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Liquid Crystals in Electric Field

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We present a general theory of electric field effects in liquid crystals where the dielectric tensor depends on the orientation order. As applications, we examine (i) the director fluctuations in nematic states in an electric field and (ii) the deformation of the nematic order around a charged particle. Some predictions are made for these effects.

KEYWORDS: liquid crystals, ions, electric field, topological defects
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1. Introduction

Phase transitions occur in various systems in an electric field. To treat such problems we need to construct a Ginzburg–Landau free energy including electrostatic interactions in a static electric field.[1] The gross variables include the order parameter ψ, the polarization $\boldsymbol{p}$, and the charge density ρ. (Note $\psi = \boldsymbol{p}$ in ferroelectric systems.) In this letter we present such a theory for liquid crystals in nematic states,[2] since there seems to be no systematic theory for anisotropic fluids. More complex phases such as smectics should be treated in the future. As a new problem, we examine the deformation of the director around a charged particle. We shall see that the charge-induced orientation is intensified with decreasing particle radius R and/or increasing charge number Z, as in the case of the solvation of polar molecules around an ion.[3,4] It is worth noting that the nematic order around a neutral colloid particle or emulsion droplet has been extensively studied,[5,6] where the surface anchoring of a neutral particle can be achieved for a large radius because the penalty of the Frank free energy needs to be small.

2. Liquid Crystals between Capacitor Plates

In liquid crystals the order parameter ψ represents the orientation tensor near the isotropic–nematic transition or the director $\boldsymbol{n}$ in nematic states. We also use the vector notation $\boldsymbol{\rho}$ to represent the set $\{\rho_\alpha\}$ for the ion densities ρ_α ($\alpha = 1, 2, \ldots$). We divide the total free energy functional $F = F_{\rm ch} + F_{\rm st}$ into a chemical part $F_{\rm ch}$ and an electrostatic part $F_{\rm st}$. Here,

$$F_{\rm ch} = F_0\{\psi, \boldsymbol{\rho}\} + \int d\boldsymbol{r} \frac{1}{2} \sum \chi^{ij} p_i p_j. \tag{1}$$

The first contribution F_0 is assumed to be independent of $\boldsymbol{p}$, but there arises a coupling between ψ and $\boldsymbol{p}$ in the presence of flexoelectricity.[2,7] The tensor χ^{ij} is the inverse matrix of the the electric susceptibility tensor χ_{ij}. We shall see that the local dielectric tensor ε_{ij} is related to χ_{ij} as

$$\varepsilon_{ij} = \delta_{ij} + 4\pi\chi_{ij}. \tag{2}$$

In particular, for nematics the following form has been assumed in agreement with experiments,[2]

$$\varepsilon_{ij} = \varepsilon_0 \delta_{ij} + \varepsilon_1 n_i n_j. \tag{3}$$

The coefficients ε_0 and ε_1 satisfy $\varepsilon_0 > 1$ and $\varepsilon_0 + \varepsilon_1 > 1$ because χ_{ij} should be a positive-definite matrix from the thermodynamic stability.

Next we consider the electrostatic part $F_{\rm st}$. A typical experimental geometry is shown in Fig. 1(a), where we insert our system between two parallel metallic plates each with an area S and separated by a distance L. We assume $S^{1/2} \gg L$ and neglect the effects of edge fields. The z axis is taken as being perpendicular to the plates. Let the average surface charge density of the upper plate be $\sigma_{\rm ex}$ and that of the lower plate be $-\sigma_{\rm ex}$. The total charge on the upper plate is $Q = S\sigma_{\rm ex}$. The electric potential ϕ satisfies $\phi = 0$ at the bottom $z = 0$ and $\phi = \Phi$ at the top $z = L$, where Φ is the potential difference between the two capacitor plates. The electric induction $\boldsymbol{D} = \boldsymbol{E} + 4\pi\boldsymbol{p}$ satisfies

$$\nabla \cdot \boldsymbol{D} = -\nabla^2\phi + 4\pi\nabla \cdot \boldsymbol{p} = 4\pi\rho, \tag{4}$$

where $\rho = \sum_\alpha eZ_\alpha\rho_\alpha$ is the charge density with $Z_\alpha e$ being the charge of the ion species α. The boundary conditions at $z = 0$ and L are $E_x = E_y = 0$ and $D_z = -4\pi\sigma_{\rm ex}$.[8] With these relations $F_{\rm st}$ is

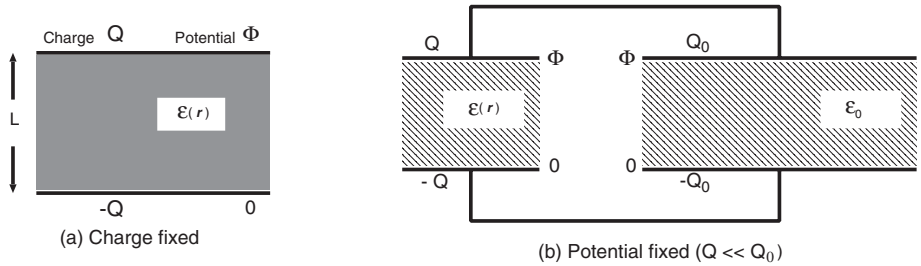

Fig. 1. (a) System of a capacitor and an inhomogeneous dielectric material at fixed capacitor charge Q. The potential difference Φ is a fluctuating quantity. (b) Two capacitors connected in parallel with charges Q and Q_0. The smaller one contains an inhomogeneous dielectric material, and the larger one a homogeneous dielectric material. In the limit $Q/Q_0 \to 0$, the potential difference Φ becomes fixed, while Q is a fluctuating quantity.

$$F_{\rm st} = \int {\rm d}\boldsymbol{r} \boldsymbol{E}^2/8\pi. \tag{5}$$

In fact, if infinitesimal deviations $\delta\boldsymbol{p}$, $\delta\rho$, and δQ are superimposed on $\boldsymbol{p}$, ρ, and Q, the incremental change in $F_{\rm st}$ is given by

$$\delta F_{\rm st} = \int {\rm d}\boldsymbol{r}[-\boldsymbol{E}\cdot\delta\boldsymbol{p} + \phi\delta\rho] + \Phi\delta Q, \tag{6}$$

where use is made of $\delta(\boldsymbol{E}^2) = -2\nabla\phi\cdot\delta\boldsymbol{D} - 8\pi\boldsymbol{E}\cdot\delta\boldsymbol{p} = -2\nabla(\phi\delta\boldsymbol{D}) + 8\pi(\phi\delta\rho - \boldsymbol{E}\cdot\delta\boldsymbol{p})$. The right-hand side of eq. (6) represents the increase of the electrostatic free energy due to the small variations of $\boldsymbol{p}$, ρ, and Q.

If we minimize F with respect to $\boldsymbol{p}$ for fixed ψ, $\boldsymbol{\rho}$, and Q, we require $\delta F/\delta\boldsymbol{p} = \boldsymbol{0}$. Then eqs. (1) and (6) give

$$\boldsymbol{p} = \overleftrightarrow{\boldsymbol{\chi}}\cdot\boldsymbol{E}, \quad \boldsymbol{D} = \overleftrightarrow{\boldsymbol{\varepsilon}}\cdot\boldsymbol{E}, \tag{7}$$

which yield eq. (2). Then we may rewrite F as $F = F_0 + F_{\rm e}$ with $F_{\rm e} = \int {\rm d}\boldsymbol{r}\sum_{ij}\chi^{ij}p_ip_j/2 + F_{\rm st}$, so

$$F_{\rm e} = \frac{1}{8\pi}\int {\rm d}\boldsymbol{r}\boldsymbol{E}\cdot\overleftrightarrow{\boldsymbol{\varepsilon}}\cdot\boldsymbol{E} = \frac{1}{8\pi}\int {\rm d}\boldsymbol{r}\boldsymbol{E}\cdot\boldsymbol{D}. \tag{8}$$

Under these relations and using $\delta\chi^{ij} = -\sum_{k\ell}\chi^{ik}\chi^{j\ell}\delta\chi_{k\ell}$ we obtain

$$\delta F = \delta F_0 + \int {\rm d}\boldsymbol{r}\left[\phi\delta\rho - \frac{1}{8\pi}\boldsymbol{E}\cdot\delta\overleftrightarrow{\boldsymbol{\varepsilon}}\cdot\boldsymbol{E}\right] + \Phi\delta Q. \tag{9}$$

From eqs. (4) and (7) the electric potential satisfies

$$-\nabla\cdot\overleftrightarrow{\boldsymbol{\varepsilon}}\cdot\nabla\phi = 4\pi\rho. \tag{10}$$

Thus ϕ and $\boldsymbol{E} = -\nabla\phi$ depend on the orientation order via eq. (3) and on ρ under each boundary condition. In the literature,[2] however, the electric field $\boldsymbol{E}$ in eq. (9) has been replaced by the average constant field $\boldsymbol{E}_0$, where $F = F_0 - \varepsilon_1\int {\rm d}\boldsymbol{r}(\boldsymbol{E}_0\cdot\boldsymbol{n})^2/8\pi + {\rm const} + O(\varepsilon_1^2)$. This is a first-order approximation with respect to ε_1 valid for $|\varepsilon_1| \ll \varepsilon_0$. If $\varepsilon_1 + \varepsilon_0$ is considerably smaller or larger than ε_0, there can be unexplored regimes of strong polarization anisotropy.

Thus the capacitor charge Q is a control parameter and the potential difference Φ is a fluctuating quantity dependent on $\boldsymbol{p}$ and $\boldsymbol{\rho}$. We may also control Φ using (i) a battery at a fixed potential difference or (ii) connecting another large capacitor in parallel to the capacitor containing our system as in Fig. 1(b). As will be discussed in the appendix, the appropriate free-energy functional is given by the Legendre transformation,[8]

$$G = F - \Phi Q = F_0 + \int {\rm d}\boldsymbol{r}\big[\phi\rho - \boldsymbol{E}\cdot\boldsymbol{D}/8\pi\big]. \tag{11}$$

From eq. (9) the incremental change in G is obtained as

$$\delta G = \delta F_0 + \int {\rm d}\boldsymbol{r}\left[\phi\delta\rho - \frac{1}{8\pi}\boldsymbol{E}\cdot\delta\overleftrightarrow{\boldsymbol{\varepsilon}}\cdot\boldsymbol{E}\right] - Q\delta\Phi. \tag{12}$$

3. Director Fluctuations in Nematic States

As the first application of our theory, we apply an electric field E_0 to a nematic liquid crystal considerably below the transition without charges ($\rho = 0$), where the orientation order is represented by the director vector $\boldsymbol{n}$. Here we do not perform the expansion with respect to ε_1. For simplicity, we assume that $\boldsymbol{n}$ is along the z-axis on the average under the homeotropic boundary condition and $\varepsilon_1 > 0$. If $\varepsilon_1 < 0$, the orientation along the z-axis becomes unstable with increasing E_0 above a critical value ($\propto L^{-1}$).[2] Then $\boldsymbol{n}$ is written as $\boldsymbol{e}_z + \delta\boldsymbol{n}$ with $\delta n_z = -[(\delta n_x)^2 + (\delta n_y)^2]/2$, where $\boldsymbol{e}_z$ is the unit vector along the z-axis and $\delta\boldsymbol{n}$ is the deviation nearly perpendicular to the z axis. By solving eq. (10) under eq. (3), we may expand the electrostatic free energy $F_{\rm e} = F - F_0$ in powers of $\delta\boldsymbol{n}$. The fluctuation contributions on the bilinear order are written as

$$\Delta F_{\rm e} = \frac{\varepsilon_1}{8\pi}E_0^2\int_{\boldsymbol{q}}\left[|\delta\boldsymbol{n}(\boldsymbol{q})|^2 + \frac{\varepsilon_1}{\varepsilon_0 + \varepsilon_1\hat{\boldsymbol{q}}_z^2}|\hat{\boldsymbol{q}}\cdot\delta\boldsymbol{n}(\boldsymbol{q})|^2\right], \tag{13}$$

where $\hat{\boldsymbol{q}} = q^{-1}\boldsymbol{q}$ represents the direction of $\boldsymbol{q}$ and $\boldsymbol{n}(\boldsymbol{q})$ is the Fourier transform of $\delta\boldsymbol{n}$. The wave number $|\boldsymbol{q}|$ is assumed to be much larger than the inverse system width L^{-1}. The large-scale fluctuations are omitted in eq. (13).

Expressing F_0 in terms of the Frank constants K_1, K_2, and K_3, we obtain the director correlation functions,

$$\frac{1}{k_{\rm B}T}\langle\delta n_i(\boldsymbol{q})\delta n_j(\boldsymbol{q})^*\rangle = \frac{\delta_{ij}}{r_2} + \frac{q_iq_j}{q_\perp^2}\left(\frac{1}{r_1} - \frac{1}{r_2}\right), \tag{14}$$

where $i,j = x,y$, $q_\perp^2 = q_x^2 + q_y^2$, and

$$r_1 = K_3q_z^2 + K_1q_\perp^2 + \varepsilon_1(\varepsilon_0 + \varepsilon_1)(\varepsilon_0 + \varepsilon_1\hat{\boldsymbol{q}}_z^2)^{-1}E_0^2/4\pi, \tag{15}$$

$$r_2 = K_3q_z^2 + K_2q_\perp^2 + \varepsilon_1E_0^2/4\pi. \tag{16}$$

If $\varepsilon_1 > 0$, the correlation length ξ is given by $\xi = (4\pi K/\varepsilon_1)^{1/2}E_0^{-1}$, where K represents the magnitude of the Frank constants The coefficient r_1 depends on $\hat{\boldsymbol{q}}$ even in the limit $q \to 0$, which has not been the case in previous literature. The scattered light intensity is proportional to[2]

$$\frac{\langle|\boldsymbol{f}\cdot\overleftrightarrow{\boldsymbol{\varepsilon}}(\boldsymbol{q})\cdot\boldsymbol{i}|^2\rangle}{k_{\rm B}T\varepsilon_1^2} = \frac{|\boldsymbol{a}|^2}{r_2} + \left(\frac{1}{r_1} - \frac{1}{r_2}\right)\frac{|\boldsymbol{q}\cdot\boldsymbol{a}|^2}{q_\perp^2}, \tag{17}$$

where $\boldsymbol{i}$ and $\boldsymbol{f}$ represent the initial and final polarizations. The vector $\boldsymbol{a}$ is defined by

$$a_x = i_zf_x + f_zi_x, \quad a_y = i_zf_y + f_zi_y, \quad a_z = 0. \tag{18}$$

In addition we previously examined the anisotropy of the turbidity (form dichroism) in a nematic state under an electric field.[1]

4. Orientation around a Charged Particle

We place a charged particle with radius R and charge Ze in a nematic state, where $\boldsymbol{n}$ is aligned along the z axis or $\boldsymbol{n} \to \boldsymbol{e}_z$ far from the particle. Let the Coulomb potential of the particle be not screened over a long distance λ. From eqs. (3) and (9) the free energy change due to the orientation change $\delta\boldsymbol{n}$ is given by

$$\delta F = -\int {\rm d}\boldsymbol{r}\left[K\nabla^2\boldsymbol{n} + \frac{\varepsilon_1}{4\pi}(\boldsymbol{E}\cdot\boldsymbol{n})\boldsymbol{E}\right]\cdot\delta\boldsymbol{n}, \tag{19}$$

where we assume the single Frank constant K ($K_1 = K_2 = K_3 = K$), so $F_0 = \int {\rm d}\boldsymbol{r}K|\nabla\boldsymbol{n}|^2/2$. If the coefficient ε_1 is considerably smaller than ε_0, the electric field $\boldsymbol{E}$ near the particle is of the form $-(Ze/\varepsilon_0r^2)\hat{\boldsymbol{r}}$ and the electrostatic energy $F_{\rm e}$ is approximated by

$$F_{\rm e} \cong -\varepsilon_1\frac{Z^2e^2}{8\pi\varepsilon_0^2}\int_{r>R}{\rm d}\boldsymbol{r}\frac{1}{r^4}(\boldsymbol{n}\cdot\hat{\boldsymbol{r}})^2. \tag{20}$$

The origin of the reference frame is taken at the center of the charged particle and $\hat{\boldsymbol{r}} = r^{-1}\boldsymbol{r}$. Then, for $\varepsilon_1 > 0$ (or $\varepsilon_1 < 0$),

$\boldsymbol{n}$ tends to be parallel (or perpendicular) to $\hat{\boldsymbol{r}}$ near the charged particle. For $\varepsilon_1 > 0$, $(\boldsymbol{e}_z \cdot \hat{\boldsymbol{r}})^2 \cong 1$ around the particle and the decrease in the electrostatic energy is estimated as

$$\Delta F_{\rm e} \cong -\varepsilon_1 \frac{Z^2 e^2}{3\varepsilon_0^2}\left(\frac{1}{R}-\frac{1}{\ell}\right), \tag{21}$$

where the radius R plays the role of the lower cutoff length and the upper cutoff length ℓ is assumed to be longer than R and shorter than the screening length λ. Note that the factor $(\boldsymbol{n}\cdot\hat{\boldsymbol{r}})^2$ in eq. (20) tends to 1/3 far from the particle. For $\varepsilon_1 < 0$, ε_1 in eq. (21) should be replaced by $|\varepsilon_1|/2$. In the literature of physical chemistry, much attention has been paid to the decrease in the electrostatic energy around a charged particle due to polarization in the surrounding fluid (solvation free energy). Its first theoretical expression is the Born formula $\Delta E = Z^2e^2(1/\varepsilon_0 - 1)/2R$.[1,3,4] The additional orientation degrees of freedom in liquid crystals yield eq. (21).

We are assuming that $\boldsymbol{n}$ is appreciably distorted from $\boldsymbol{e}_z$ in the space region $R \lesssim r \lesssim \ell$. The Frank free energy is estimated as

$$F_0 \sim \pi K \ell. \tag{22}$$

Here $F_0 + \Delta F_{\rm e}$ is minimized at $\ell = \ell_{\rm c}$, where

$$\begin{aligned}\ell_{\rm c} &= (|\varepsilon_1|/3\pi\varepsilon_0^2 K)^{1/2} Ze \\ &= (|\varepsilon_1|/3\pi\varepsilon_0)^{1/3}(a\ell_{\rm B})^{1/2} Z.\end{aligned} \tag{23}$$

Here $\ell_{\rm B} = e^2/\varepsilon_0 k_{\rm B} T$ is the Bjerrum length and we set $K = k_{\rm B}T/a$ with a being a microscopic length. To produce strong orientation deformation we furthermore require the negativity of the minimum of $F_0 + \Delta F_{\rm e}$ to obtain $R < \ell_{\rm c}/2$ or

$$R/Z < (12\pi)^{-1/2}(|\varepsilon_1| a\ell_{\rm B}/\varepsilon_0)^{1/2}. \tag{24}$$

If this condition does not hold, the effect of the electric field on the nematic order becomes weak. In eq. (24) the factor $(12\pi)^{-1/2}$ has no significant meaning and the right-hand side only gives the order of magnitude. Here, $\ell_{\rm B} \sim 100\,$Å typically for $\varepsilon_0 \sim 10$ and $T \sim 300\,$K. Therefore, for a microscopic radius R, eq. (24) can hold well unless $|\varepsilon_1|/\varepsilon_0$ is very small. For salts with a low concentration of ions with charge Z_α and density ρ_α ($\alpha = 1, 2, \ldots$), the screening length is given by the Debye–Hückel expression $\lambda^{-2} = 4\pi e^2 \sum_\alpha Z_\alpha^2 \rho_\alpha/\varepsilon_0 k_{\rm B} T$. The criterion (24) is satisfied only for $\ell_{\rm c} < \lambda$. If $R < \lambda < \ell_{\rm c}$, the director orientation is deformed in the space region $R < r < \lambda$ for $(F_0 + \Delta F_{\rm e})_{\ell=\lambda} < 0$.

To illustrate the deformation of $\boldsymbol{n}$ around charged objects in equilibrium, we have numerically solved

$$\boldsymbol{n} \times \left[K\nabla^2 \boldsymbol{n} + \frac{\varepsilon_1}{4\pi}(\boldsymbol{E}\cdot\boldsymbol{n})\boldsymbol{E}\right] = \boldsymbol{0}, \tag{25}$$

and eq. (10) in two dimensions by assuming $\boldsymbol{n} = (\cos\theta, \sin\theta)$ (or $n_z = 0$). A charge is placed in the hard-core region $(x^2 + y^2)^{1/2} < R$. In three dimensions this is the case of an infinitely long charged wire with radius R and charge density σ, in which all the quantities depend only on x and y. The solution can be characterized by the three normalized quantities, $\varepsilon_1/\varepsilon_0$, $\sigma^* \equiv \sigma/(\varepsilon_0 K)^{1/2}$, and $R/\ell_{\rm B}$. Here, we set $\sigma^* = 2.4$ and $R/\ell_{\rm B} = 2$. We discretize the space into a 200×200 lattice in units of $\ell_{\rm B}$ under the periodic boundary condition in the x direction, so the system width is $L = 200\ell_{\rm B}$. The electric potential vanishes at $y = 0$ and L. In Fig. 2, $\boldsymbol{n}$ tends to be parallel to the y axis far from the origin and the spacing between the adjacent bars is $2\ell_{\rm B}$. The director is in the radial direction for $\varepsilon_1/\varepsilon_0 = 0.4$ in (a) and is perpendicular to $\boldsymbol{r}$ for $\varepsilon_1/\varepsilon_0 = -0.4$ in (b) near the origin. A pair of defects are aligned in the x direction in (a) and in the y direction in (b). Similar defect formation was numerically realized in two dimensions for a neutral particle with the surface interaction (26) described below.[9,10]

5. Charged Colloidal Suspension

The nematic orientation around a large particle without charges[5,6] is determined by competition of the Frank free energy F_0 and a microscopic anchoring interaction at the particle surface expressed as

$$F_{\rm a} = -\frac{1}{2} W_{\rm a} \int {\rm d}S (\boldsymbol{n}\cdot\hat{\boldsymbol{r}})^2. \tag{26}$$

Here, $\int {\rm d}S$ is the surface integration, and $\hat{\boldsymbol{r}}$ is the normal unit vector at the surface. The degree of anchoring is represented by the dimensionless parameter,

$$\mu_{\rm a} = W_{\rm a} R/K. \tag{27}$$

In charged colloidal suspensions, the distortion of $\boldsymbol{n}$ due to the surface charge can be more important than that due to the anchoring interaction (26). Note that eq. (24) is well satisfied even for large R if the ratio Z/R can be increased with increasing R. Notice that the ionizable points on the surface are proportional to the surface area $4\pi R^2$. However, the problem is very complex, because the counterions themselves can induce large deformation of the nematic order (because of their small size) and tend to accumulate near the large particles.

For simplicity let the deformation of $\boldsymbol{n}$ around the counterions be weak. Furthermore, we assume that the screening length λ is shorter than R and the nematic order does not vary on the spacial scale of λ except for the defect-core regions. Then $F_{\rm e}$ is approximated from eq. (20) as $F_{\rm e} \cong -W_{\rm e}\int {\rm d}S(\boldsymbol{n}\cdot\hat{\boldsymbol{r}})^2/2$ with

$$W_{\rm e} = \varepsilon_1 Z^2 e^2 \lambda/4\pi\varepsilon_0^2 R^4. \tag{28}$$

This is of the same form as $F_{\rm a}$ in eq. (26) and the strength of anchoring is represented by $\mu_{\rm eff} = (W_{\rm a} + W_{\rm e})R/K$. Here, the Debye–Hückel screening becomes extended in the dilute limit. In such cases and in the limit of large Z/R, the electric field around a large particle decays on the spatial scale of the Gouy–Chapman length[11],

$$\lambda = k_{\rm B}T/eE_{\rm s} = R^2/\ell_{\rm B} Z, \tag{29}$$

where $E_{\rm s} = Ze/4\pi\varepsilon_0 R^2$ is the electric field at the surface. If $\ell_{\rm B} Z/R \gg 1$, we have $\lambda \ll R$. Then we obtain $W_{\rm e} = (\varepsilon_1 k_{\rm B}T/4\pi\varepsilon_0)Z/R^2$ and

$$\mu_{\rm eff} = (W_{\rm a}/K)R + (\varepsilon_1 k_{\rm B}T/4\pi\varepsilon_0 K)Z/R. \tag{30}$$

If the second term dominates over the first, charge-induced anchoring can be expected.

6. Summary and Concluding Remarks

In §2, we have presented the scheme of Ginzburg–Landau theory for the electric field effects in liquid crystals, where the dielectric tensor depends on the orientation order as in

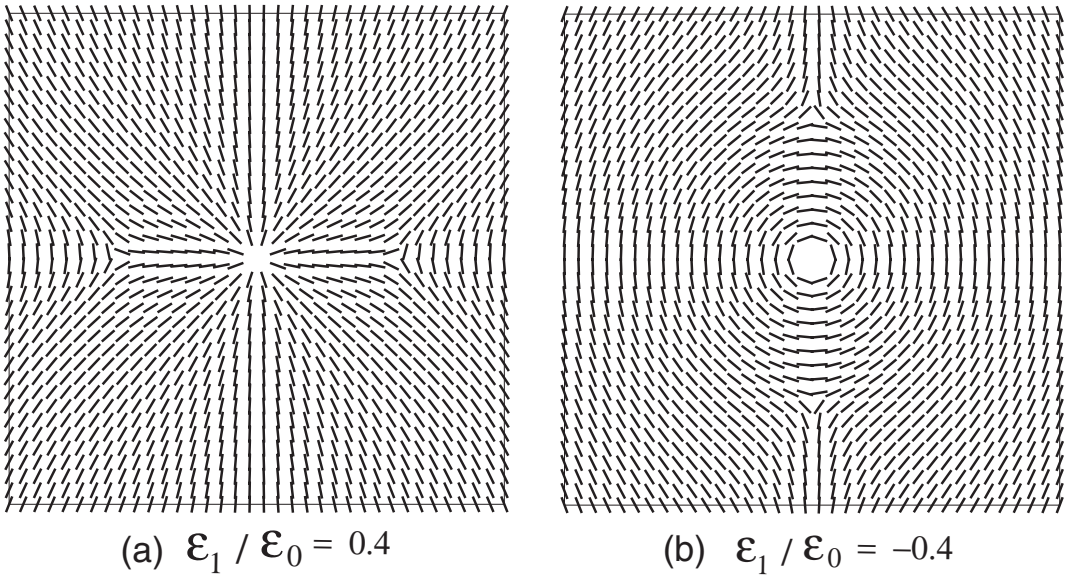

Fig. 2. The director field in two dimensions for $\varepsilon_1/\varepsilon_0 = 0.4$ in (a) and for $\varepsilon_1/\varepsilon_0 = -0.4$ in (b) around a charged wire at the origin. The field tends to be along the y axis (in the vertical direction) far from the origin. The spacing between the adjacent bars is $2\ell_B$.

eq. (3). Generalizations to more complex situations such as ferroelectric cases are straightforward. In §3, the director fluctuations have been examined in an applied electric field where the dielectric anisotropy needs not be small. It is desirable if eq. (17) could be confirmed by light scattering experiments in systems with not small $\varepsilon_1/\varepsilon_0$. In §4 and 5, the distortion of the nematic order around a charged particle has been studied for the first time. The condition of strong orientation deformation due to the charge effect is given by eq. (24) if the charge is not screened in the range $r < \ell_c$ with ℓ_c being defined by eq. (23). Even if a charged particle is an ion with a microscopic radius $R \sim 1$ Å, its solvation range ($\sim \ell_c$) can be much longer than R and defects can be produced around the particle. This effect might explain the observed anomalously small mobility of ions in nematic liquid crystals (see 5.4.4.3 of ref. 2). In colloidal suspensions the presence of the counterions makes the problem very complex, but we have obtained eq. (30) for the case in which the colloidal surface charges are screened within a thin layer with thickness given by eq. (29).

In future work we will perform simulations in three dimensions to calculate the mobility of an ion in nematics. Furthermore, we will study the phase transitions of liquid crystals with increasing the ion density. Electric field effects in an ac field should also be studied.

We finally mention a similar charge effect recently predicted for a near-critical polar binary mixture.[1)] In such fluids the dielectric constant $\varepsilon(c)$ strongly depends on the composition c and, as a result, the phase separation behavior is strongly affected by doped ions. In particular, if charged colloidal particles are suspended, a charge-density-wave phase should be realized for $(|\varepsilon_1|/4\varepsilon_0)Z/R > (\pi C_0/\ell_B)^{1/2}$ at low temperatures, where $\varepsilon_1 = \partial\varepsilon(c)/\partial c$ and C_0 is a microscopic wave number (= the coefficient in the gradient free energy). Here a large $(|\varepsilon_1|/\varepsilon_0)Z/R$ is required as in eq. (24).

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Appendix

We connect two capacitors in parallel as in Fig. 1(b). One contains an inhomogeneous dielectric material under investigation and the other is a large capacitor serving as a charge reservoir. The area S_0 and the charge Q_0 of the large capacitor are much larger than S and Q of the smaller capacitor, respectively. We consider an experiment in which the total charge $Q_{tot} = Q_0 + Q$ is fixed and the potential difference is commonly given by $\Phi = Q_0/C_0$, where C_0 is the capacitance of the large capacitor. Obviously, in the limit $Q/Q_0 \sim S/S_0 \to 0$, the deviation of Φ from the upper bound $\Phi_{tot} = Q_{tot}/C_0$ becomes negligible. Because the electrostatic energy of the large capacitor is given by $E_0 = Q_0^2/2C_0 = (Q_{tot}^2/2C_0)(1 - Q/Q_{tot})^2$, we obtain

$$E_0 \cong (Q_{tot}^2/2C_0) - \Phi Q, \tag{A·1}$$

where the first term is constant and the term of order $(Q/Q_{tot})^2$ is neglected. Therefore, for the total system including the two capacitors, the relevant free energy is given by G in eq. (11).

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