\mathbf{q}_{sc}}$ in the system with $\varepsilon_1 = \varepsilon_3 = 3$ and $\varepsilon_2 = 7$ are very similar to the dependences in the system with $\varepsilon_1 = \varepsilon_2 = 3$ and $\varepsilon_3 = 7$; however, according to Eq. (4.7), there is "competition" between the geometric multiplier $\cos^2\varphi_s$ and the correlation function $G_{\mathbf{q}_{sc}}$. It turns out that multiplying by a geometric factor $\cos^2\varphi_s$ allows obvious small differences of the correlation functions, shown in Figs. 4(a) and 4(b). Thus we can see that the angular dependences of the light scattering intensity in the systems with $\varepsilon_1 = \varepsilon_3 = 3$ and $\varepsilon_2 = 7$ and with $\varepsilon_1 = \varepsilon_2 = 3$ and $\varepsilon_3 = 7$ are quite different, as shown in Figs. 4(c) and 4(d). For films with the same average permittivity, the light intensity may differ by about 20% at the same angle of scattering. Also, we can see that when $P \to 0$ the correlation function $G_{\mathbf{q}_{sc}}$ and the scattered intensity become
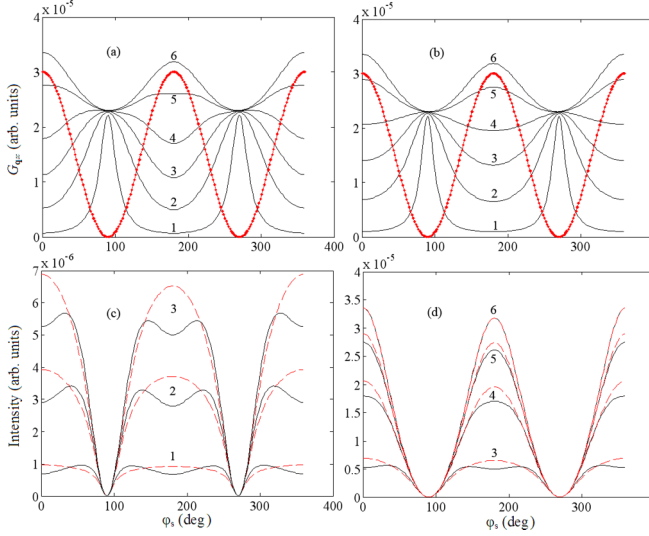
FIG. 4. (a) and (b) Angular dependence of the Fourier image of the **c**-director fluctuation correlation function $G_{\mathbf{q}_{sc}}$ for various values of spontaneous polarization and (a) $\varepsilon_1 = \varepsilon_3 = 3$ and $\varepsilon_2 = 7$ and (b) $\varepsilon_1 = \varepsilon_2 = 3$ and $\varepsilon_3 = 7$. The solid black lines 1, 2, 3, 4, 5, and 6 correspond to $P = 15, 5, 3, 2, 1$, and 0 stC/cm^2, respectively. The dotted red lines show the geometrical factor $\sim\cos^2\varphi_s$ in Eq. (4.7). (c) and (d) Angular dependence of the light scattering intensity for various values of spontaneous polarization. The solid black lines and dashed red lines 1, 2, 3, 4, 5, and 6 correspond to $P = 15, 7, 5, 2, 1$, and 0 stC/cm^2, respectively. The solid black lines correspond to $\varepsilon_1 = \varepsilon_3 = 3$ and $\varepsilon_2 = 7$. The dashed red lines correspond to $\varepsilon_1 = \varepsilon_2 = 3$ and $\varepsilon_3 = 7$.

independent of the anisotropy of the Coulomb interaction of polarization charges. The increase in magnitude of the spontaneous polarization leads to a decrease of the correlation function $G_{\mathbf{q}_{sc}}$ and the intensity of scattered light. We can say that the system becomes more rigid with increasing spontaneous polarization. In addition, the anisotropy of the Coulomb interaction between polarization charges should lead to additional anisotropy in light scattering, as shown in Figs. 3 and 4. The obtained results are consistent with those found earlier for bulk samples in Ref. [17].

V. SUMMARY

The polarization charges in ferroelectric smectic liquid crystals have attracted the attention of researchers for more than a decade. This interest is caused by the fact that the polarization charges appear mainly due to spatial fluctuations of spontaneous polarization **P**. In turn these charges can interact with each other and with impurity particles. This interaction affects primarily the orientation of the director fluctuations. So the influence of polarization charges can be seen in experiments of light scattering from Sm-C^* films. In this study we analyzed theoretically the role of the Coulomb interaction anisotropy in free-standing Sm-C^* films. For a film of finite thickness, the calculations were performed, taking into account the inhomogeneity of the director fluctuations throughout the film's volume. Deriving the correlation function of the thermal **c**-director fluctuations, we have calculated the angular dependences of the scattered light intensity. We have

shown that the dependence of the scattered light intensity on the azimuth angle becomes nonmonotonic in relatively thick films, in the presence of the Coulomb interaction anisotropy. We think such a dependence could be observed experimentally.

APPENDIX: CALCULATION OF THE COULOMB TERM

The last line in Eq. (2.9) is the contribution of the Coulomb interaction of polarization charges to the free energy:

$$F_C = \frac{P^2}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\frac{\partial \varphi(\mathbf{r}')}{\partial x'} \frac{\partial \varphi(\mathbf{r})}{\partial x}}{\sqrt{\det \hat{\varepsilon} (\hat{\varepsilon}^{-1})_{ik} (\mathbf{r} - \mathbf{r}')_i (\mathbf{r} - \mathbf{r}')_k}}. \quad (A1)$$

Introducing the notation

$$f(\mathbf{r}_\perp, z) = f(\mathbf{r}) = \frac{1}{\sqrt{\det \hat{\varepsilon} (\hat{\varepsilon}^{-1})_{ik} (\mathbf{r})_i (\mathbf{r})_k}} \quad (A2)$$

and performing a Fourier transform in the x-y plane, we have

$$F_C = \frac{P^2}{2} \int_{-L/2}^{L/2} dz \int_{-L/2}^{L/2} dz' \int \frac{d\mathbf{q}_\perp}{(2\pi)^2} q_x^2 f_{-\mathbf{q}_\perp}(z - z')$$
$$\times \varphi_{\mathbf{q}_\perp}(z) \varphi_{\mathbf{q}_\perp}^*(z'). \quad (A3)$$

To calculate the function $f_{-\mathbf{q}_\perp}(z - z')$ we can use the result obtained in [17] in infinite three-dimensional space

$$f_{-\mathbf{q}} = \frac{4\pi \bar{\varepsilon}}{\varepsilon_1 \varepsilon_3 q_x^2 + \varepsilon_2 \bar{\varepsilon} q_y^2 + [q_x(\varepsilon_3 - \varepsilon_1) \sin\theta \cos\theta + q_z \bar{\varepsilon}]^2}. \quad (A4)$$

If we replace q_z by $-q_z$ in the function $f_{-\mathbf{q}_\perp, -q_z}$ given by Eq. (A4) we get the function $f_{-\mathbf{q}_\perp, q_z}$, which allows us to find $f_{-\mathbf{q}_\perp}(z)$ via

$$f_{-\mathbf{q}_\perp}(z) = \int_{-\infty}^{+\infty} \frac{dq_z}{2\pi} e^{iq_z z} f_{-\mathbf{q}_\perp, q_z}. \quad (A5)$$

The function $f_{-\mathbf{q}_\perp, q_z}$ has two poles at

$$q_z = A q_x \pm i Q(\mathbf{q}_\perp), \quad (A6)$$

where A and $Q(\mathbf{q}_\perp)$ are given in Eq. (2.18). Hence the integral in Eq. (A5) is reduced to the contour integral on the complex plane and can be easily calculated by residues. As a result we obtain

$$f_{-\mathbf{q}_\perp}(z) = \frac{2\pi}{\bar{\varepsilon} Q(\mathbf{q}_\perp)} \exp[i A q_x z - Q(\mathbf{q}_\perp) |z|]. \quad (A7)$$

If the expression given by Eq. (A7) is substituted into the formula (A3) we obtain the Coulomb term in the expression (2.17).

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