Q-tensor model for electrokinetics in nematic liquid crystals

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Abstract

We use a variational principle to derive a mathematical model for a nematic electrolyte in which the liquid crystalline component is described in terms of a second-rank order tensor. The model extends the previously developed director-based theory and accounts for presence of disclinations and possible biaxiality. We verify the model by considering a simple but illustrative example of liquid crystal-enabled electro-osmotic flow (LCEO) around a stationary dielectric spherical particle placed at the center of a large cylindrical container filled with a nematic electrolyte. Assuming homeotropic anchoring of the nematic on the surface of the particle and uniform distribution of the director on the surface of the container, we consider two configurations with a disclination equatorial ring and with a hyperbolic hedgehog, respectively. The computed electro-osmotic flows show a strong dependence on the director configurations and on the anisotropies of dielectric permittivity and electric conductivity of the nematic characteristic of liquid crystal-enabled electrokinetics. Further, the simulations demonstrate space charge separation around the dielectric sphere, even in the case of isotropic permittivity and conductivity. This is in agreement with the induced-charge electro-osmotic effect described for isotropic electrolytes surrounding dielectric spheres.

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I. INTRODUCTION

Recent advancements in micro- and nanofluidics motivated a significant interest in electrokinetic phenomena, both from the theoretical and applied points of view [1, 2]. These phenomena occur in systems that exhibit spatial separation of charges and fall into one of the two categories: an electrically driven transport of particles in a fluid (electrophoresis) and electrically driven flows of fluids with respect to their containers (electro-osmosis).

Separation of charges typically results from dissociation of polar chemical groups at the solidfluid electrolyte interface and formation of an equilibrium electric double layer. Application of the electric field causes electrokinetic flows with a characteristic velocity proportional to the applied field. Besides this classic effect, there is a broad class of phenomena, in which separation of charges is caused by the electric field itself [3]-[7]. Since the induced charge is proportional to the applied field, the resulting flow velocities grow with the square of the field, $v \sim E^2$, [3]-[7]. These phenomena, called collectively an induced-charge electro-kinetics (ICEK) [3], are most often considered for ideally polarizable (conducting) solid particles, in which case the velocity scale is $v^{metal} \sim \varepsilon_0 \varepsilon_{medium} E^2 a/\eta$, where and a is the radius of the colloid while $\varepsilon_0 \varepsilon_{medium}$ and η are the dielectric permittivity and viscosity of the electrolyte, respectively [3, 6, 7]. If the particle is a solid dielectric with permittivity $\varepsilon_0 \varepsilon_p$, the ICEO flows are still present but with a much reduced velocity, $v^{diel} \sim \varepsilon_0 \varepsilon_p E^2 \lambda_D / \eta$, where λ_D is the Debye screening length [6, 7]. In aqueous electrolytes λ_D is typically much smaller than a (tens of nanometers vs micrometers).

Another mechanism to achieve charge separation—even without a solid component—is to use an anisotropic fluid, such as a nematic liquid crystal as an electrolyte [8–13]. The anisotropy of the medium in presence of spatial gradients of the orientational order makes it possible to move charged ions to different locations. The subsequent motion of the fluid induced by the electric field give rise to nonlinear effects [10] called the liquid crystal-enabled electrokinetics (LCEK) [8–12, 14, 15]. Both the experiments and theoretical considerations demonstrate that the LCEK flow velocities are proportional to the square of the electric field [8–12, 14, 15]. Because the flow direction is independent of the field polarity, LCEK transport can be driven by an alternating current, a feature desired in technological applications.

In this paper we derive a mathematical model for electrokinetic flows in nematic liquid crystals, where the nematic component is described by the second-rank tensor order parameter, or a socalled Q-tensor. The model generalizes our previous work that extended Ericksen-Leslie formalism [16–18] to nematic electrolytes, where we established a system of governing equations from the local form of balance of linear and angular momentum within the framework of the director-based theory. An alternative derivation can be found in [15], where we arrived at the same system of equation in a more formal, but probably more efficient manner following a variational formulation of nematodynamics, as proposed in [19, 20]. Because the director models have a limited applicability in that they cannot model nematic biaxiality and topological defects—other than vortices—here we use the strategy in [15, 19, 20] to arrive at the appropriate Q-tensor-based-theory.

As an illustrative example, we consider a stationary, relatively small (sub-micrometer) colloidal sphere that sets a perpendicular surface anchoring of the preferred orientation of the nematic. The director field around the particle is either of the quadrupolar type with an equatorial disclination loop [21] or of dipolar symmetry, with a point defect, a hyperbolic hedgehog residing on one side of the sphere [22]. Numerical simulations demonstrate electro-osmotic flows around these two configurations that are in qualitative agreement with the experimental data [12] but also highlight features characteristic for the ICEK around a dielectric sphere in absence of materials anisotropies [4, 6, 7].

The paper is organized as follows. In Section II we recall the principle of minimum energy dissipation and then use this principle in Section III to derive the system of governing equations for our model. In Section IV we solve the governing system numerically to obtain the flow and charge patterns for electrokinetic flows around a stationary spherical particle in a cylindrical column of a nematic electrolyte.

II. PRINCIPLE OF MINIMUM ENERGY DISSIPATION

There is a variety of variational principles governing behavior of evolutionary systems [23]. In classical mechanics, for instance, irreversible dynamics of a system can be described by means of a Rayleigh dissipation function $\mathcal{R} = \frac{1}{2}\xi_{ij}\dot{q}_i\dot{q}_j$ quadratic in generalized velocities $\dot{q} = (\dot{q}_1, ..., \dot{q}_M)$ (summation over repeated subscripts is implied hereafter). The basic idea is to balance frictional and conservative forces in Lagrange's dynamical equations

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{q}_m} - \frac{\partial \mathcal{L}}{\partial q_m} + \frac{\partial \mathcal{R}}{\partial \dot{q}_m} = 0, \tag{1}$$

where $q = (q_1, ..., q_M)$ are generalized coordinates conjugated with the velocities \dot{q} and $\mathcal{L} = \frac{1}{2}a_{ij}(q)\dot{q}_i\dot{q}_j - \mathcal{U}(q)$ is the Lagrangian of the system, defined as the difference between the kinetic energy $\frac{1}{2}a_{ij}(q)\dot{q}_i\dot{q}_j$ and the potential energy $\mathcal{U}(q)$. In what follows, we assume that the matrices (ξ_{ij}) and (a_{ij}) are symmetric.

Similarly to their non-dissipative counterparts, Eqs. (1) can be recast into a variational problem as their solutions provide a critical points of the functional

$$\int_{\Omega} d^3r \left\{ \dot{\mathcal{E}} + \mathcal{R} \right\}$$

with respect to a special class of variations $\delta \dot{q}$ of the generalized velocities \dot{q} . Here $\Omega \subset \mathbb{R}^3$ is the region occupied by the system, $\mathcal{E} = \mathcal{L} + 2\mathcal{U}$ is the total energy and the superimposed dot (as well as $\frac{d}{dt}$) denotes the total or material time derivative. Unlike Hamilton's principle of stationary action, the current approach "freezes" both the configuration q and the generalized forces $X_m := \frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{q}_m} - \frac{\partial \mathcal{L}}{\partial q_m}, m = 1, \dots, M$ acting on the system at a give time. The state of the system is then varied by imposing arbitrary instantaneous variations $\delta \dot{q}$ of the velocities \dot{q} . Note that variations δq , $\delta \dot{q}$, and $\delta \ddot{q}$ are mutually independent except for the condition that the generalized forces $X_m, m = 1, \dots, M$ should remain unaltered [24]. Then, by using the product rule and relabeling, we indeed have

$$\frac{\delta}{\delta \dot{q}_m} \int_{\Omega} d^3 r \left\{ \dot{\mathcal{E}} + \mathcal{R} \right\} = \frac{\delta}{\delta \dot{q}_m} \int_{\Omega} d^3 r \left\{ a_{ij} \ddot{q}_j \dot{q}_i + \frac{1}{2} \frac{\partial a_{ij}}{\partial q_k} \dot{q}_k \dot{q}_j \dot{q}_i + \frac{\partial \mathcal{U}}{\partial q_i} \dot{q}_i + \mathcal{R} \right\}$$

$$= \frac{\delta}{\delta \dot{q}_m} \int_{\Omega} d^3 r \left\{ \left[\frac{d}{dt} \left(a_{ij} \dot{q}_j \right) - \frac{1}{2} \frac{\partial a_{kj}}{\partial q_i} \dot{q}_k \dot{q}_j + \frac{\partial \mathcal{U}}{\partial q_i} \right] \dot{q}_i + \mathcal{R} \right\} = \frac{\delta}{\delta \dot{q}_m} \int_{\Omega} d^3 r \left\{ X_i \dot{q}_i + \mathcal{R} \right\}$$

$$= X_m + \frac{\partial \mathcal{R}}{\partial \dot{q}_m} = \frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{q}_m} - \frac{\partial \mathcal{L}}{\partial q_m} + \frac{\partial \mathcal{R}}{\partial \dot{q}_m}, \quad (2)$$

for every $m = 1, \ldots, M$. Hence, the Euler-Lagrange equations

$$\frac{\delta}{\delta \dot{q}} \int_{\Omega} d^3 r \left\{ \dot{\mathcal{E}} + \mathcal{R} \right\} = 0 \tag{3}$$

are identical to the generalized equations of motion (1) and thus govern dynamics of a dissipative mechanical system. Since the conservative forces are assumed to be fixed here and \mathcal{R} is a positivedefinite function, the equations (3) yield a minimum of energy dissipation [19, 20]. It is worth noting that for overdamped systems—where $\ddot{q} = 0$ —this principle of minimum energy dissipation is equivalent to the Onsager's variational approach [25].

III. NEMATIC ELECTROLYTE

In this section, we apply the principle (3) to a nematic electrolyte subject to an external electric field. It was shown earlier that under an appropriate choice of the generalized velocities this framework is capable of reproducing the classical Ericksen-Leslie equations of nematodynamics [19, 20]. Below we demonstrate that it can be extended so as to take into account the presence of an ionic subsystem.

A. Energy of the system

Consider a nematic liquid crystal that contains an ideal gas of N species of ions with valences z^{α} at concentrations c^{α} , where $1 \leq \alpha \leq N$. Assuming that the ions do not interact with the liquid crystal one can write the density of the ionic subsystem energy in the form of entropic and Coulombic contributions

$$\mathcal{E}_{ion} = k_B \Theta \sum_{\alpha=1}^{N} c^{\alpha} \ln c^{\alpha} + \sum_{\alpha=1}^{N} e c^{\alpha} z^{\alpha} \Phi, \qquad (4)$$

where k_B and Θ stand for the Boltzmann constant and the absolute temperature, respectively, Φ denotes the electric potential, and e the elementary charge. Under the action of the field, the ions move with velocities \mathbf{u}^{α} which satisfy the continuity equations

$$\frac{\partial c^{\alpha}}{\partial t} + \nabla \cdot (c^{\alpha} \mathbf{u}^{\alpha}) = 0.$$
(5)

Nematics themselves are anisotropic ordered fluids. A typical nematic consists of elongated molecules whose local orientation can be described by a coarse-grained vector field $\mathbf{n} \equiv -\mathbf{n}$ with non-polar symmetry, the director. This unit-length vector field appropriately describes uniaxial nematic states with constant degree of orientational order S.

In general, the degree of orientational order may not be constant, a nematic may contain disclinations, or be in a biaxial state (characterized by a spatially varying degree of biaxiality $P(\mathbf{r})$ and a set of not one, but two mutually orthogonal unit-length vector fields). Neither of these effects can be modeled within the framework of the standard director theory. The appropriate order parameter to characterize all available nematic states is a symmetric traceless second rank tensor \mathbf{Q} with three, possibly different, eigenvalues. In the uniaxial limit, two of the eigenvalues are equal so that

$$\mathbf{Q}_{ij} = S(n_i n_j - \frac{1}{3}\delta_{ij}). \tag{6}$$

Then the free energy per a unit volume of a nematic liquid crystal can be written in the following form

$$\mathcal{E}_{LdG} = -\frac{A}{2} \mathsf{Q}_{ij} \mathsf{Q}_{ij} + \frac{B}{3} \mathsf{Q}_{ij} \mathsf{Q}_{jk} \mathsf{Q}_{ki} + \frac{C}{4} (\mathsf{Q}_{ij} \mathsf{Q}_{ij})^2 + \frac{L}{2} (\partial_k \mathsf{Q}_{ij}) (\partial_k \mathsf{Q}_{ij}), \tag{7}$$

where the first three terms represent the so-called Landau-de Gennes potential

$$\mathcal{E}_{LdG}^{p} = -\frac{A}{2} \mathsf{Q}_{ij} \mathsf{Q}_{ij} + \frac{B}{3} \mathsf{Q}_{ij} \mathsf{Q}_{jk} \mathsf{Q}_{ki} + \frac{C}{4} (\mathsf{Q}_{ij} \mathsf{Q}_{ij})^{2}, \tag{8}$$

given by an expansion of the free energy of the nematic in terms of the order parameter. The last term $\frac{L}{2}(\partial_k \mathbf{Q}_{ij})(\partial_k \mathbf{Q}_{ij}) = \mathcal{E}^e_{LdG}$ in (7) accounts for elasticity of the liquid crystal with one elastic constant approximation being adopted from now on.

In order to take into account the interaction between the electric field $\mathbf{E} = -\nabla \Phi$ and the liquid crystal, we have to supplement the potential energy (7) of the nematic by

$$\mathcal{E}_E = -\frac{1}{2}\mathbf{D}\cdot\mathbf{E},\tag{9}$$

where \mathbf{D} denotes the electric displacement vector that satisfies

$$\nabla \cdot \mathbf{D} = \sum_{\alpha=1}^{N} e c^{\alpha} z^{\alpha}.$$
 (10)

It should be noted that care must be taken in dealing with the electric field in this problem. The field is substantially nonlocal, that is, its changes can affect the system even if they occur outside the region Ω occupied by the system. In order to avoid dealing with the field outside of Ω , we assume that the system under investigation is surrounded by conductors that are held at a prescribed potential $\Phi_{\partial\Omega}$. Then the electric field exists in Ω only, so that $D_i = \varepsilon_0 \varepsilon_{ij} E_j$ where

$$\varepsilon_{ij} = \frac{1}{3} (\varepsilon_{\parallel} + 2\varepsilon_{\perp}) \delta_{ij} + \Delta \varepsilon \mathbf{Q}_{ij}$$
(11)

with $\Delta \varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$, ε_{\perp} and ε_{\parallel} being dielectric permittivities perpendicular and along the director, respectively, measured in units of the vacuum permittivity ε_0 . Equation (11) is, in fact, used as an implicit phenomenological definition of the tensor order parameter Q.

Thus, neglecting inertia of molecular rotations $(\hat{Q}_{ij} = 0)$, one can write the total energy per unit volume of the system in the form

$$\mathcal{E} = \frac{1}{2}\rho v_i v_i + \mathcal{E}_{LdG} + \mathcal{E}_E + \mathcal{E}_{ion}$$
(12)

with $\rho = \text{const}$ being the nematic mass density and \mathbf{v} the velocity of its flow which we assume to be incompressible, $\nabla \cdot \mathbf{v} = 0$.

B. Dissipation function

We require the dissipation function to be frame-indifferent, positive-definite and quadratic in the generalized velocities. Then, choosing \mathbf{v} and $\dot{\mathbf{Q}}$ to be the generalized velocities, the dissipation function of a nematic liquid crystal \mathcal{R}_{nem} has to be quadratic in \mathbf{v} and $\dot{\mathbf{Q}}$. This restriction, however, does not specify the dependence of the dissipation function on \mathbf{Q} which, in general allows for a large number of nematic viscosity coefficients [19]. Following [26], we reduce the number of these coefficients by restricting \mathcal{R}_{nem} to the terms that at most quadratic in the scalar order parameter S. Then

$$2\mathcal{R}_{nem} = \zeta_1 \mathring{\mathsf{Q}}_{ij} \mathring{\mathsf{Q}}_{ji} + 2\zeta_2 \mathsf{A}_{ij} \mathring{\mathsf{Q}}_{ji} + 2\zeta_3 \mathsf{A}_{ij} \mathring{\mathsf{Q}}_{jk} \mathsf{Q}_{ki} + 2\zeta_4 \mathsf{A}_{ij} \mathsf{A}_{jk} \mathsf{Q}_{ki} + \zeta_5 \mathsf{A}_{ij} \mathsf{A}_{jk} \mathsf{Q}_{kl} \mathsf{Q}_{li} + \zeta_6 \left(\mathsf{A}_{ij} \mathsf{Q}_{ji}\right)^2 + \zeta_7 \mathsf{A}_{ij} \mathsf{A}_{ji} \mathsf{Q}_{kl} \mathsf{Q}_{lk} + \zeta_8 \mathsf{A}_{ij} \mathsf{A}_{ji}, \quad (13)$$

where $A_{ij} = \frac{1}{2}(\partial_j v_i + \partial_i v_j)$ represents the symmetric part of the velocity gradient and $\mathring{Q}_{ij} = \dot{Q}_{ij} - W_{ik}Q_{kj} - W_{jk}Q_{ki}$, with $W_{ij} = \frac{1}{2}(\partial_j v_i - \partial_i v_j)$, gives the rate of the Q-tensor change relative to a flow vorticity [19]. Inserting the uniaxial representation (6) of the tensorial order parameter Q in (13) and taking into account that $\mathring{n}_i = \dot{n}_i - W_{ij}n_j$ and $\dot{S} = 0$, the dissipation function takes the form

$$2\mathcal{R}_{nem}^{(\mathbf{n})} = (\alpha_3 - \alpha_2)\dot{n_i}^2 + 2(\alpha_5 - \alpha_6)\dot{n_i}\mathsf{A}_{ij}n_j + (\alpha_5 + \alpha_6)(\mathsf{A}_{ij}n_j)^2 + \alpha_4(\mathsf{A}_{ij})^2 + \alpha_1(n_i\mathsf{A}_{ij}n_j)^2, \quad (14)$$

when written in terms of the director **n**. Now one can relate the viscosities ζ_i to the Leslie's viscosities α_j [27]:

$$\alpha_{3} - \alpha_{2} = 2S^{2}\zeta_{1}, \qquad \alpha_{6} - \alpha_{5} = 2S\zeta_{2} + \frac{1}{3}S^{2}\zeta_{3}, \alpha_{1} = S^{2}\zeta_{6}, \qquad \alpha_{5} + \alpha_{6} = S\zeta_{4} + \frac{1}{2}S^{2}\zeta_{5}, \alpha_{4} = \zeta_{8} - \frac{1}{3}S\zeta_{4} + \frac{1}{3}S^{2}\left(\frac{1}{3}\zeta_{5} + 2\zeta_{7}\right).$$
(15)

It follows from (15) that the viscosities ζ_3 , ζ_5 , and ζ_7 are higher-order corrections to the Leslie's viscosities in terms of the scalar order parameter S. Thus, one can set $\zeta_3 = \zeta_5 = \zeta_7 = 0$ and arrive at a simpler form of the dissipation function

$$2\mathcal{R}_{nem} = \zeta_1 \mathring{\mathsf{Q}}_{ij} \mathring{\mathsf{Q}}_{ji} + 2\zeta_2 \mathsf{A}_{ij} \mathring{\mathsf{Q}}_{ji} + 2\zeta_4 \mathsf{A}_{ij} \mathsf{A}_{jk} \mathsf{Q}_{ki} + \zeta_6 \left(\mathsf{A}_{ij} \mathsf{Q}_{ji}\right)^2 + \zeta_8 \mathsf{A}_{ij} \mathsf{A}_{ji}, \tag{16}$$

which involves only five nematic viscosities.

For the nematic electrolyte, we also need to incorporate dissipation due to the motion of ions. Taking into account that the mobilities of ions along and perpendicular to the director **n** are different and treating \mathbf{u}^{α} with $1 \leq \alpha \leq N$ as the generalized velocities, the contribution of ions to dissipation is given by [28]

$$2\mathcal{R}_{ion} = k_B \Theta \sum_{\alpha_1}^N c^{\alpha} (\mathsf{D}_{ij}^{\alpha})^{-1} (u_i^{\alpha} - v_i) (u_j^{\alpha} - v_j).$$

$$(17)$$

Here the diffusion matrix D_{ij}^{α} reflects the anisotropy of the liquid crystal conductivity.

Thus, the total energy dissipation rate in the nematic electrolyte is equal to the sum $\mathcal{R} = \mathcal{R}_{nem} + \mathcal{R}_{ion}$ with \mathcal{R}_{nem} as specified in (16).

C. Governing equations

Once the energy \mathcal{E} , the dissipation \mathcal{R} , and the generalized velocities of the system are specified, we are in a position to derive equations describing electro-osmotic flows in nematics. The equations are implicitly given by

$$\frac{\delta}{\delta \mathbf{v}} \int_{\Omega} d^{3}r \left\{ \dot{\mathcal{E}} + \mathcal{R} - p'(\partial_{i}v_{i}) - \Lambda \mathbf{Q}_{ii} \right\} = 0,$$

$$\frac{\delta}{\delta \dot{\mathbf{Q}}} \int_{\Omega} d^{3}r \left\{ \dot{\mathcal{E}} + \mathcal{R} - p'(\partial_{i}v_{i}) - \Lambda \mathbf{Q}_{ii} \right\} = 0,$$

$$\frac{\delta}{\delta \mathbf{u}^{\alpha}} \int_{\Omega} d^{3}r \left\{ \dot{\mathcal{E}} + \mathcal{R} - p'(\partial_{i}v_{i}) - \Lambda \mathbf{Q}_{ii} \right\} = 0,$$
(18)

where two Lagrange multipliers, p' and Λ , associated, respectively, with the flow incompressibility and the tracelessness of the tensor order parameter.

But before deriving the explicit form of (18), let us specify the boundary conditions for our problem. Although one can simply use the natural boundary conditions that follow from the principle of minimum energy dissipation (3), here we impose Dirichlet conditions on $\partial\Omega$. In particular,

$$\mathbf{v} = 0, \quad \dot{\mathbf{Q}} = 0, \quad \mathbf{u}^{\alpha} = 0 \quad \text{on } \partial\Omega.$$
 (19)

This choice of boundary conditions slightly simplifies further consideration and corresponds to a majority of experimental setups.

Next, we calculate the rate of change of the energy in Eq. (18): we start by computing

$$\frac{d}{dt} \int_{\Omega} d^3 r \left\{ \frac{1}{2} \rho \mathbf{v}^2 + \mathcal{E}_{LdG} \left(\mathbf{Q}, \nabla \mathbf{Q} \right) \right\} = \\
= \int_{\Omega} d^3 r \left\{ \left[\rho \dot{v}_l + \partial_k \left(\frac{\partial \mathcal{E}_{LdG}}{\partial (\partial_k \mathbf{Q}_{ij})} (\partial_l \mathbf{Q}_{ij}) \right) \right] v_l + \left[\frac{\partial \mathcal{E}_{LdG}}{\partial \mathbf{Q}_{ij}} - \partial_k \left(\frac{\partial \mathcal{E}_{LdG}}{\partial (\partial_k \mathbf{Q}_{ij})} \right) \right] \dot{\mathbf{Q}}_{ij} \right\}, \quad (20)$$

and

$$\frac{d}{dt} \int_{\Omega} d^3 r \mathcal{E}_E(\mathbf{Q}, \nabla \Phi) = \int_{\Omega} d^3 r \left\{ \frac{\partial \mathcal{E}_E}{\partial \mathbf{Q}_{ij}} \dot{\mathbf{Q}}_{ij} + \frac{\partial \mathcal{E}_E}{\partial (\partial_i \Phi)} (\partial_i \dot{\Phi}) - \frac{\partial \mathcal{E}_E}{\partial (\partial_i \Phi)} (\partial_k \Phi) (\partial_i v_k) \right\},$$
(21)

with help of the identity $(\partial_k \dot{\mathbf{Q}}_{ij}) = \partial_k \dot{\mathbf{Q}}_{ij} - (\partial_k v_l)(\partial_l \mathbf{Q}_{ij}).$

Recall that

$$\mathcal{E}_E = -\varepsilon_0 (\bar{\varepsilon} \delta_{ij} + \Delta \varepsilon \mathbf{Q}_{ij}) (\partial_i \Phi) (\partial_j \Phi) / 2,$$

where $\bar{\varepsilon} = (\varepsilon_{\parallel} + 2\varepsilon_{\perp})/3$. Then

$$\frac{\partial \mathcal{E}_E}{\partial \mathsf{Q}_{ij}} = -\frac{1}{2} \varepsilon_0 \Delta \varepsilon (\partial_i \Phi) (\partial_j \Phi) \quad \text{and} \quad \frac{\partial \mathcal{E}_E}{\partial (\partial_i \Phi)} = -\varepsilon_0 \varepsilon_{ij} (\partial_j \Phi).$$
(22)

Hence

$$\frac{d}{dt} \int_{\Omega} d^3 r \mathcal{E}_E(\mathbf{Q}, \nabla \Phi) = \\
= \int_{\Omega} d^3 r \left\{ -\frac{1}{2} \varepsilon_0 \Delta \varepsilon E_i E_j \dot{\mathbf{Q}}_{ij} - (\partial_i D_i) \dot{\Phi} - \partial_i (\varepsilon_0 \varepsilon_{ij} E_j E_k) v_k \right\} + \int_{\partial \Omega} d^2 r \left\{ (\nu_i \varepsilon_0 \varepsilon_{ij} E_j) \dot{\Phi} \right\}. \quad (23)$$

On a conductor-dielectric interface, the normal component of the displacement, $D_i\nu_i$, is given by the surface charge density σ . It follows from (19) and the definition of a material derivative that the surface integral in (23) can be written as

$$\int_{\partial\Omega} d^2r \left\{ (\nu_i \varepsilon_0 \varepsilon_{ij} E_j) \dot{\Phi} \right\} = \int_{\partial\Omega} d^2r \, D_i \nu_i \frac{\partial\Phi}{\partial t} = \int_{\partial\Omega} d^2r \, \sigma \frac{\partial\Phi}{\partial t}.$$
 (24)

This integral gives the power spent by charges located at $\partial\Omega$ and can be omitted when $\Phi_{\partial\Omega}$ varies slowly compared to the timescales of the dynamics associated with \mathbf{v} , \mathbf{u}^{α} and $\dot{\mathbf{Q}}$.

For the ionic subsystem, we have

$$\frac{d}{dt} \int_{\Omega} d^3 r \mathcal{E}_{ion}(c^{\alpha}, \Phi) = \int_{\Omega} d^3 r \sum_{\alpha=1}^{N} \left\{ (\partial_i \mu^{\alpha}) c^{\alpha} (u_i^{\alpha} - v_i) + e c^{\alpha} z^{\alpha} \dot{\Phi} - \mu^{\alpha} c^{\alpha} (\partial_i v_i) \right\},$$
(25)

where $\mu^{\alpha} = \frac{\partial \mathcal{E}_{ion}}{\partial c^{\alpha}} = k_B \Theta(\ln c^{\alpha} + 1) + ez^{\alpha} \Phi$ is the chemical potential of the α -th ion species [29].

Note that $\dot{\mathcal{E}}_{ion}$ includes the term $\sum_{\alpha} ec^{\alpha} z^{\alpha} \dot{\Phi}$ whereas $\dot{\mathcal{E}}_E$ contains $-(\partial_i D_i) \dot{\Phi}$; these terms cancel out when combined together in the expression for the total power $\dot{\mathcal{E}}$. This is due to the fact that the electric field obeys the Maxwell's equation (10).

We could have instead obtained the same equation (10) for **D** from (3), if we chose to treat Φ as a generalized velocity. Then

$$\frac{\delta}{\delta\dot{\Phi}} \int_{\Omega} d^3 r \left\{ \dot{\mathcal{E}} + \mathcal{R} - p'(\partial_i v_i) - \Lambda \mathsf{Q}_{ii} \right\} = -\partial_i D_i + \sum_{\alpha=1}^N e c^\alpha z^\alpha = 0.$$
(26)

Since the present framework deals with the energy of the entire system this derivation properly addresses the nonlocality of the field.

Now we write down the variational derivatives of the total dissipation function \mathcal{R} . We have

$$\frac{\delta}{\delta \dot{\mathbf{Q}}_{ij}} \int_{\Omega} d^3 r \mathcal{R} = \frac{\partial \mathcal{R}_{nem}}{\partial \dot{\mathbf{Q}}_{ij}} = \zeta_1 \dot{\mathbf{Q}}_{ij} + \zeta_2 \mathbf{A}_{ij}, \tag{27}$$

$$\frac{\delta}{\delta u_i^{\alpha}} \int_{\Omega} d^3 r \mathcal{R} = k_B \Theta c^{\alpha} (\mathsf{D}_{ij}^{\alpha})^{-1} (u_j^{\alpha} - v_j), \tag{28}$$

$$\frac{\delta}{\delta v_i} \int_{\Omega} d^3 r \mathcal{R} = \frac{\delta}{\delta v_i} \int_{\Omega} d^3 r \mathcal{R}_{nem} - k_B \Theta \sum_{\alpha=1}^N c^\alpha (\mathsf{D}_{ij}^\alpha)^{-1} (u_j^\alpha - v_j).$$
(29)

Using the explicit form (16) of \mathcal{R}_{nem} and the chain rule

$$\frac{\partial}{\partial(\partial_j v_i)} = \frac{\partial}{\partial \mathsf{A}_{ij}} + \mathsf{Q}_{ki} \frac{\partial}{\partial \mathring{\mathsf{Q}}_{jk}} - \mathsf{Q}_{kj} \frac{\partial}{\partial \mathring{\mathsf{Q}}_{ik}},$$

we obtain that

$$\frac{\delta}{\delta v_i} \int_{\Omega} d^3 r \mathcal{R}_{nem} = -\partial_j \mathsf{T}_{ij}^V,$$

where the viscous stress tensor

$$T_{ij}^{V} = \zeta_{1} \left(\mathring{Q}_{jk} Q_{ki} - \mathring{Q}_{ik} Q_{kj} \right) + \zeta_{2} \mathring{Q}_{ij} + (\zeta_{4} + \zeta_{2}) A_{jk} Q_{ki} + (\zeta_{4} - \zeta_{2}) A_{ik} Q_{kj} + \zeta_{6} \left(A_{kl} Q_{lk} \right) Q_{ij} + \zeta_{8} A_{ij} \quad (30)$$

is identical to that suggested in [30].

Thus, it follows from (25) and (28) that

$$\frac{\delta}{\delta u_i^{\alpha}} \int_{\Omega} d^3 r \left\{ \dot{\mathcal{E}} + \mathcal{R} - p'(\partial_i v_i) - \Lambda n_i \dot{n}_i \right\} = c^{\alpha} \left(\partial_i \mu^{\alpha} + k_B \Theta(\mathsf{D}_{ij}^{\alpha})^{-1} (u_j^{\alpha} - v_j) \right) = 0.$$
(31)

Combining this with the continuity equation (5), we arrive at

$$\frac{\partial c^{\alpha}}{\partial t} + \partial_j \left[c^{\alpha} v_j - \frac{c^{\alpha}}{k_B \Theta} \mathsf{D}^{\alpha}_{ij} (\partial_i \mu^{\alpha}) \right] = 0.$$
(32)

Likewise, equations (20), (23) and (27) yield

$$\frac{\delta}{\delta \dot{\mathsf{Q}}_{ij}} \int_{\Omega} d^3 r \left\{ \dot{\mathcal{E}} + \mathcal{R} - p'(\partial_i v_i) - \Lambda \mathsf{Q}_{ii} \right\} = \\ = \frac{\partial \mathcal{E}_{LdG}}{\partial \mathsf{Q}_{ij}} - \partial_k \left[\frac{\partial \mathcal{E}_{LdG}}{\partial (\partial_k \mathsf{Q}_{ij})} \right] - \Lambda \delta_{ij} - \frac{1}{2} \varepsilon_0 \Delta \varepsilon E_i E_j + \zeta_1 \mathring{\mathsf{Q}}_{ij} + \zeta_2 \mathsf{A}_{ij} = 0.$$
(33)

Finally, combining (20), (23), (25), (29) and (31) we arrive at

$$\frac{\delta}{\delta v_i} \int_{\Omega} d^3 r \left\{ \dot{\mathcal{E}} + \mathcal{R} - p'(\partial_i v_i) - \Lambda \mathbf{Q}_{ii} \right\} = \\ = \rho \dot{v}_i + \partial_k \left[\frac{\partial \mathcal{E}_{LdG}}{\partial (\partial_k \mathbf{Q}_{mn})} (\partial_i \mathbf{Q}_{mn}) - \mathsf{T}_{ik}^V - \varepsilon_0 \varepsilon_{kj} E_j E_i \right] + \partial_i p' + \partial_i \left[\sum_{\alpha=1}^N c^\alpha \mu^\alpha \right] = 0. \quad (34)$$

The sum $p' + \sum_{\alpha} c^{\alpha} \mu^{\alpha}$ can be defined as the total pressure p, thus yielding an alternative form

$$\rho \dot{v_i} + \partial_k \left[\frac{\partial \mathcal{E}_{LdG}}{\partial (\partial_k \mathbf{Q}_{mn})} (\partial_i \mathbf{Q}_{mn}) + p \delta_{ik} - \mathsf{T}^V_{ik} - \varepsilon_0 \varepsilon_{kj} E_j E_i \right] = 0$$
(35)

of (34). Equations (10), (32), (33) and (35) along with the definition of the chemical potential

$$\mu^{\alpha} = \frac{\partial \mathcal{E}_{ion}}{\partial c^{\alpha}} = k_B \Theta(\ln c^{\alpha} + 1) + e z^{\alpha} \Phi$$
(36)

and constraints $\nabla \cdot \mathbf{v} = 0$, $\mathbf{Q}_{ii} = 0$ constitute the full set of equations governing electro-osmosis in nematic liquid crystals, which can be written in the following invariant form

$$\begin{cases} \frac{\partial c^{\alpha}}{\partial t} + \operatorname{div} \left[c^{\alpha} \mathbf{v} - \frac{c^{\alpha}}{k_{B}\Theta} \mathsf{D}^{\alpha} (\nabla \mu^{\alpha}) \right] = 0, \\ \frac{\partial \mathcal{E}_{LdG}}{\partial \mathsf{Q}} - \operatorname{div} \left[\frac{\partial \mathcal{E}_{LdG}}{\partial (\nabla \mathsf{Q})} \right] - \Lambda \mathsf{I} - \frac{1}{2} \varepsilon_{0} \Delta \varepsilon \mathbf{E} \otimes \mathbf{E} + \zeta_{1} \mathring{\mathsf{Q}} + \zeta_{2} \mathsf{A} = 0, \\ \rho \dot{\mathbf{v}} + \operatorname{div} \left[-\mathsf{T}^{\mathrm{el}} + p \mathsf{I} - \mathsf{T}^{V} - \varepsilon_{0} \mathbf{E} \otimes \hat{\varepsilon} \mathbf{E} \right] = 0, \\ \operatorname{div} \left[\frac{1}{3} \left(\varepsilon_{\parallel} + 2\varepsilon_{\perp} \right) \mathbf{E} + \Delta \varepsilon \mathsf{Q} \mathbf{E} \right] = \frac{e}{\varepsilon_{0}} \sum_{\alpha=1}^{N} c^{\alpha} z^{\alpha}, \\ \mu^{\alpha} = k_{B} \Theta(\ln c^{\alpha} + 1) + e z^{\alpha} \Phi, \\ \operatorname{div} \mathbf{v} = 0, \\ \operatorname{Tr} \mathsf{Q} = 0, \end{cases}$$
(37)

where the elastic stress tensor $\mathsf{T}^{\mathrm{el}} = -\frac{\partial \mathcal{E}_{LdG}}{\partial (\partial_k \mathsf{Q}_{mn})} (\partial_i \mathsf{Q}_{mn}) \mathbf{e}_i \otimes \mathbf{e}_k$, the dielectric tensor $\hat{\varepsilon} = \varepsilon_{ij} \mathbf{e}_i \otimes \mathbf{e}_j$ and I is the identity tensor.

IV. ELECTRO-OSMOTIC FLOW AROUND A SPHERICAL PARTICLE

In this section, we consider a simple but illustrative example of liquid crystal-enabled electroosmotic flow (LCEO) around an immobilized spherical particle placed at the center of a large cylindrical domain filled with a nematic electrolyte. Recently, a similar problem in a rectangular container was experimentally examined in [12]. Despite the difference in geometry, the physical mechanism of LCEO is essentially the same in both cases. The colloidal inclusion distorts the otherwise uniform ordering of the liquid crystal molecules, inducing spatial variations of the order tensor \mathbf{Q} field. In the presence of an electric field, inhomogeneities of \mathbf{Q} , along with the anisotropy of dielectric permittivity and conductivity of the liquid crystal give rise to spatial separation of electric charges present in the system. This field-induced charging of distorted regions of the nematic electrolyte is a distinctive feature of LCEO, which consequently yields electrokinetic flow with the velocity quadratic in the electric field. The profile of the flow, as will be seen below, depends on the symmetry of the tensor field \mathbf{Q} as well as on anisotropies of ionic conductivities and the dielectric permittivity of the nematic.

Let us consider a micron-sized spherical colloidal particle suspended in a nematic electrolyte subject to a uniform electric field $\mathbf{E} = (0, 0, -E)$. For the sake of simplicity, assume that the ionic subsystem consists of two species with valences $z^+ = 1$ and $z^- = -1$ and concentrations c^+ and c^{-} , respectively. We assume equal mobility matrices

$$\mathsf{D}^{+} = \mathsf{D}^{-} = \mathsf{D}_{ij} = \bar{\mathsf{D}}(\bar{\lambda}_{\sigma}\delta_{ij} + (\lambda_{\sigma} - 1)\mathsf{Q}_{ij})\,\mathbf{e}_i \otimes \mathbf{e}_j,$$

where $\{\mathbf{e}_i\}_{i=1,2,3}$ is a set of mutually orthonormal vectors in \mathbb{R}^3 and $\lambda_{\sigma} = \sigma_{\parallel}/\sigma_{\perp} > 0$ denotes the ratio of the conductivity along and perpendicular to the nematic director, respectively; $\bar{\lambda}_{\sigma} = \frac{1}{3}(\lambda_{\sigma}+2)$ and $\bar{\mathbf{D}} > 0$.

For further analysis of the system of governing equations (37), it is convenient to introduce nondimensional variables

$$\tilde{\mathbf{r}} = \frac{\mathbf{r}}{a}, \qquad \tilde{t} = \frac{t}{\bar{v}}, \qquad \tilde{\Phi} = \frac{\Phi}{Ea}, \qquad \tilde{c}^{\pm} = \frac{c^{\pm}}{\bar{c}}, \\ \tilde{v} = \frac{\mathbf{v}}{\bar{v}}, \qquad \tilde{p} = \frac{p}{\bar{p}}, \qquad \tilde{\mathsf{D}}_{ij} = \frac{\mathsf{D}_{ij}}{\bar{\mathsf{D}}}, \qquad \tilde{\mathsf{T}}_{ij}^{V} = \mathsf{T}_{ij}^{V} \frac{a}{\zeta_{8}\bar{v}},$$
(38)

where a is the radius of the particle and \bar{x} denotes the characteristic value of x. Then omitting the tildes for notational simplicity, one can rewrite the system (37) in the following nondimensional form

$$\begin{cases} \operatorname{Pe}\left(\frac{\partial c^{\pm}}{\partial t} + \operatorname{div}\left[c^{\alpha}\mathbf{v}\right]\right) - \operatorname{div}\left[\mathsf{D}\left(\nabla c^{\pm} \mp c^{\pm}G\mathbf{E}\right)\right] = 0, \\ \frac{\partial \mathcal{E}_{LdG}}{\partial \mathsf{Q}} - \operatorname{div}\left[\frac{\partial \mathcal{E}_{LdG}}{\partial(\nabla\mathsf{Q})}\right] - \Lambda \mathsf{I} - \frac{1}{2}\frac{a^{2}}{\xi_{E}^{2}}\mathbf{E}\otimes\mathbf{E} + \operatorname{Er}\left(\frac{\zeta_{1}}{\zeta_{8}}\mathring{\mathsf{Q}} + \frac{\zeta_{2}}{\zeta_{8}}\mathsf{A}\right) = 0, \\ \operatorname{Re}\dot{\mathbf{v}} + \operatorname{div}\left[-\frac{1}{\operatorname{Er}}\mathsf{T}^{\operatorname{el}} + p\mathsf{I} - \mathsf{T}^{V} - \mathbf{E}\otimes\frac{\hat{\varepsilon}}{\varepsilon_{\perp}}\mathbf{E}\right] = 0, \\ \operatorname{div}\left[\frac{1}{3}\left(\lambda_{\varepsilon} + 2\right)\mathbf{E} + \left(\lambda_{\varepsilon} - 1\right)\mathbf{Q}\mathbf{E}\right] = B\left(c^{+} - c^{-}\right), \\ \operatorname{div}\mathbf{v} = 0, \\ \operatorname{Tr}\mathbf{Q} = 0, \end{cases}$$
(39)

which implies $\bar{p} = \frac{\zeta_8 \bar{v}}{a}$ and $\bar{v} = \frac{\varepsilon_0 \varepsilon_\perp a E^2}{\zeta_8}$, and where the nondimensional parameters

$$Pe = \frac{\bar{v}a}{\bar{D}}, \qquad Er = \frac{\zeta_8 \bar{v}a}{L}, \qquad \frac{a^2}{\xi_E^2} = \frac{\varepsilon_0 \Delta \varepsilon E^2 a^2}{L},$$

$$Re = \frac{\rho \bar{v}a}{\zeta_8}, \qquad B = \frac{e\bar{c}a}{\varepsilon_0 \varepsilon_\perp E}, \qquad G = \frac{eaE}{k_B \Theta}$$
(40)

along with $\lambda_{\varepsilon} = \varepsilon_{\parallel}/\varepsilon_{\perp}$ are introduced. Here $\xi_E = \sqrt{L/(\varepsilon_0 | \Delta \varepsilon | E^2)}$ is the electric coherence length. We consider the colloidal sphere to be relatively small, $a \approx 1 \mu m$; the rest of the parameters are close to the ones used in typical experiments on LCEO: $\rho \approx 1 \text{ g/cm}^3$, $\Delta \varepsilon \approx 10$, $\varepsilon_{\perp} \approx 10$, $L \approx 10 \text{ pN}$, $\overline{D} \approx 5 \cdot 10^{-11} \text{ m}^2/\text{s}$, $\zeta_8 \approx 0.1 \text{ Pa} \cdot \text{s}$, $\overline{c} = 10^{19} \text{ m}^{-3}$, and $\Theta = 293 \text{ K}$. To simplify computations we assume that the radius of the particle $a \approx 1 \mu \text{m}$ and the field strength $E \approx 40 \text{ mV}/\mu \text{m}$ are somewhat smaller than those used in experiments, so that

Pe
$$\approx 0.03$$
, Er ≈ 0.01 , $\frac{a^2}{\xi_E^2} \approx 0.01$, Re $\approx 1 \cdot 10^{-8}$, $B \approx 0.45$, $G \approx 1.6$. (41)

Smallness of the first three characteristic numbers is of particular importance in what follows. Since diffusive transport of ions prevails over advective (the Peclet number $Pe \ll 1$) and the elasticity of the liquid crystal dominates over its viscosity (the Ericksen number $Er \ll 1$), the order parameter Q and the concentrations of ions c^+ and c^- are not significantly affected by the liquid crystal flow. Moreover, due to the small ratio of the particle radius a to the electric coherence length ξ_E , we can also neglect the influence of the electric field on the molecular alignment.

Note that in [12], for a particle of radius $25 \ \mu m$, the experimentally observed velocity of propagation was $4 \ \mu m/s$, which corresponds to Er = O(1). The system (37) can still be solved numerically for this situation, but the equations remain fully coupled.

Thus, the system of equations (39) can be solved in three consecutive steps. First, we find the alignment tensor Q from

$$\begin{cases} \frac{\partial \mathcal{E}_{LdG}}{\partial \mathsf{Q}} - \operatorname{div} \left[\frac{\partial \mathcal{E}_{LdG}}{\partial (\nabla \mathsf{Q})} \right] - \Lambda \mathsf{I} = 0, \\ \operatorname{Tr} \mathsf{Q} = 0, \end{cases}$$
(42)

then calculate the concentrations $c^{\pm}(\mathbf{r})$ and the electric field $\mathbf{E} = -\nabla \Phi$ given by

$$\begin{cases} \operatorname{div} \left[\mathsf{D} \left(\nabla c^{\pm} \mp c^{\pm} G \mathbf{E} \right) \right] = 0, \\ \operatorname{div} \left[\frac{1}{3} \left(\lambda_{\varepsilon} + 2 \right) \mathbf{E} + \left(\lambda_{\varepsilon} - 1 \right) \mathsf{Q} \mathbf{E} \right] = B \left(c^{+} - c^{-} \right), \end{cases}$$
(43)

and finally, solve

$$\begin{cases} \operatorname{div}\left[-\frac{1}{\mathrm{Er}}\mathsf{T}^{\mathrm{el}} + p\mathsf{I} - \mathsf{T}^{V} - \frac{1}{\varepsilon_{\perp}}\mathbf{E}\otimes\hat{\varepsilon}\mathbf{E}\right] = 0,\\ \operatorname{div}\,\mathbf{v} = 0 \end{cases}$$
(44)

for the pressure $p(\mathbf{r})$ and the velocity field $\mathbf{v}(\mathbf{r})$.

A. Alignment tensor

The non-dimensionalized Landau-de Gennes free energy \mathcal{E}_{LdG} , which enters (39) and subsequently (42) and (44), reads in the nondimensional form as

$$\mathcal{E}_{LdG} = \left(\frac{a}{\xi}\right)^2 \left\{ -\frac{1}{2} \operatorname{Tr} \, \mathsf{Q}^2 + \frac{B}{3A} \operatorname{Tr} \, \mathsf{Q}^3 + \frac{C}{4A} \left(\operatorname{Tr} \, \mathsf{Q}^2\right)^2 \right\} + \frac{1}{2} \left|\nabla \mathsf{Q}\right|^2, \tag{45}$$



Figure 1. Domain of simulation. The mesh was generated by Gmsh [31]. Thick red lines depict physical boundaries of the domain.

where $\xi = \sqrt{L/A} \sim 10$ nm stands for the nematic coherence length and A, B, and C are constant at a given temperature. The Landau-de Gennes potential \mathcal{E}_{LdG}^p defined in (7) determines whether the nematic phase is thermodynamically stable. It is minimized by a uniaxial tensor $\mathbf{Q} = S_0(\mathbf{n} \otimes \mathbf{n} - \frac{1}{3}\mathbf{I})$ with $S_0 = \frac{1}{4C} \left(-B + \sqrt{B^2 + 24AC}\right)$ for any $\mathbf{n} \in \mathbb{S}^2$. Following Fukuda *et al.* [32, 33], we set C = -B = 3A so as $S_0 = 1$. Assuming the same scalar order parameter $S_0 = 1$ at the particle surface and introducing a unit-length vector $\boldsymbol{\nu}$ normal to it, we impose the Dirichlet boundary condition $\mathbf{Q} = \boldsymbol{\nu} \otimes \boldsymbol{\nu} - \frac{1}{3}\mathbf{I}$ corresponding to the strong homeotropic anchoring of the nematic. At infinity we assume that the alignment uniform, i.e., $\mathbf{Q} = \mathbf{n}^0 \otimes \mathbf{n}^0 - \frac{1}{3}\mathbf{I}$, where $\mathbf{n}^0 = (0, 0, 1)$. The topological constraints imposed by our choice of boundary data produce either a line or point singularity in the vicinity of the particle. Theoretical [32, 34, 35] and experimental [36, 37] studies show that a small particle $(a/\xi \leq 60)$ will be encircled by a disclination loop, known as a Saturn ring, whereas a point defect, a hyperbolic hedgehog, will be energetically favorable provided that $a/\xi \gtrsim 60$. Note that both configurations are axisymmetric with respect to \mathbf{n}^0 . Therefore, in cylindrical coordinates $\{\rho, \phi, z\}$ with the z-axis pointing along the director at infinity \mathbf{n}^0 , the alignment tensor $\mathbf{Q} = \mathbf{Q}(\rho, z)$ does not depend on the azimuthal angle ϕ .

While the problem (42) was solved explicitly in the limit of small particles [38], there is no

analytical solution for large a/ξ in three dimensions. In two dimensions the solution, however, it is well known [39]. Indeed, the director field $\mathbf{n}^{2D} = (\cos \psi, \sin \psi)$ around a circular particle located at the origin of Cartesian coordinate system $\{x, y\}$ and a pointlike topological defect at $(0, -y_0)$ is given by

$$\psi = 2 \arctan \frac{x}{y} - \arctan \frac{x}{y+y_0} - \arctan \frac{x}{y+1/y_0}.$$
(46)

In our study, this two-dimensional solution \mathbf{n}^{2D} is used as an initial guess for the axially symmetric problem. We use the nonlinear variational solver developed by the FEniCS Project—a collection of open source software for automated solution of differential equations by finite element methods [40–51]. In the case of small particles ($a/\xi \lesssim 60$), the initial state relaxes to a Saturn ring configuration, while for large particles ($a/\xi \gtrsim 60$) it results in a hedgehog-like solution that, in agreement with [32, 35, 52], is in fact a small ring disclination rather than a point defect.

The computed solutions of the problem (42) for $a/\xi = 30$ and $a/\xi = 70$ are visualized in Fig. 2 by means of a scalar criterion u proposed in [53]. Note that in the absolute units, the radius of the colloidal spheres is rather small, 0.3 microns and 0.7 microns, respectively; experiments reported so far deal with bigger spheres, a = 25 microns [12]. The criterion utilizes the fact that the eigenvalues of the tensor order parameter \mathbf{Q} corresponding to a uniaxial nematic state can be written as -s, -s, 2s. Then Tr $\mathbf{Q}^2 = 6s^2$ and det $\mathbf{Q} = 2s^3$ and one can introduce a scalar quantity

$$u = \frac{(\det \mathbf{Q})^2}{(\mathrm{Tr} \ \mathbf{Q}^2)^3} - \frac{1}{54},\tag{47}$$

whose nonzero values indicate biaxial alignment of the liquid crystal molecules.

B. Charge separation

Once the tensor field Q is known, we solve the problem (43) for the ionic concentrations $c^{\pm} = c^{\pm}(\rho, z)$ and the electric potential $\Phi = \Phi(\rho, z)$, subject to Dirichlet boundary conditions $c^{\pm} = 1$ and $\Phi = z$ at $z = \pm Z$ (see Fig. 1). Here, the Maxwell equation in (43) should also be solved inside the particle. Therefore, the dielectric permittivity ϵ_p of the particle has to be specified as it determines the distribution of ions in the system and thus influences the flow. In the present study, we focus on dielectric colloids which are commonly used in practice. In particular, Fig. 3 shows nondimensional charge density $q = c^+ - c^-$ around a dielectric spherical particle with $\epsilon_p = 0.4\varepsilon_{\perp}$.

Note that the separation of charges in the system arises from an interplay between the orientational ordering of the nematic and its anisotropic permittivity and conductivity, determined



Figure 2. Spherical particle accompanied by a Saturn ring (a) and a hyperbolic hedgehog (b) topological defects. Nonzero values of the biaxiality parameter u given by (47) indicate biaxial alignment of the liquid crystal molecules.

by the tensor field \mathbf{Q} and the parameters λ_{ε} and λ_{σ} , respectively. This result is in line with the expectations that the space charge around colloidal spheres is proportional to the anisotropy of dielectric permittivity and electric conductivity [12]. A similar, but probably simpler, interplay in patterned nematics [14, 15, 28], where spatially varying director field is induced by means of specific anchoring at the substrates, yields the electrokinetic charge density $q_{\text{pat}} \propto \lambda_{\varepsilon} - \lambda_{\sigma}$. In the system under investigation, the charge distribution $q(\mathbf{r})$ is also sensitive to the values of λ_{σ} and λ_{ε} , but it does not vanish when $\lambda_{\varepsilon} = \lambda_{\sigma}$. This is not surprising, given the fact that even in isotropic electrolytes – where $\lambda_{\varepsilon} = \lambda_{\sigma} = 1$ – a dielectric sphere in presence of an applied electric field is capable of generating space charges and cause induced-charge electro-osmosis (ICEO) [3, 4, 6]. This effect is especially pronounced when the Debye screening length $\lambda_D = \frac{1}{e} \sqrt{\frac{\varepsilon_0 \varepsilon_{medium} k_B T}{n}}$ (where *e* is the elementary charge, k_B is the Boltzmann constant, and *T* is the absolute temperature) around the colloid is comparable to the radius of the colloid, as will be discussed later in the context of the field-induced electro-osmotic velocities.

C. Flow profile

We are now in a position to solve the system of equations (44) for the pressure $p = p(\rho, z)$ and the velocity $\mathbf{v} = \mathbf{v}(\rho, z)$ of the electro-osmotic flow. One can further simplify the problem by



Figure 3. Nondimensional charge density $q = c^+ - c^-$ around a spherical particle with: a Saturn ring (a),(c),(e); and a hedgehog (b),(d),(f) topological defect. Here $\lambda_{\varepsilon}=1$, $\lambda_{\sigma}=2$ in (a),(b); $\lambda_{\varepsilon}=2$, $\lambda_{\sigma}=1$ in (c),(d); and $\lambda_{\varepsilon} = \lambda_{\sigma}=2$ in (e),(f).



Figure 4. Velocity field around a spherical particle with: a Saturn ring (a),(c),(e); and a hedgehog (b),(d),(f) defect. Here $\lambda_{\varepsilon}=1$, $\lambda_{\sigma}=2$ in (a),(b); $\lambda_{\varepsilon}=2$, $\lambda_{\sigma}=1$ in (c),(d); and $\lambda_{\varepsilon}=\lambda_{\sigma}=2$ in (e),(f). The nondimensional viscosities are as follows: $\tilde{\zeta}_1=0.3$, $\tilde{\zeta}_2=0$, $\tilde{\zeta}_4=1.3$, $\tilde{\zeta}_6=-0.15$. 19

taking advantage of the fact that $\operatorname{Er} \ll 1$ and $a^2/\xi_E^2 \ll 1$. Since these two parameters are small, the elastic stress tensor $\mathsf{T}^{\mathrm{el}} = -\frac{\partial \mathcal{E}_{LdG}}{\partial (\partial_k \mathsf{Q}_{mn})} (\partial_i \mathsf{Q}_{mn}) \mathbf{e}_i \otimes \mathbf{e}_k$ is determined by the order parameter Q that satisfies (42). It follows then that $\operatorname{div} \mathsf{T}^{\mathrm{el}} = -\nabla \mathcal{E}_{LdG}$. Now splitting the total pressure p into the static $p^0 = \operatorname{const} - \mathcal{E}_{LdG}/\operatorname{Er}$ and hydrodynamic p^h parts [54], we arrive at the following system

$$\begin{cases} \operatorname{div}\left[p^{h}\mathbf{I}-\mathbf{T}^{V}-\frac{1}{\varepsilon_{\perp}}\mathbf{E}\otimes\hat{\varepsilon}\mathbf{E}\right]=0,\\ \operatorname{div}\,\mathbf{v}=0. \end{cases}$$
(48)

Here the viscous stress is

$$\mathsf{T}^{V} = \tilde{\zeta}_{1} \left(\mathsf{Q} \mathring{\mathsf{Q}} - \mathring{\mathsf{Q}} \mathsf{Q} \right) + \tilde{\zeta}_{2} \mathring{\mathsf{Q}} + \left(\tilde{\zeta}_{4} + \tilde{\zeta}_{2} \right) \mathsf{Q} \mathsf{A} + \left(\tilde{\zeta}_{4} - \tilde{\zeta}_{2} \right) \mathsf{A} \mathsf{Q} + \tilde{\zeta}_{6} \operatorname{Tr} \left(\mathsf{Q} \mathsf{A} \right) \mathsf{Q} + \mathsf{A}, \tag{49}$$

where $\tilde{\zeta} = \zeta/\zeta_8$, $2\mathsf{A} = \nabla \mathbf{v} + (\nabla \mathbf{v})^T$, and $\mathring{\mathsf{Q}} = \dot{\mathsf{Q}} - \mathsf{W}\mathsf{Q} + \mathsf{Q}\mathsf{W}$ with $2\mathsf{W} = \nabla \mathbf{v} - (\nabla \mathbf{v})^T$.

Solutions to (48) computed under no-slip conditions ($\mathbf{v} = 0$) at the physical boundaries of the domain of simulation (see Fig. 1) are depicted in Fig. 4. Similar to the charge density qdiscussed above, the flow \mathbf{v} is sensitive to the degree of anisotropy λ_{ε} and λ_{σ} , as well as to the symmetry of the director field. In particular, the flow profiles around the particle encircled by an equatorial Saturn ring are symmetric with respect to the plane of the defect. On the contrary, the particle accompanied by a hedgehog gives rise to the velocity fields \mathbf{v} of dipolar symmetry, which is in qualitative agreement with [12]. Unlike the LCEO in patterned nematics [14, 15, 28] which vanishes when λ_{ε} and λ_{σ} are equal, here we observe nonzero velocity field \mathbf{v} even in the case of $\lambda_{\varepsilon} = \lambda_{\sigma}$. As mentioned above, this effect is in line with the model developed for ICEO flows around dielectric spheres [3, 4, 6]. We now discuss the issue in a greater detail.

Considering an uncharged immobilized dielectric sphere placed in a uniform electric field, Murtsovkin found the analytical solutions for the radial and azimuthal ICEO flows that show a quadrupolar symmetry [6] and a typical amplitude near the surface

$$v^{diel} = \beta \frac{\varepsilon_0 \varepsilon_{medium}}{\eta} \frac{aE^2}{1 + \frac{\varepsilon_{medium}a}{\varepsilon_p \lambda_D}},\tag{50}$$

where β is a scalar coefficient that depends on the geometry of the system (for an infinite system with $\lambda_D \ll a$ and $\beta = \frac{9}{32\pi} \approx 0.1$). For an aqueous electrolyte we have that $\varepsilon_{medium} \approx 80$, $\lambda_D \approx 50$ nm, thus for a typical dielectric particle of a micron size and a permittivity of glass, $\varepsilon_p \approx 5$, one can safely assume $\varepsilon_{medium}a \gg \varepsilon_p \lambda_D$ so that $v^{diel} = \beta \frac{\varepsilon_0 \varepsilon_p}{\eta} \lambda_D E^2$. This velocity is, by a factor about λ_D/a , smaller than the ICEO flow velocities around ideally polarizable (conductive) spheres [3, 6]. The smallness of this effect around dielectric spheres has been confirmed experimentally

by a direct comparison of ICEO velocities around conducting (gold) and dielectric (glass) spheres of the same size in the same aqueous electrolyte [55]. In the case of a nematic electrolyte, the ratio $\varepsilon_{medium} a / \varepsilon_p \lambda_D$ is not necessarily very large, as ε_{medium} and ε_p are often of the same order of magnitude and the Debye screening length is in the range $0.1 - 1 \,\mu m$ [56–58]. For the micron-size particles considered in this study, $\varepsilon_{medium} a/\varepsilon_p \lambda_D$ is of order 1. On the other hand, analytical estimates of the LCEK flows velocities yield a typical amplitude $v^{LCEK} = \alpha \frac{\varepsilon_0 \varepsilon_\perp}{\eta} \left(\frac{\varepsilon}{\varepsilon_\perp} - \frac{\sigma}{\sigma_\perp} \right) a E^2$ where α is an unknown dimensionless parameter of order 0.1 - 1 that is expected to depend on the director field, strength of anchoring, etc. [12]. The ICEO and LCEO flow velocities around dielectric spheres in the nematic electrolyte can thus be of comparable magnitudes. When $\frac{\varepsilon}{\varepsilon_{\perp}} - \frac{\sigma}{\sigma_{\perp}} = 0$, the total velocity around the sphere would not vanish, being determined by the isotropic contribution (50). For example, with $\varepsilon_{medium} = \varepsilon_p = 7$, $\eta = 0.1$ Pas, $a = \lambda_D = 0.3 \,\mu\text{m}$, $E = 40 \times 10^3 \,\mathrm{V/m}$, the estimate is $v^{diel} = 0.01 \,\mu\mathrm{m/s}$. The ICEO effect is apparently more pronounced around smaller particles explored in this work; as the particles become larger as in the experiments [12], this effect would become of a lesser importance. On the other hand, the LCEK effect is expected to diminish as the particle becomes smaller, since the smaller (submicrometer and less) particles are not capable to produce strong director gradients needed for charge separation. It would be of interest to explore the relative strength of ICEK and LCEK in the isotropic and the nematic phases of the same liquid crystal material for particles of a different size.

We conclude that the flow profiles shown in Fig. 4 significantly differ from those observed experimentally in [12] due to different geometry of the experiment [12] where the electrolyte was confined to a planar cell of thickness comparable to the particle diameter. Furthermore, the differences between the results reported here and in [12] stem from the fact that the particles considered in this study are much smaller than those in [12].

It is also worth noting that, if the applied electric field reverses, the charge distributions depicted in Fig. 3 will be inverted while the flow profiles shown in Fig. 4 will remain unaltered (compare, for instance, Fig. 5 to Fig. 3b and Fig. 4b).

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Figure 5. Charge density and velocity of LCEO around the particle with a hedgehog generated by the electric field of inverted polarity. Here $\lambda_{\varepsilon} = 1$, $\lambda_{\sigma} = 2$, $\tilde{\zeta}_1 = 0.3$, $\tilde{\zeta}_2 = 0$, $\tilde{\zeta}_4 = 1.3$, $\tilde{\zeta}_6 = -0.15$.

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- A. Ramos, *Electrokinetics and electrohydrodynamics in microsystems*, Vol. 530 (Springer Science & Business Media, 2011).
- [2] H. Morgan and N. Green, "AC electrokinetics: colloids and nanoobjects," (2003).
- [3] M. Z. Bazant and T. M. Squires, Physical Review Letters 92, 066101 (2004).
- [4] N. Gamayunov, V. Murtsovkin, and A. Dukhin, Colloid J. USSR (Engl. Transl.); (United States)
 48, 233 (1986).
- [5] A. Dukhin and V. Murtsovkin, Colloid J. USSR (Engl. Transl.); (United States) 48, 240 (1986).
- [6] V. A. Murtsovkin, Colloid journal of the Russian Academy of Sciences 58, 341 (1996).
- [7] T. M. Squires and M. Z. Bazant, Journal of Fluid Mechanics 509, 217 (2004).
- [8] S. Hernàndez-Navarro, P. Tierno, J. Ignés-Mullol, and F. Sagués, Soft Matter 9, 7999 (2013).
- [9] S. Hernàndez-Navarro, P. Tierno, J. Ignés-Mullol, and F. Sagués, The European Physical Journal Special Topics 224, 1263 (2015).
- [10] O. D. Lavrentovich, I. Lazo, and O. P. Pishnyak, Nature 467, 947 (2010).
- [11] I. Lazo and O. D. Lavrentovich, Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences 371, 20120255 (2013).

- [12] I. Lazo, C. Peng, J. Xiang, S. V. Shiyanovskii, and O. D. Lavrentovich, Nature Communications 5, 5033 (2014).
- [13] Y. Sasaki, Y. Takikawa, V. S. Jampani, H. Hoshikawa, T. Seto, C. Bahr, S. Herminghaus, Y. Hidaka, and H. Orihara, Soft Matter 10, 8813 (2014).
- [14] C. Peng, Y. Guo, C. Conklin, J. Viñals, S. V. Shiyanovskii, Q.-H. Wei, and O. D. Lavrentovich, Physical Review E 92, 052502 (2015).
- [15] O. M. Tovkach, M. C. Calderer, D. Golovaty, O. Lavrentovich, and N. J. Walkington, Phys. Rev. E 94, 012702 (2016).
- [16] F. M. Leslie, Continuum Mechanics and Thermodynamics 4, 167 (1992).
- [17] F. Leslie, Advances in liquid crystals 4, 1 (1979).
- [18] N. J. Walkington, ESAIM: Mathematical Modelling and Numerical Analysis 45, 523 (2011).
- [19] A. M. Sonnet, P. L. Maffettone, and E. G. Virga, Journal of Non-Newtonian Fluid Mechanics 119, 51 (2004).
- [20] A. M. Sonnet and E. G. Virga, Physical Review E 64, 031705 (2001).
- [21] O. Kuksenok, R. Ruhwandl, S. Shiyanovskii, and E. Terentjev, Physical Review E 54, 5198 (1996).
- [22] P. Poulin, H. Stark, T. Lubensky, and D. Weitz, Science 275, 1770 (1997).
- [23] A. Mielke, in Analysis and Computation of Microstructure in Finite Plasticity (Springer, 2015) pp. 125–155.
- [24] A. M. Sonnet and E. G. Virga, Dissipative ordered fluids: theories for liquid crystals (Springer Science & Business Media, 2012).
- [25] M. Doi, Journal of Physics: Condensed Matter 23, 284118 (2011).
- [26] J. Ericksen, Arch Rath. Mech. Anal. **113**, 97 (1991).
- [27] N. Kuzuu and M. Doi, J. Phys. Soc. Japan 53, 1031 (1984).
- [28] M. C. Calderer, D. Golovaty, O. Lavrentovich, and N. J. Walkington, SIAM J. Appl. Math. 76, 2260 (2016).
- [29] Y. Hyon, B. Eisenberg, and C. Liu, Commun. Math. Sci 9, 459 (2011).
- [30] T. Qian and P. Sheng, Physical Review E 58, 7475 (1998).
- [31] C. Geuzaine and J.-F. Remacle, International Journal for Numerical Methods in Engineering 79, 1309 (2009).
- [32] J.-I. Fukuda, M. Yoneya, and H. Yokoyama, Physical Review E 65, 041709 (2002).
- [33] J.-I. Fukuda, H. Stark, M. Yoneya, and H. Yokoyama, Journal of Physics: Condensed Matter 16,

S1957 (2004).

- [34] H. Stark, The European Physical Journal B-Condensed Matter and Complex Systems 10, 311 (1999).
- [35] M. Ravnik and S. Zumer, Liquid Crystals **36**, 1201 (2009).
- [36] J. Loudet and P. Poulin, Physical Review Letters 87, 165503 (2001).
- [37] C. Völtz, Y. Maeda, Y. Tabe, and H. Yokoyama, Physical Review Letters 97, 227801 (2006).
- [38] S. Alama, L. Bronsard, and X. Lamy, Physical Review E 93, 012705 (2016).
- [39] T. Lubensky, D. Pettey, N. Currier, and H. Stark, Physical Review E 57, 610 (1998).
- [40] M. S. Alnæs, J. Blechta, J. Hake, A. Johansson, B. Kehlet, A. Logg, C. Richardson, J. Ring, M. E. Rognes, and G. N. Wells, Archive of Numerical Software 3 (2015), 10.11588/ans.2015.100.20553.
- [41] A. Logg, K.-A. Mardal, G. N. Wells, et al., Automated Solution of Differential Equations by the Finite Element Method (Springer, 2012).
- [42] A. Logg, G. N. Wells, and J. Hake, "DOLFIN: a C++/Python finite element library," in Automated Solution of Differential Equations by the Finite Element Method, Volume 84 of Lecture Notes in Computational Science and Engineering, edited by A. Logg, K.-A. Mardal, and G. N. Wells (Springer, 2012) Chap. 10.
- [43] A. Logg and G. N. Wells, ACM Transactions on Mathematical Software 37 (2010), 10.1145/1731022.1731030.
- [44] R. C. Kirby and A. Logg, ACM Transactions on Mathematical Software 32 (2006), 10.1145/1163641.1163644.
- [45] A. Logg, K. B. Ølgaard, M. E. Rognes, and G. N. Wells, "FFC: the FEniCS form compiler," in Automated Solution of Differential Equations by the Finite Element Method, Volume 84 of Lecture Notes in Computational Science and Engineering, edited by A. Logg, K.-A. Mardal, and G. N. Wells (Springer, 2012) Chap. 11.
- [46] K. B. Ølgaard and G. N. Wells, ACM Transactions on Mathematical Software 37 (2010), 10.1145/1644001.1644009.
- [47] M. S. Alnæs, A. Logg, K. B. Ølgaard, M. E. Rognes, and G. N. Wells, ACM Transactions on Mathematical Software 40 (2014), 10.1145/2566630.
- [48] M. S. Alnæs, "UFL: a finite element form language," in Automated Solution of Differential Equations by the Finite Element Method, Volume 84 of Lecture Notes in Computational Science and Engineering, edited by A. Logg, K.-A. Mardal, and G. N. Wells (Springer, 2012) Chap. 17.
- [49] R. C. Kirby, ACM Transactions on Mathematical Software **30**, 502 (2004).

- [50] M. S. Alnæs, A. Logg, K.-A. Mardal, O. Skavhaug, and H. P. Langtangen, International Journal of Computational Science and Engineering 4, 231 (2009).
- [51] M. S. Alnæs, A. Logg, and K.-A. Mardal, "UFC: a finite element code generation interface," in Automated Solution of Differential Equations by the Finite Element Method, Volume 84 of Lecture Notes in Computational Science and Engineering, edited by A. Logg, K.-A. Mardal, and G. N. Wells (Springer, 2012) Chap. 16.
- [52] X. Wang, Y.-K. Kim, E. Bukusoglu, B. Zhang, D. S. Miller, and N. L. Abbott, Phys. Rev. Lett. 116, 147801 (2016).
- [53] P. Kaiser, W. Wiese, and S. Hess, Journal of Non-Equilibrium Thermodynamics 17, 153 (1992).
- [54] H. Stark and D. Ventzki, Physical Review E 64, 031711 (2001).
- [55] C. Peng, I. Lazo, S. V. Shiyanovskii, and O. D. Lavrentovich, Physical Review E 90, 051002 (2014).
- [56] R. Thurston, J. Cheng, R. B. Meyer, and G. D. Boyd, Journal of applied physics 56, 263 (1984).
- [57] V. Nazarenko and O. Lavrentovich, Physical Review E 49, R990 (1994).
- [58] F. Ciuchi, A. Mazzulla, A. Pane, and J. A. Reyes, Applied Physics Letters 91, 232902 (2007).