Defect structures in nematic liquid crystals around charged particles

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Abstract. We numerically study the orientation deformations in nematic liquid crystals around charged particles. We set up a Ginzburg-Landau theory with inhomogeneous electric field. If the dielectric anisotropy \( \varepsilon_1 \) is positive, Saturn-ring defects are formed around the particles. For \( \varepsilon_1 < 0 \), novel “ansa” defects appear, which are disclination lines with their ends on the particle surface. We find unique defect structures around two charged particles. To lower the free energy, oppositely charged particle pairs tend to be aligned in the parallel direction for \( \varepsilon_1 > 0 \) and in the perpendicular plane for \( \varepsilon_1 < 0 \) with respect to the background director. For identically charged pairs the preferred directions for \( \varepsilon_1 > 0 \) and \( \varepsilon_1 < 0 \) are exchanged. We also examine competition between the charge-induced anchoring and the short-range anchoring. If the short-range anchoring is sufficiently strong, it can be effective in the vicinity of the surface, while the director orientation is governed by the long-range electrostatic interaction far from the surface.


1 Introduction

A variety of mesoscopic structures have been found in liquid crystals around inclusions such as colloids and water droplets [1–3]. In nematics, inclusions distort the orientation order over long distances, inducing topological defects [4–13]. We mention the formation of structures or phases, such as string-like aggregates [2,12,14,15], soft solids supported by a jammed cellular network of particles [16], and a transparent phase including microemulsions [17,18]. The origin of the long-range distortions has been ascribed to the anchoring of the liquid crystal molecules on the inclusion surface [4–13,19,20]. It arises from the short-range molecular interactions between the liquid crystal molecules and the surface molecules. In the Ginzburg-Landau-de Gennes theory, we have a surface free energy depending on the orientation of liquid crystal molecules on the surface.

In this paper, we are interested in another anchoring mechanism. That is, electrically charged inclusions align the liquid crystal molecules in their vicinity to lower the electrostatic energy [21–23], which can be relevant for ions and charged particles. In fact, de Gennes [24,25] attributed the origin of the small size of the ion mobility in nematics to a long-range deformation of the orientation order around ions. However, the effect of charges in liquid crystals remains complicated and has rarely been studied, despite its obvious fundamental and technological importance. It is of great interest how the electric-field anchoring mechanism works and how it is different from the usual short-range anchoring mechanism.

The electric-field and the liquid crystal orientation are coupled because the dielectric tensor \( \varepsilon_{ij} \) depends on the local orientation tensor \( Q_{ij} \) (see eq. (15)). The alignment along a homogeneous electric field is well known [25], but the alignment in an inhomogeneous electric field has not yet been well studied. When the dielectric tensor is inhomogeneous, it is a difficult task to solve the Poisson equation and seek the electric potential \( \Phi \). We here perform numerical simulations placing charged particles in liquid crystals in a three-dimensional cell. We use the Ginzburg-Landau-de Gennes scheme in terms of the orientation tensor \( Q_{ij} \) [23,25–27]. A similar approach has recently been used to calculate the polarization and composition deformations around charged particles in electrolytes [28]. It is worth noting that hydration of water molecules around ions is analogous to the orientation anchoring of liquid crystal molecules around charged particles, as pointed out by de Gennes [24,25].
In sect. 2, we will present a Ginzburg-Landau-de Gennes theory for liquid crystals containing charged particles. In particular, we will give two general forms of the electrostatic free energy for the fixed-charge and fixed-potential cases (which can be used for any dielectric fluids containing charges). In sect. 3, we will explain the numerical method adopted in this work. In sect. 4, we will present numerical results of equilibrium configurations of the orientation order around charged particles. We will also examine competition of the short-range and electric-field anchoring mechanisms. In sect. 5, a summary and critical remarks will be given.

2 Theoretical background

We consider a liquid crystal system in a cubic box and place one or two charged spherical particles with radius \( R \) inside the box. The particle positions are written as \( \mathbf{R}_n \) (\( n = 1, 2 \)). The liquid crystal order is described in terms of the symmetric orientational tensor \( Q_{ij}(\mathbf{r}) \) with the traceless condition \( Q_{ii} = 0 \) [25]. We place one or two charged particles with radius \( R \) considerably longer than the radius of the solvent molecules. In this work the Boltzmann constant is set equal to unity and the temperature \( T \) is assumed to be independent of \( T \), while the coefficients \( A \) is 0, \( B \) is dependent on the temperature. For the uniaxial form \( Q_{ij} = S(n_i n_j - \delta_{ij}/3) \), we have \( F_a = wS \int \rho(1/3) - (\nu \cdot \mathbf{n})^2 \). Thus, for neutral particles, positive and negative values of \( w \) lead to homeotropic and planar anchoring, respectively.

We explain the electrostatic part \( F_e \), which depends on the experimental method. As a generalization of the theory by one of the present authors [21], we allow that the fluid region can contain a net charge \( Q_{in} = \int d\mathbf{r} \rho(\mathbf{r}) \) inside the fluid. As in fig. 1, we insert the fluid between parallel metallic plates in the region \( 0 < z < H \). The surface charge and the potential of the lower plate at \( z = 0 \) are \( Q_b \) and \( \Phi_b \), while those of the upper plate are \( Q_t \) and \( \Phi_t \). We require the overall charge neutrality condition,

\[
Q_{in} + Q_b + Q_t = 0,
\]

since the electric field in the metal plates should vanish. In terms of \( Q = (Q_t - Q_b)/2 \), we may set

\[
Q_b = -Q - Q_{in}/2, \quad Q_t = Q - Q_{in}/2.
\]

i) In fig. 1(a), \( Q \) can be fixed and can be a control parameter, where the potential difference,

\[
V = \Phi_t - \Phi_b,
\]

depends on the fluid inhomogeneity induced by the charged particles. Here the electrostatic energy of the surface charges of the plates is fixed, the appropriate form of \( F_e \) is

\[
F_e = \frac{1}{8\pi} \int d\mathbf{r} \mathbf{D} \cdot \mathbf{E} = \int d\mathbf{r} \frac{\rho(\mathbf{r})}{2} \left( \frac{\Phi_t + \Phi_b}{2} \right) + \frac{QV}{2},
\]

in eqs. (2) and (4) are to be performed only outside the particles \( |\mathbf{r} - \mathbf{R}_n| > R \). It is convenient to define the length

\[
d = T/L,
\]

which is the typical molecular size of liquid crystal. The term \( F_a \) represents the short-range anchoring free energy. It is expressed as the integral on the particle surfaces

\[
F_a = -w \int d\mathbf{a} \nu_j Q_{ij},
\]

where \( d\mathbf{a} \) is the surface element, \( \nu \) is the outward normal unit vector to the surface, and \( w \) represents the strength of the anchoring. For the uniaxial form \( Q_{ij} = S(n_i n_j - \delta_{ij}/3) \), we have \( F_a = wS \int \rho(1/3) - (\nu \cdot \mathbf{n})^2 \). Thus, for neutral particles, positive and negative values of \( w \) lead to homeotropic and planar anchoring, respectively.

The first term is of the Landau-de Gennes form,

\[
F_0 = \int' d\mathbf{r} \left[ \frac{A}{2} J_2 - \frac{B}{3} J_3 + \frac{C}{4} J_2^2 \right],
\]

where we introduce

\[
J_2 = Q_{ij}^2, \quad J_3 = Q_{ij} Q_{jk} Q_{ki}.
\]

Hereafter repeated indices are implicitly summed over. The coefficient \( A \) is dependent on the temperature \( T \), while the coefficients \( B \) and \( C \) are positive constants assumed to be independent of \( T \). The second term is the gradient free energy in the one-constant approximation,

\[
F_g = \frac{L}{2} \int' d\mathbf{r} (\nabla_k Q_{ij})^2,
\]

where \( \nabla_k = \partial/\partial x_k \) (\( x_k = x, y, z \)) are the space derivatives and \( L \) is a positive constant. The space integrals \( \int' d\mathbf{r} \) in eqs. (2) and (4) are to be performed only outside the particles \( |\mathbf{r} - \mathbf{R}_n| > R \). It is convenient to define the length

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d = T/L,
\]

where \( d\mathbf{a} \) is the surface element, \( \nu \) is the outward normal unit vector to the surface, and \( w \) represents the strength of the anchoring. For the uniaxial form \( Q_{ij} = S(n_i n_j - \delta_{ij}/3) \), we have \( F_a = wS \int \rho(1/3) - (\nu \cdot \mathbf{n})^2 \). Thus, for neutral particles, positive and negative values of \( w \) lead to homeotropic and planar anchoring, respectively.

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\[
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\]
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tions [24], where the amplitude from that in eq. (11). It is worth noting that the sec-

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2.2 Equilibrium conditions

In our numerical work we will adopt the geometry of fig. 1(b) and set \( V = 0 \). The charge density \( \rho \) is fixed. We define the tensor, \( h_{ij} \equiv \delta \mathcal{F}/\delta Q_{ij} + \lambda \delta_{ij} \), where \( \lambda \) is chosen such that \( h_{ij} \) becomes traceless. Some calculations give

\[ h_{ij} = (A + CJ_2)Q_{ij} - B \left( Q_{ik}Q_{kj} - \frac{1}{3} J_2 \delta_{ij} \right) \]

\[ -L \nabla^2 Q_{ij} - \frac{\epsilon_1}{8\pi} \left( E_i E_j - \frac{1}{3} E^2 \delta_{ij} \right). \]  

In equilibrium, minimization of \( \mathcal{F} \) yields

\[ h_{ij} = 0, \]  

in the particle exterior. The boundary condition of \( Q_{ij} \) on the particle surface is given by

\[ L \mathbf{v} \cdot \nabla Q_{ij} + w(\nu_i \nu_j - \delta_{ij}/3) = 0. \]

Obviously, the defect structure is independent of the sign of the particle charge, since \( Q_{ij} \) is coupled to the bilinear terms of \( \mathbf{E} \) in eq. (16).

For \( B > 0 \) uniaxial states are selected in the bulk region below the isotropic-nematic transition \( A < A_t \) [25], where \( Q_{ij} = S(n_i n_j - \delta_{ij}/3) \) and

\[ A_t = B^2/27C. \]

Substituting the uniaxial form into the first line of eq. (16), we obtain

\[ 2CS^2 - BS + \epsilon_1 A = 0, \]

which is solved to give

\[ S = B/4C + [(B/4C)^2 - 3 \epsilon_1 / 2C]^{1/2}. \]

Just below the transition we have \( S = S_t \equiv B/3C \). However, it is known that the liquid crystal order is considerably biaxial inside defect cores [8,23,26]. See fig. 3 of ref. [23] for the biaxiality of the Saturn-rank core (where the spatial mesh size is finer than in this work). Note that \( Q_{ij} \) can generally be expressed as

\[ Q_{ij} = S_1(n_i n_j - \delta_{ij}/3) + S_2(m_i m_j - \ell_i \ell_j), \]

where \( n, m, \) and \( \ell \) constitute three orthogonal unit vectors. Inside defect cores, the amplitude \( S_2 \) of biaxial order is of the same order as the amplitude \( S_1 (= S \) in this work) of uniaxial order. Outside the defect cores, \( S_2 \) nearly vanishes and the orientation order becomes uniaxial.

In addition, the polarization vector of the liquid crystal is given by \( \mathbf{P} = \chi_{ij} E_j \) in terms of the susceptibility tensor \( \chi_{ij} \). From \( \epsilon_1 E_j = E_j + 4\pi P_j \), we have

\[ \chi_{ij} = (\epsilon_{ij} - \delta_{ij})/4\pi. \]

This tensor should be positive-definite in equilibrium to ensure the thermodynamic stability in the (paraelectric) nematic phase [23]. For the special form (15) this requirement becomes

\[ \epsilon_0 - 1 + \epsilon_1 q_\alpha > 0, \]

where \( q_\alpha \) (\( \alpha = 1, 2, 3 \)) are the eigenvalues of \( Q_{ij} \).

where \( E_i = -\partial \Phi / \partial x_i \) is the electric field and \( D_i = \epsilon_{ij} E_j \) is the electric induction with \( \epsilon_{ij} \) being the dielectric tensor. Here we superimpose small variations \( \delta Q_b \), \( \delta Q_i \), \( \delta \rho \), and \( \delta \varepsilon_{ij} \) on \( Q_b \), \( Q_i \), \( \rho \), and \( \varepsilon_{ij} \), respectively. We use the relation

\[ \int d\mathbf{r} \mathbf{E} \cdot \delta \mathbf{D}/4\pi = \Phi_b \delta Q_b + \Phi_i \delta Q_i + \int d\mathbf{r} \delta \Phi \delta \rho. \]

We then obtain the incremental change of \( \mathcal{F}_c \) as

\[ \delta \mathcal{F}_c = V \delta Q + \int d\mathbf{r} \delta \rho \left( \Phi - \frac{\Phi_i + \Phi_b}{2} \right) - \frac{1}{8\pi} \int d\mathbf{r} \delta \varepsilon_{ij} E_i E_j, \]

\[ \delta \mathcal{F}_c = \frac{1}{8\pi} \int d\mathbf{r} \mathbf{D} \cdot \mathbf{E} - V Q \]

where the second line follows from the second line of eq. (10). This is the Legendre transformation of the electrostatic free energy in the fixed-charge case. Here we use the same notation \( \mathcal{F}_c \) in the two cases. Then the incremental form of \( \mathcal{F}_c \) reads

\[ \delta \mathcal{F}_c = -Q \delta V + \int d\mathbf{r} \delta \rho \left( \Phi - \frac{\Phi_i + \Phi_b}{2} \right) - \frac{1}{8\pi} \int d\mathbf{r} \delta \varepsilon_{ij} E_i E_j, \]

where the first term on the right-hand side is different from that in eq. (11). It is worth noting that the second line of eq. (12) yields the frequency used expression \( \mathcal{F}_c = -\int d\mathbf{r} \mathbf{D} \cdot \mathbf{E}/8\pi \) in the fixed-potential condition for dielectric fluids without charge (\( \rho = 0 \)) (see ref. [24] for example).

The potential \( \Phi \) satisfies the Poisson equation,

\[ \nabla_i (\varepsilon_{ij} \nabla_j \Phi) = -4\pi \rho. \]

We assume the linear form of the dielectric tensor,

\[ \varepsilon_{ij}(\mathbf{r}) = \varepsilon_0 \delta_{ij} + \varepsilon_1 Q_{ij}(\mathbf{r}), \]

in the liquid crystal region (the particle exterior)\(^1\). Defining \( \Phi \) in the whole space, we may solve eq. (14) by setting

\[ \varepsilon_{ij}(\mathbf{r}) = \varepsilon_0 \rho \delta_{ij} \]

in the particle interior. Then the integrals in eqs. (10) and (12) are over the whole cell region. We then have \( \delta \mathcal{F}_c/\delta Q_{ij} = -\varepsilon_1 E_i E_j/8\pi \) both at fixed \( Q \) and at fixed \( V \).

\(^1\) In the nematic state we have \( \varepsilon_{ij} = \varepsilon_0 + 2S \epsilon_1 / 3 \) along the director \( \mathbf{n} \) and \( \varepsilon_{\perp} = \varepsilon_0 - SC \epsilon_1 / 3 \) in the perpendicular directions [24], where the amplitude \( S \) is given in eq. (20).
2.3 Electric-field effect near the surface

Let us consider the electric-field effect near a particle surface. For simplicity, we assume $|\varepsilon_1| \lesssim \varepsilon_0$. Then the surface electric field $E_s$ is estimated to be of order $\varepsilon Z/\varepsilon_0 R^2$, where $Z$ is the particle charge (with $\varepsilon$ being the elementary charge). i) Far above the transition $A \gg A_t$ in the isotropic phase, we neglect the terms proportional to $B$, $C$, and $L$ in eq. (17) to obtain $Q_{ij} \approx \varepsilon_1 E^2 r^2 - \delta_{ij}/3)/8\pi A$, which grows as $A$ is decreased as a pretransitional effect. ii) Just below the transition, a nonlinear deformation occurs for $|\varepsilon_1| E^2/8\pi \gtrsim A_s S_i = B^3/81 C^2$, which is easily realized for small $B$. iii) In the nematic phase far below the transition, strong nonlinear deformations of $Q_{ij}$ are induced on the surface for $R \ll \ell$, with [23]

$$\ell = |Z|/|\varepsilon_1| \ell_B d/12\pi \varepsilon_0 S)^{1/2},$$

where $d$ is defined by eq. (5) and

$$\ell_B = c^2/\varepsilon_0 T$$

is the Bjerrum length. This criterion arises from the balance of the gradient term ($\sim LSR^{-2}$) and the electrostatic term ($\sim \varepsilon_1 E^2/8\pi \propto R^4$) in $h_{ij}$ in eq. (17). Furthermore, for sufficiently large $\ell/R$, a defect is formed around the particle, where the distance from the surface is of order $\ell - R$.

It is important to clarify the condition of defect formation in real systems. Let us assume $\varepsilon_0 \sim 2$, $|\varepsilon_1| \sim \varepsilon_0$, $S \sim 1$, $d \sim 2$ nm, and $\ell_B \sim 24$ nm. Then $\ell \sim |Z|$ nm. Thus, the relation $R < \ell$ holds for microscopic ions, though our coarse-grained model is inaccurate on the angstrom scale. See remark 3) in the last section for a comment on ions in liquid crystal. We may also consider a large particle with a constant surface charge density

$$\sigma = Z/4\pi R^2.$$  

It may be difficult to induce sufficient ionization on colloidal surfaces in liquid crystal solvents. One method of realizing charged surfaces will be to attach ionic surfactant molecules on colloidal surfaces. For such a particle, the condition of defect formation becomes $R \gg R_c$, where

$$R_c = (3c_0 S/4\pi |\varepsilon_1| \ell_B d)^{1/2} \sigma^{-1}.$$  

(27)

Using the above parameter values, we have $R_c \sim 0.1 \sigma^{-1}$ nm (with $\sigma$ in units of nm$^{-2}$). For example, if $\sigma = 0.0624$ nm$^{-2}$ or $c_0 = 1 \mu$C/cm$^2$, we obtain $R_c = 1.6$ nm. Here the electric field at the surface is $c_0 \sigma/4\pi \varepsilon_0 \approx 100$ V/\mu m, which is strong enough to align the director field. Electric field applied macroscopically is typically of order 1 V/\mu m [29,30].

3 Simulation method

We give our simulation method in the Landau-de Gennes scheme under the condition of $V = 0$. For simplicity, we impose the periodic boundary condition in the $x'y$-plane. We suppose nanoscale particles confined between a thin layer.

In the previous section we have assumed sharp boundaries between the particles and the liquid crystal region. However, precise simulations are not easy in the presence of sharp curved boundaries on a cubic lattice, unless the mesh size is very small. In this work, to overcome this difficulty, we employed the smooth particle method. That is, we introduce diffusive particle profiles by [9, 11, 12, 19, 20]

$$\phi_n(r) = 1/2 \tanh \left( R - |R_n - r| / d \right) + 1/2,$$

where the surface is treated to be diffuse with thickness $d = T/L$ in eq. (5), $R_n$ represents the particle center, and $R$ is the particle radius.

In terms of $\phi_n(r)$, the overall particle and charge distributions are expressed as

$$\phi(r) = \sum_n \phi_n(r),$$

$$\rho(r) = \frac{1}{v} \sum_n Z_n \phi_n(r),$$

where $Z_n e$ are the particle charges and $v = 4\pi R^2/3$ is the particle volume. The charge distribution is assumed to be homogeneous inside the particles. In $\mathcal{F}_0$ in eq. (2) and $\mathcal{F}_g$ in eq. (4), the space integrals outside the particles $\int d^3 r$ should be redefined as

$$\int d^3 r (\cdots) = \int d^3 r [1 - \phi(r)] (\cdots).$$

(31)

The surface integral in eq. (6) is also redefined as

$$\int da (\cdots) = \int d^2 r \nabla \phi ^2 (\cdots).$$

(32)

Then, the short-range anchoring free energy (6) is rewritten as

$$\mathcal{F}_a = -w \int d^2 r Q_{ij}(\nabla_i \phi) (\nabla_j \phi) / |\nabla \phi|.$$  

(33)

The dielectric tensor is space-dependent as

$$\varepsilon_{ij}(r) = [\varepsilon_0 + (\varepsilon_p - \varepsilon_0) \phi] \delta_{ij} + \varepsilon_1 (1 - \phi) Q_{ij},$$

(34)

where $\varepsilon_p$ is the dielectric constant inside the particles.

To seek $Q_{ij}$ satisfying eqs. (17) and (18), we treated $Q_{ij}(r, t)$ as a time-dependent tensor variable obeying the evolution equation

$$\frac{1}{\zeta} \frac{\partial}{\partial t} Q_{ij}(r, t) = -\frac{\delta \mathcal{F}}{\delta Q_{ij}} + \lambda \delta_{ij}$$

$$= -(1 - \phi) \delta_{ij} - L(\nabla_k \phi) (\nabla_k Q_{ij})$$

$$+ \frac{w}{|\nabla \phi|} (\nabla_i \phi \nabla_j \phi - |\nabla \phi|^2 \delta_{ij} / 3),$$  

(35)

where $\zeta$ is a constant kinetic coefficient. In the first line, the functional derivative is taken both inside and outside
conditions. The potential \( \Phi \) for the director \( \mathbf{n} \) is lowest for the selected director alignments both at \( z \) and is periodic in the \( \lambda \) the particles with the redefinitions (29)-(34), with \( n_{ij} \) and \( \mathbf{n} \) and the parallel alignment \( d \).

In the second line, \( n_{ij} \) is defined in eq. (16) and \( \nabla \phi \) arises from the factor 1 – \( \phi \) in eq. (31). On a cubic \( 64 \times 64 \times 64 \) lattice, we integrated the above equation for \( Q_{ij} \). Space and time are measured in units of \( d \) and \( \tau = d^2 / \zeta L \).

respectively. The space mesh size is \( d \) and the time mesh size is \( \Delta t = 0.01 \tau \) in the integration. The cell interior is in the region \( 0 \leq x, y, z \leq 64d \).

We solved the Poisson equation (14) at each integration step using a Crank-Nicolson method [23].

As the boundary conditions of \( Q_{ij} \) at \( z = 0 \) and \( 64d \), we assume the homeotropic anchoring \( n_i = \delta_{i2} \) for \( \epsilon_1 > 0 \) and the parallel alignment \( n_i = \delta_{i2} \) for \( \epsilon_1 < 0 \), where \( n = (n_x, n_y, n_z) \) is the director with \( i = x, y, z \). Those of \( Q_{ij} \) in the \( x \) and \( y \) directions are the periodic boundary conditions. The potential \( \Phi \) vanishes at \( z = 0 \) and \( 64d \) and is periodic in the \( xy \) plane. Note that the electric field at \( z = 0 \) and \( 64d \) is along the \( z \) axis, so the electrostatic energy is lowest for the selected director alignments both for \( \epsilon_1 > 0 \) and \( \epsilon_1 < 0 \). In order to approach a steady state, we performed the integration until \( dF/\text{dt} \) became less than \( 10^{-3} T/\tau \).

In our steady states thus attained, we confirmed that both eqs. (17) and (18) excellently hold in the bulk liquid crystal region and near the particle surfaces, respectively. Mathematically, they should hold in the thin-interface limit \( d \ll R \), where \( -\nabla \phi \equiv \delta (r - R) \mathbf{u} \) around a spherical surface with \( \mathbf{v} \) being the normal unit vector.

In fig. 2, we show our numerical result of the derivative \( \partial J_2/\partial r \) in units of \( d^{-1} \) and gradient free-energy density \( f_g = L(\nabla_i Q_{ij})^2/2 \) in units of \( T d^{-3} \) vs. normalized distance \( (r - R)/R \) from the surface of a charged spherical particle. The path starts from a surface position and passes through a Saturn ring (see fig. 3).
Fig. 6. Normalized gradient free energy $F_g$ vs. charge number $Z$ of a particle. Arrows indicate the point of defect formation. A jump appears for $\varepsilon_1 > 0$, while there is no jump for $\varepsilon_1 < 0$.

4.1 A single particle in nematic liquid

We first consider a single charged particle for the two cases, $\varepsilon_1 > 0$ and $\varepsilon_1 < 0$. Its charge number $Z$ is in the range [60, 160]. The orientation tensor $Q_{ij}$ is independent of the sign of $Z$.

Figure 3 displays the director field $\mathbf{n} = (n_x, n_y, n_z)$ around a single particle with $Z = 60, 100, 160$. Here we set $\varepsilon_1 = 1.8\varepsilon_0$, and $R = 12.5d$. The liquid crystal is deeply in the nematic phase. At the particle surface one of the perpendicular alignment is selected, which is analogous to the case of a neutral particle in the homeotropic anchoring condition realized for $w > 0$. The system is axysymmetric, as assumed in our previous simulation [23].

For small $Z$ in fig. 3(a), no defect is formed, while the orientation field is largely distorted. For large $Z$ in fig. 3(b) and (c), a Saturn-ring disclination line of the topological charge $s = -1/2$ appears near the equator of the particle. In our small system, the Saturn ring is confined within the box. However, if the system size is larger, the defect should be more extended, since its radius is predicted to be of order $\ell$ in eq. (24) [23].

Figure 4 displays the orientation field around a particle with $R = 12.5d$ for $\varepsilon_1 = -1.8\varepsilon_0$. The other parameters are the same as in fig. 3. For $\varepsilon_1 < 0$, the director tends to be along the particle surface, analogously to the case of a neutral particle with planar anchoring realized for $w < 0$. For not large $Z$ in fig. 4(a), the director is distorted around the particle without defects. Slightly above the threshold in fig. 4(b), defects are formed at the two poles of the particle. For a neutral particle, a similar defect structure is called “boojum” [1, 7, 31]. For larger $Z$ in fig. 4(c), two “ansa”-shaped defects emerge with their ends on the particle surface, as a novel defect structure. Here a boojum-like structure in fig. 4(b) grows into a curved disclination line of topological strength $s = -1/2$. The director is perpendicular to the plane formed by each ansa. In fig. 5 we show the top and side views of the director field around the ansae at $Z = 160$ in fig. 4. Here the axial symmetry is broken, so the previous simulation did not detect this structure [23] (where an axially symmetric, biaxial defect was instead detected).

For $\varepsilon_1 > 0$ it was shown [23] that a Saturn ring appears discontinuously with increasing $\ell$ ($\propto Z$) in eq. (24). Also in the case of a neutral particle [9], its appearance is discontinuous with increasing $wR$. In fig. 6, we show...
the normalized gradient free energy $F_g/T$ versus $Z$ for $\varepsilon_1/\varepsilon_0 = \pm 1.8$, since $F_g$ in eq. (4) is sensitive to the defect formation. The arrows indicate the point of the defect formation on the curves. Remarkably, for $\varepsilon_1 = 1.8\varepsilon_0 > 0$, $F_g$ changes discontinuously at $Z \approx 136$ with increasing $Z$ and at $Z \approx 80$ with decreasing $Z$, where $\ell/R \approx 5$ and 9, respectively, using eq. (24). This hysteretic behavior demonstrates that the system is bistable with and without a Saturn ring (in the range of $80 < Z < 136$ in the present example). On the other hand, for $\varepsilon_1 < 0$, $F_g$ increases smoothly as $Z$ increases. This is because the ansa defects gradually protrude from the particle surface into the liquid crystal.

### 4.2 A pair of charged particles

We first place a pair of positively and negatively charged particles with $R = 6.25$, which form a dipole. Their distance is fixed at $|R_1 - R_2| = 2R$. In fig. 7, we show snapshots of the director and the defect structure around the two particles. Here $\varepsilon_1 = 1.8\varepsilon_0$ and $Z_1 = -Z_2 = 50$ in the upper plates (a) and (b), while $\varepsilon_1 = -1.8\varepsilon_0$ and $Z_1 = -Z_2 = 100$ in the lower plates (c) and (d). The particles are aligned in the parallel direction (left) and in one of the perpendicular directions (right) with respect to the background director direction (along the $z$ axis for $\varepsilon_1 > 0$ and along the $x$ axis for $\varepsilon_1 < 0$). We can see Saturn rings in fig. 7(a) and (b), while there are four ansae in fig. 7(c) and two ansae in fig. 7(d). In the lower panel of fig. 8, we show the sequence of this topological change of the defect structure with varying the angle $\theta$ between the background director and the vector connecting the particle centers. In the upper panel of fig. 8, we show the free energy $F = F(\theta)$ measured from its minimum $F(\theta_{\text{min}})$ as a function of $\theta$. The angle $\theta_{\text{min}}$ at the minimum is $0$ for $\varepsilon_1 > 0$ and $\pi/2$ for $\varepsilon_1 < 0$. We can see Saturn ring (in the range of 80
We next place identically charged particles separated by 2R. In fig. 9, we display the defect structures around two positively charged particle with \( Z_1 = Z_2 \). Remarkably, the topology of the defects around a pair is the same as that of a single particle. That is, we find only one disclination loop for \( \varepsilon_1 > 0 \) and two ansa defects for \( \varepsilon_1 < 0 \). Notice that a pair may be regarded as a non-spherical particle [10] with charge 2Ze. Figure 10 displays the free energy \( F = \mathcal{F}(\theta) \) measured from its minimum as a function of the angle \( \theta \). The angle \( \theta_{\text{min}} \) at the minimum is \( \pi/2 \) for \( \varepsilon_1 > 0 \) and 0 for \( \varepsilon_1 < 0 \).

### 4.3 A charged particle with nonvanishing \( w \)

In this subsection, we discuss the effect of the short-range anchoring free energy \( F_a \) in eq. (6) supposing a single particle. As illustrated so far, the electric field for positive and negative \( \varepsilon_1 \) serves to induce homeotropic and planar alignment, respectively. Therefore, the two anchoring mechanisms can compete for (i) \( \varepsilon_1 > 0 \) and \( w < 0 \) and for (ii) \( \varepsilon_1 < 0 \) and \( w > 0 \).

In fig. 11, we set \( \varepsilon_1 = 1.8\varepsilon_0 > 0 \) and choose various negative \( w \). In fig. 11(a), \( f_g d^3/T = 0.03 \) on the surfaces (in green). This threshold is small and the right two snapshots do not involve defects. We can see that the region having large \( f_g \) moves from the vicinity of the Saturn ring to upper and lower surface parts of the particle. The Saturn ring remains nonvanishing for small \( w \), but the director field around the equator tends to be tangential to the surface (parallel to the background director direction along the \( z \) axis) and the Saturn ring disappears with increasing \( |w| \). The director field changes steeply near the surface away from the equator for large \( |w| \). This changeover occurs discontinuously with sudden disappearance of the Saturn ring at \( w = w_c \), where \( w_c \approx -3.4Td^{-2} \) in the present case.

In fig. 12, we set \( \varepsilon_1 = -1.8\varepsilon_0 < 0 \) and choose various positive \( w \). In fig. 12(a), the ansa defects shrink into two point defects and disappear with increasing \( w \). The top and side views of the director are shown for \( w = 2Td^{-2} \) in fig. 12(b) and for \( w = 5Td^{-2} \) in fig. 12(c) around the particle. For large \( w \), the defect structure becomes axisymmetric without defects and the regions of large \( f_g \) cover the particle surface. This crossover is continuous with increasing \( w \). In the above examples, the short-range anchoring is effective close to the surface for sufficiently large \( |w| \), while the electric-field anchoring is dominant far from the surface. A similar problem is encountered in the Fredericks transition in magnetic field as the strength of the surface anchoring is varied [25,32]. The crossover from weak to
strong short-range anchoring occurs for

$$|w| > L/\xi_c = T/d\xi_c,$$  \hspace{3cm} (37)

where $\xi_c$ is the thickness of this transition layer. For $|\varepsilon_1| < \varepsilon_0$ this length is determined by

$$\xi_c^{-2} = E_s^2/8\pi,$$  \hspace{3cm} (38)

where $E_s = Ze/\varepsilon_0 R^2$ is the surface electric field. This estimation is obtained from $h_{ij} = 0$ in eq. (17). On the right-hand sides of eq. (16), the gradient term becomes $-L S \nabla^2 \varphi$ in the nematic phase, where $\varphi$ is the angle of the director with respect to the surface normal. The balance of this term with the last electrostatic term ($\sim \varepsilon_1 E_s^2/8\pi$) at the surface yields eq. (38). For our parameters chosen in figs. 11 and 12, eq. (38) gives $\xi_c = 0.9d$ and the right-hand side of eq. (37) becomes $1.17d^{-2}$, which are consistent with our numerical results.

5 Summary and remarks

We have performed three-dimensional simulations in the presence of charged particles in nematic liquid crystals. We first give a summary.

(i) The director tends to be parallel (perpendicular) to the electric field for positive (negative) $\varepsilon_1$. In fig. 3, a Saturn-ring defect is formed, as $l$ in eq. (24) much exceeds the particle radius $R$. In figs. 4 and 5, we have found novel anna defects without axial symmetry in a nematic solvent with $\varepsilon_1 < 0$. In our previous simulation [23], a boojum-like defect was derived for $\varepsilon_1 < 0$, since it was based on the assumption of axial symmetry. In fig. 6, the formation of a Saturn ring due to the electric field is first order, while that of anna defects is continuous.

(ii) We have also examined the director in the presence of two charged particles in nematic liquid crystals. Results for $Z_1 = -Z_2$ are in figs. 7 and 8, while those for $Z_1 = Z_2$ are in figs. 9 and 10. We have found that oppositely charged particle pairs are likely to be aligned in the parallel direction for $\varepsilon_1 > 0$ and in the perpendicular plane for $\varepsilon_1 < 0$ with respect to the background director direction. We conjecture that polar molecules composed of oppositely charged particles can be aligned in nematic liquid crystals even on microscopic scales. On the other hand, fig. 10 shows that the preferred alignment directions are exchanged for identically charged particles.

(iii) We have examined the competition of the charge-induced anchoring and the short-range anchoring in figs. 11 and 12. These two anchoring mechanisms can compete when $\varepsilon_1$ and $w$ have different signs. Under the condition (37), the short-range anchoring can be effective near the surface with a distance shorter than $\xi_c$ in eq. (38).

We supplement the discussion in sect. 2.3. For microscopic particles (ions), observation of nanoscale defects should be difficult, but there might be some indication of the defect formation in the behavior of the electric conductivity [24, 25]. For colloidal particles, the condition $R > R_c$ can be satisfied only when the ionization on the surface occurs to a sufficient level in a liquid crystal. We may also suspend a macroscopic particle in a liquid crystal. We mention an experiment [29], in which an electric field was applied to nematics containing silicone oil particles to produce field-dependent defects. We may even propose to suspend metallic particles or water droplets containing salt in a liquid crystal, where a surface charge appears in an applied electric field. Recently, electric field was applied to two-dimensional colloidal crystals in nematic solvent [30], where the lattice spacing changes up to 20% in one direction in response to the applied field.

Further remarks are as follows.

1) The competition of the short-range and charge anchoring mechanisms should be investigated furthermore, since our examples of a single particle are very fragmentary. The interaction among charged particles in liquid crystal solvent should be much complicated in such situations.

2) The liquid crystal order $S$ increases with increasing $|A|$ in the nematic phase and its discontinuity at the transition decreases with decreasing $B$ in eq. (2). For small $B$ (for weakly first-order phase transition), therefore, the defect formation takes place considerably far below the nematic-isotropic transition. The ion mobility in nematics [24, 25] might decrease discontinuously at the Saturn-ring formation with lowering the temperature.

3) Light scattering should be sensitive to doped ions in nematics, where even a small amount of ions should strongly distort the nematic order. This is analogous to the role of microemulsions in nematics [17, 18].

4) As discussed below, eq. (26), we should examine how ionic surfactant molecules can be attached to surfaces of colloids and microemulsions in liquid crystal solvents [33]. It is worth noting that an ionic surfactant was attached to microemulsion surfaces in the previous experiment [17].

5) Intriguing also are effects of salt at weakly first-order nematic-isotropic phase transition and the ion distribution around isotropic-nematic interfaces. Such theoretical studies were already reported for electrolytes with binary mixture solvents [28, 34].

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References

4. O.D. Lavrentovich, P. Pasini, C. Zannoni, S. Zumer (Editors), Defects in Liquid Crystals: Computer Simulation,