Nematic caps on colloidal particles in a nematogenic liquid under an electric field

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We examine the localized nematic regions (caps) on spherical colloidal particles suspended in a nematogenic liquid in the isotropic phase in the bulk by solving the Poisson equation with an orientation-dependent dielectric tensor. These caps appear and grow with an increasing applied electric field. We assume positive dielectric anisotropy of the nematogenic liquid and a high dielectric constant of the particles. Then, the electric field becomes the strongest near the poles of each particle along the field direction, leading to nematic caps. This cap formation occurs continuously for homeotropic anchoring, but is a discontinuous transition otherwise. We also discuss how the nematic caps can be observed in dielectric response, birefringence, and depolarized light scattering.

1 Introduction

Recently, much attention has been paid to the behavior of suspended particles in nematogenic liquids, where anchoring on the particle surfaces distorts the orientation field around the particles over long distances.1–3 Remarkably, topological defects appear for strong anchoring interactions and/or for a large particle radius.1–3 Moreover, even when the suspended particles are very small and do not induce defects, they can greatly change the physical properties and the phase transition behavior of the host liquid.4–8 If the particles have magnetic or electric dipole moments, coupling between these moments and the applied field enhances or alters the response to the applied field.9–11 Indeed, addition of small ferroelectric particles gives rise to an intriguing dielectric response and a large shift of the transition temperature.10,11 Under an applied electric field in liquid crystals, Loudet and Poulin14 examined defects around a large particle, while Qi et al.7 found a strong influence of gold nanoclusters on the Fredericksz transition.

The electric field can induce anisotropic molecular alignment if the dielectric tensor $\varepsilon_{ij}$ depends on the local orientation tensor $Q_{ij}$. The usually assumed form is given by15,16

$$\varepsilon_{ij} = \varepsilon_0 \delta_{ij} + \varepsilon_1 Q_{ij},$$

(1)

where $\varepsilon_0$ and $\varepsilon_1$ are constants. While alignment in the uniform electric field follows from minimization of the Landau-de Gennes free energy,15,16 alignment in the inhomogeneous electric field has not yet been well studied. This is because it is not easy to solve the Poisson equation with inhomogeneous $\varepsilon_{ij}$ to calculate the local electric field $E_i$. We stress that inhomogeneous $Q_{ij}$ and $E_i$ are strongly coupled in various situations with the addition of charged, metallic, and ferroelectric particles under an applied field. We should also investigate the role of inhomogeneous electric field in the ferroelectric and flexoelectric phenomena17–19 and the field-induced orientation transition.16,20 Though still fragmentary, we previously solved the Poisson equation for charged particles in liquid crystals to find charge-induced anchoring and defects.21–24 For example, for positive (negative) $\varepsilon_1$ in eqn (1), the director $n_i$ tends to be parallel (perpendicular) to $E_i$ around charged particles,21–24 which is analogous to hydration of ions in water.25

In this paper, we first present a theoretical scheme of applying an electric field to nematogenic liquids containing neutral colloidal particles. We also present a method of solving the Poisson equation with eqn (1). As an application, we consider a colloidal particle with a high dielectric constant in the applied field, where the surrounding nematogenic liquid is in the isotropic phase slightly above the isotropic–nematic transition far from the particle. In this situation, the electric field $E_i$ is the strongest at the poles of the particle. Then, for positive dielectric anisotropy $\varepsilon_1 > 0$, small nematic regions, called nematic caps, can appear close to the poles with the director nearly parallel to $E_i$. Obviously, such local orientational order is due to the high inhomogeneity of $E_i$, so it can be expected also for charged, metallic, and ferroelectric particles in the applied field above the bulk transition temperature. Furthermore, narrow nematic regions can appear on a patterned or non-smooth wall in regions with a relatively high electric field. It is worth noting that local phase separation or wetting occurs around a charged particle in binary fluid mixtures, where the dielectric constant depends on the concentration.16,26 In addition, we present some predictions on the dielectric response, birefringence, and depolarized light...
scattering at small concentrations of particles with nematic caps in the isotropic phase.

This paper is organized as follows. In Section 2, we will describe the Landau-de Gennes model with inhomogeneous $E_c$. In Sections 3 and 4, we will present numerical results for a spherical particle in a nematicogenic liquid without and with the surface anchoring interaction, respectively. In Section 4, we will propose some experiments to detect nematic caps.

2 Theoretical background

2.1 Free energy

We consider equilibrium states of a one-component nematicogenic liquid in the presence of colloidal particles with radius $R$. Here, we neglect surface charges on the colloid surface and mobile charges in the cell.

The order parameter is the traceless, symmetric tensor $Q_{ij}$ and the total free energy $F$ is written as

$$F = \int dr \left[ f_L + \frac{K}{2} \nabla \cdot \nabla Q_{ij}^2 \right] - \frac{w}{4} \int dS Q_{ij}p_ip_j + F_{el},$$

(2)

where $\int dr$ represents the space integral in the colloid exterior within the cell and $\int dS$ the surface integral on the colloid surface with $v = (v_x, v_y, v_z)$ being the outward normal unit vector. Hereafter, $i, j, f$ and $k$ stand for $x, y, z$ and we set $(\nabla_x, \nabla_y, \nabla_z) = (\partial/\partial x, \partial/\partial y, \partial/\partial z)$. The $f_L$ is the Landau-de Gennes free energy density expressed as

$$f_L = \frac{A}{2} Q_{ij}^2 - \frac{B}{3} Q_{ij} Q_{kl} Q_{ij} + \frac{C}{4} \left( Q_{ij}^2 \right)^2.$$

(3)

The coefficient $A$ depends on the temperature $T$, while $B, C$, and $K$ are positive constants. The second term in eqn (2) is the anchoring free energy with $w$ being the anchoring strength parameter. For simplicity, we assume no anchoring ($w = 0$) on the cell surface. The last term $F_{el}$ is the electrostatic free energy to be explained below.

In terms of the director $n = (n_x, n_y, n_z)$ and the other orthogonal unit vectors $m = (m_x, m_y, m_z)$ and $\ell = (\ell_x, \ell_y, \ell_z)$, we can express $Q_{ij}$ generally as

$$Q_{ij} = \left( \frac{\nu_i \cdot \nu_j}{3} \right) S \cos \chi + \left( \nu_i \cdot \ell \right) \left( \nu_j \cdot \ell \right) \frac{S \sin \chi}{\sqrt{3}},$$

(4)

where $S(=0)$ is the order parameter amplitude and $\chi$ is the biaxial angle in the range $|\chi| \leq \pi/3$. Then, we find $Q_{ij}^2 = 2S^2/3$ and $S^3 \cos(3\chi) = 9Q_{ij} Q_{kl} Q_{ij}$. Therefore,

$$f_L = \frac{A}{3} S^2 - \frac{B}{27} S^3 \cos(3\chi) + \frac{C}{9} S^4.$$

(5)

In homogeneous states, $f_L$ is minimized in uniaxial states with $\chi = 0$ due to the cubic term with $B > 0$. For $A > A_0$, $f_L$ is minimized in the isotropic phase with $S = 0$. At $A = A_0$, we have $f_L = CS^2(S - S_0)^2/9$, so a nematic phase with $S = S_0$ can coexist with the isotropic phase. Here,

$$A_0 = B^2/27C.$$

(6)

At $A = A_0$, we also have $\partial f_L / \partial S = 2C(S - S_0)(2S - S_0)/9$, so $f_L$ attains a local maximum $f_{L1}$ at $S = S_0/2$, where

$$f_{L1} = A_0 S_0^2 / 48 = B^2/1164 C^3.$$

(8)

In terms of $s = S/S_0$, we obtain the scaling form,

$$f_L = 16A_0 [4I(s)^2 - 2s^3 \cos(3\chi) + s^4].$$

(9)

At $A = A_0$, eqn (2) yields the nematic–isotropic surface tension $A = 16A_0^2 S_0^2/3$ when the director $n_0$ is perpendicular to the interface. The $\xi_t$ is the correlation length in the isotropic phase at $A = A_t$ given by

$$\xi_t = (K/4A_0)^{1/2}.$$

(10)

Hereafter, space is measured in units of $\xi_t$. For small $B$, $A_0$ is small and the transition is weakly first-order, where $\xi_t$ can be considerably long. We may set $A = A_t + c(T - T_t)$ near the transition $T \sim T_t$, where $c$ is a constant positive.

For example, for 5CB, we have $B = 7.2 \text{ J cm}^{-3}$, $C = 8.8 \text{ J cm}^{-3}$ and $K = 4.5 \times 10^{-14} \text{ J cm}^{-1}$, which yield $A_t = 0.22 \text{ J cm}^{-3}$, $S_0 = 0.27$, $f_{L1} = 3.3 \times 10^{-14} \text{ J cm}^{-3}$, and $\xi_t = 4.5 \text{ nm}$. In this case, if we suppose a particle with radius $R = 60$ in units of $\xi_t$, we have $R = 270 \text{ nm}$.

2.2 Electrostatics

2.2.1 Poisson equation. We place metal walls at the bottom $z = -H/2$ and at the top $z = H/2$ in a cylindrical capacitor cell with radius $L$ and height $H$. The $z$ axis is along the cylinder axis and the origin is at the center of the cell.

The dielectric tensor $\varepsilon_{ij}$ depends on $Q_{ij}$ as in eqn (1) in the liquid and is a constant $\varepsilon_0\delta_{ij}$ in the colloid interior. We assume $\varepsilon_1 > 0$ and $\varepsilon_0 > 0$. The electric potential $\Phi(r)$ is defined in the cell including the colloid interior. The electric field is given by $E_i = -\nabla_i \Phi$ and the electric induction by $D_i = \varepsilon_0 \varepsilon_i E_i$. The Poisson equation in the charge-free condition is given by

$$\nabla \cdot D = -\nabla_i \varepsilon_{ij} \nabla_j \Phi = 0.$$

(11)

This equation is rewritten in the colloid exterior as

$$\varepsilon_0 \nabla^2 \Phi + \varepsilon_1 \nabla_i Q_{ij} \nabla_j \Phi = 0,$$

(12)

while we have $\nabla^2 \Phi = 0$ in the colloid interior. We impose the metallic boundary condition at $z = \pm H/2$ as

$$\Phi(x, y, \pm H/2) = \Phi_e = H \varepsilon_0 \Phi(x, y, H/2) = 0.$$

(13)

We fix the potential difference $\Phi_e$ or the applied electric field $E_e = \Phi_e/H$. We need to solve the Poisson eqn (12) or (13) for inhomogeneous $Q_{ij}$ under the fixed potential conditions. See Appendix A for its numerical method.

2.2.2 Electrostatic free energy. The (total) capacitor charge at $z = -H/2$ is written as $q_0$. Then, the charge at $z = H/2$ is $-q_0$. 

$S_i = B/3C.$

(7)
due to the charge neutrality. At \( z = -H/2 \), the surface charge density is \( D_e/\pi \), so

\[
q_0 = \frac{1}{4\pi} \int dS \langle x, y, -H/2 \rangle.
\]

where \( dS = \int dxdy \) denotes the integral on the bottom surface. The electrostatic free energy is given by

\[
F_{el} = -\frac{1}{8\pi} \int dE \cdot D = -\frac{1}{2} q_0 \Phi_e,
\]

at fixed \( \Phi_e \). We consider infinitesimal changes \( Q_{ij} \to Q_{ij} + \delta Q_{ij} \) and \( \Phi_e \to \Phi_e + \delta \Phi_e \). From \( \delta (D \cdot E) = -2 \nabla \cdot \delta \Phi D - E_i \delta E_i \), the incremental change of \( F_{el} \) is written as

\[
\delta F_{el} = -\frac{1}{8\pi} \int dE_i E_j \delta E_i Q_{ij} - q_0 \delta \Phi_e.
\]

Thus, \( \delta F_{el} / \delta Q_{ij} = -\epsilon_i E_i E_j / 8\pi \) in the colloid exterior.

We give other expressions for \( F_{el} \). Without charges in the cell, we use eqn (11) to obtain the relationship \( \nabla \cdot [\langle z - H/2 \rangle D] = D_e \). From eqn (14) its integration in the cell gives

\[
4\pi H q_0 = \int dE \cdot D = V(D_e).
\]

Here, \( V \) is the cell volume and \( \langle \cdots \rangle \) represents the space average in the cell. Thus,

\[
F_{el} = -VE_e(D_e)/8\pi.
\]

We treat situations where \( D_e \) tends to \( iE_e \) far from the particles, where \( i \) is the \( z \) component of the dielectric tensor far from them. We may calculate \( i \) in the homogeneous state in the absence of colloidal particles as

\[
i = e_0 + \Delta e_i + e_i Q_{zz}^h.
\]

Here, \( \Delta e_i \) is the fluctuation contribution to be calculated in Appendix B. The third term is the homogeneous part (see eqn (25)). From \( \int dE_e = -\int dE \delta \Phi \langle z \rangle = V(D_e) \), eqn (18) yields

\[
F_{el} = -\frac{1}{8\pi} V E_e D_e - \frac{N_{eo}}{8\pi} \int \langle D_z - \tau E_x \rangle.
\]

The first term is a constant. In the second term, \( N_{eo} \) is the particle number and \( \int \langle D_z - \tau E_x \rangle \) is the integral performed around one particle. We assume \( N_{eo} R^3 \ll V \) and the particles are much separated from one another.

2.2.3 Remarks. To account for flexo- and order-electricity,17-19 we need to include coupling terms between \( E_i \) and \( \nabla \cdot Q_{ij} \) in the free energy, though they are neglected in this paper. See remark (2) in the Summary section.

In real nematogenic fluids, a very small amount of ions are usually present.17 Notice that there is no accumulation of ions on the surfaces of neutral dielectric particles, around which no minimum and no maximum of \( \Phi \) appears. (However, ion accumulation occurs around ferroelectric ones.19) We can also neglect ion accumulation on the capacitor walls if the experimental times are shorter than the accumulation time \( H/\kappa \), where \( D \) is the ion diffusion constant, and \( \kappa \) is the Debye wavenumber. In stationary states, ions do accumulate on the walls for \( \kappa \Phi_e/k_\text{B}T \ll 1 \), but the screening can be neglected far from the walls if \( e_0 H \ll \kappa a_0 \sim e_0 E_e \), where \( n_i \) is the ion density and \( a_0 \) is the surface charge density at \( z = 0 \). For example, let us set \( \Phi_e = 1 \), \( H = 1 \mu \text{m} \), and \( e_0 = 1 \); then, this condition becomes \( n_i \ll e_0 \Phi_e \kappa H^2 \sim 10^{-5} \text{ mol L}^{-1} \).

We may impose another boundary condition at fixed surface charge \( q_0 \). The corresponding electrostatic free energy is given by the Legendre transformation \( F_{el} + q_0 \Phi_e = q_0 \Phi_e / 2 \).

2.3 Equilibrium relationships

2.3.1 Equations of \( Q_{ij} \). In equilibrium, we minimize \( F \) with respect to \( Q_{ij} \) at fixed \( \Phi_e \). In the liquid, with the aid of eqn (16), we obtain the equilibrium relationship\( ^{23-24} \)

\[
(A + CJ_2 - KV^2)Q_{ij} = B(Q_{ik}Q_{kj} - J \delta_{ij}/3) - \epsilon_i (E_i E_j - |E|^2 \delta_{ij}/3) / 8\pi = 0.
\]

where all the terms are made traceless. The boundary condition on the colloid surface also follows as

\[
K \nu \cdot \nabla Q_{ij} + w(r, p, \delta_{ij}/3) = 0.
\]

On the cell surface, the gradient of \( Q_e \) in the normal direction is assumed to vanish.

As a dimensionless parameter representing strength of the applied electric field, we introduce

\[
u = \epsilon_i E_i^2 / (8\pi S_A).
\]

which is the ratio of the third to first terms of eqn (21) for \( A \sim A_i \) and \( \epsilon_i \sim \epsilon_0 \). \( E_i \sim E_e \). When \( \epsilon_i \sim \epsilon_0 \), \( u \) is the ratio of the electric field energy density by \( S_A A_i = 48f_i \). From eqn (15) and (16) the electrostatic free energy density in the colloid exterior is expanded with respect to \( Q_e \) as

\[
-D \cdot E/8\pi = \text{const.} - 48f_i u(E_i E_j E_j) Q_j / S_A + \cdots
\]

We also consider a homogeneous state without colloidal particles, where the director \( n \) is along the z axis and \( Q_e \) is a homogeneous tensor \( Q_e^h \). For small \( u \), eqn (21) yields

\[
Q_e^h = (\delta_{iz} - \delta_{iz} / 3) u(S_A) / A_i.
\]

Even for \( u \sim 1 \), we shall see that \( Q_e^h \) exceeds \( Q_e^h \) in the cap region, while \( Q_e^h \) tends to \( Q_e \) far from it.

2.3.2 Equations for a single particle. In the axisymmetric geometry with a single particle at the origin, we define the three unit vectors \( e_x = (x/r, y/r, 0, 0), e_y = (-y/r, x/r, 0, 0), \) and \( e_z = (0, 0, 1), \) where \( r = (x^2 + y^2)^{1/2} \). Without loss of generality the orientation tensor \( \bar{Q} = \langle Q_e \rangle \) is expressed as\( ^{31} \)

\[
\bar{Q} = Q_i e_i e_i + Q_{ij} e_i e_j - (Q_{iz} + Q_{zi}) e_i e_z + Q_{ij} (e_i e_j + e_j e_i),
\]

where we have \( Q_1 = (Q_{xx} x^2 + 2Q_{xy} xy + Q_{yy} y^2)/r^2 \), \( Q_2 = Q_{za} \), and \( Q_3 = (Q_{xx} x + Q_{zy} y)/r \). The equilibrium equations for \( Q_e \) will be

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presented in Appendix C. Using the relationships in the sentence after eqn (4), \( S \) and \( \chi \) are related to \( Q_k \) by

\[
(Q_k^2 - Q_1 Q_3)/2Q_2^2 - 1 = S^2/6Q_2^2 - 3/2 = (S/3Q_k)^3 \cos(3\chi) - 1, \tag{27}
\]

where \( Q_k = Q_1 + Q_3 \). The uniaxiality \( \chi = 0 \) in eqn (4) holds for \( Q_k^2 - Q_1 Q_3 = 2Q_2^2 \), where the left and right hand sides of eqn (27) vanish. Thus, if \( \chi = 0 \), we simply obtain

\[
\frac{Q_1 + Q_3}{S} = \frac{1}{3} Q_2 \quad \frac{Q_1 - Q_3}{S} = \cos \frac{2\eta}{2} = \cos \frac{1}{6} Q_2 \quad \frac{Q_1}{S} = \sin \frac{2\eta}{2}, \tag{28}
\]

where \( \eta \) is the angle between the \( x \) axis and the director \( n = (\rho^{-1}x \sin \eta, \rho^{-1}y \sin \eta, \cos \eta) \).

### 2.3.3 Field-induced phase transition.** The bulk field-induced isotropic-nematic phase transition was previously detected.** In its analysis use was made of the free energy density \( f_1(S) = (\varepsilon_0/12\pi)E_r^2S \) for \( \chi = 0 \), where the second term follows from eqn (24) for \( E_r = E_r \Delta \varepsilon \). Then, at its critical point, we have \( A = 3A_e/2 \) and \( u = 1/4 \). The corresponding critical field is \( E_c = 14.1 \text{ V m}^{-1} \) for 5CB.** In Fig. 2(a), below, these critical values will be the upper bounds of the axes in the \( A-u \) plane. This means that the threshold values of \( u \) for the cap formation can be much smaller than 1/4.

### 3 Numerical results for \( w = 0 \)

In this section, we present results for a single particle with \( w = 0 \) and \( A > A_c \) with the aid of the numerical method in Appendix A. Our cell is cylindrical with radius \( L = 256 \) and height \( H = 512 \) in units of \( \xi_0 \), so the cell volume is \( V = \pi L^2H \sim 10^9 \). In this axisymmetric geometry, \( Q_k \) in eqn (26) and \( \Phi \) depend on \( \rho = (x^2 + y^2)^{1/2} \) and \( z \). We set \( \varepsilon_1 = \varepsilon_0 \) and \( \varepsilon_d = 20\varepsilon_0 \). In typical nematogenic liquids such as 5CB, \( \Delta \varepsilon = \varepsilon_1S \) in nematic states can even be of order \( \varepsilon_0 \).

#### 3.1 Electric field

If the field strength parameter \( u \) in eqn (23) is small, the electric potential \( \Phi(\rho) \) around the sphere should be close to that \( \Phi_{iso}(\rho) \) for isotropic liquids with dielectric constant \( \varepsilon_0 \). We confirm this that this is the case even in the presence of nematic caps as long as \( u \ll 1 \). Here, \( \Phi_{iso} \) is given by

\[
\Phi_{iso} = -E_z(1 - \alpha R^2/\rho^3)z \quad (r > R)
\]

\[
-\alpha(1 - \alpha)z \quad (r < R) \tag{29}
\]

To represent the dielectric discontinuity, we define

\[
\alpha = (\varepsilon_d - \varepsilon_0)/(\varepsilon_d + 2\varepsilon_0), \tag{30}
\]

where \( \alpha = 0.864 \) for our choice of \( \varepsilon_d/\varepsilon_0 = 20 \). Here, \( \alpha \to 1 \) in the metallic limit \( \varepsilon_d/\varepsilon_0 \to \infty \).

In Fig. 1, for \( R = 60, A = 1.18A_c \), and \( u = 0.0551 \), we plot the \( z \) component of the electric field \( E_z = -\partial \Phi/\partial z \) (a) along the \( z \) axis \( (\rho = 0 \text{ and } \rho > R) \) and (b) on the horizontal midplane \( (z = 0 \text{ and } \rho > R) \). It is close to \( E_z^{iso} = -\partial \Phi_{iso}/\partial z \) where

\[
E_z^{iso}(0, z) = E_z(1 + 2\alpha R^2/\rho^3)(z > R) \tag{31}
\]

In (a), \( E_z(0, z) \) is three times larger than \( E_z \) for \( z \equiv \pm R \) and exhibits a small peak at \( z \sim 1.9R \) immediately outside the cap along the \( z \) axis. In contrast, \( D_z(0, z) \) decays monotonically with increasing \( z \) in the inset. In (b), \( E_z(\rho, 0) \) is very close to \( E_z^{iso}(\rho, 0) \) and small for \( \rho \sim R \). In (c), the amplitude \( |E| \) is shown in gradation in the \( \rho-z \) plane. Corresponding to the small peak along the \( z \) axis, it is increased in narrow regions outside the caps. In (d), the difference \( \Phi - \Phi_{iso} \) divided by \( E_c \) is displayed in the \( \rho-z \) plane, where it is about 5% of \( E_c \) around the caps.

#### 3.2 Phase diagram and cap structure

We show that if \( u \) in eqn (23) is increased above a threshold \( u_{nc} \), cap-like nematic regions appear on the top and bottom of the particle, where the electric field is the strongest. We typically obtain \( E_c \sim 1 \text{ V m}^{-1} \) with caps for \( u \sim 0.02 \) (see Section 2.3.3).

In Fig. 2(a), we display the phase diagram in the \( A-u \) plane for \( R = 60 \). The particle puts on a pair of nematic caps for \( u > u_{nc} \). We illustrate the cap patterns at \( A = 1.184 \), for (A) \( u = 0.028 \), (B) \( 0.055 \), and (C) \( 0.08 \), where \( u_{nc} = 0.0279 \). With
Further increasing \( u \), the caps touch the cell walls. Eventually, the bulk region becomes nematic, which is for \( u > 0.091 \) at \( A = 1.18A_s \). Here, a ring in the isotropic phase surrounds the particle on the horizontal plane, as in the pattern of state (D) at \( u = 0.12 \). In addition, the director \( n \) close to the colloidal surface in the caps is nearly parallel to the surface normal. Namely, the so-called homeotropic anchoring\(^2\) is realized even for \( w = 0 \). A similar anchoring effect was found for charged particles in a nematic solvent.\(^{32-34}\)

The transition between the isotropic states and those with caps is discontinuous at \( u = u_{nc} \) for \( w = 0 \). To show this, we plot the cap volume \( V_{cap} \) in (c) and (d) of Fig. 2, which is the total volume of the top and bottom regions of the particle with \( S(r)/S_t > 0.5 \). It is also nearly equal to the integral,

\[
V_{cap} \equiv \int dr \left[ \left( S(r) - S^h \right) / S_t \right],
\]

where \( S^h \) is the homogeneous part of \( S \) given by \( uS_t A_t/A \) for \( u \ll 1 \) from eqn (25). In (c) and (d), \( V_{cap} \) grows discontinuously for \( u > u_{nc} \) where the threshold \( u_{nc} \) increases with decreasing \( R \). It even exceeds the colloid volume \( 4\pi R^3/3 \) for \( u \geq 0.06 \).

We found metastable states without caps (those with caps) for \( u \) slightly larger (smaller) than \( u_{nc} \) (not shown here). In Fig. 2, we determined \( u_{nc} \) to minimize \( F \) in eqn (2); then, \( F \) is continuous at the transition. In Fig. 3, we plot \( u_{nc} \) in (a) and \( V_{cap}^{nc} \) in (b) as functions of \( R \) for \( A = 1.18A_s \), where \( V_{cap}^{nc} \) is the cap volume at the transition with \( u = u_{nc} \). In the range of \( R \) investigated, \( u_{nc} \) can well be fitted by

\[
u_{nc} \equiv u_0 + k/R,
\]

where \( u_0 = 0.0168 \) and \( k = 0.689 \) with \( R \) in units of \( \xi_g \). Thus, \( u_{nc} \ll 1 \) as long as \( R \gg 1 \), although \( u_{nc} \) increases with decreasing \( R \). We also have \( V_{cap}^{nc} \propto R^{1.75} \) in (b). The shape of the caps at \( u = u_{nc} \) is gradually flattened with increasing \( R \).

In Fig. 2, we display profiles of \( S_t, Q_{1s}, Q_{2s}, \) and \( Q_{3s} \) in the \( \rho-z \) plane for state (B) in Fig. 2. They are of order \( S_t \) in eqn (7) within the cap. In this case, the orientation is nearly uniaxial (\( \chi \equiv 0 \)) and the relationship in eqn (28) holds excellent. In fact, the angle \( \chi \) in eqn (4) increases at most up to 0.02\( \pi \) near \( \rho, z = (R, 0) \), while it is virtually zero far from it. For example, its maximum in the region \( z > R \) is \( 3.9 \times 10^{-2} \pi \) at \( (\rho, z) = (1.10R, 1.01R) \). Therefore, we have \( Q_{1s}/S_t \equiv 2/3 - n_z^2, Q_{2s}/S_t \equiv n_z^2 - 1/3, \) and \( Q_{3s}/S_t \equiv n_z(1 - n_z^2)^{1/2}S_t \). In particular, \( Q_{3s} \) vanishes on the \( z \) axis (on which \( n_z = 1 \)) and exhibits a ridge near the cap interface. As can be seen in (B) in Fig. 2(b), the director angle \( \eta = \cos^{-1} n_z \) increases from zero to attain a maximum \( \eta_m \) near the isotropic–nematic interface with increasing \( \rho \), where \( \eta_m \sim \pi/4 \) for \( z \leq R/2 \) and \( \eta_m \to 0 \) for larger \( z \).

### 3.3 Free energy deviations due to caps

When \( Q_g \) is nonvanishing around the particle, the Landau–de Gennes free energy and the gradient free energy increase, but the electrostatic free energy more largely decreases, leading to cap formation. As the densities of the former, we write

\[
\Delta f_L = f_L - f_L^h, \quad \Delta f_g = K |\nabla Q|^2/2.
\]

where \( f_L^h \) is the value of \( f_L \) in the homogeneous state at \( Q_g = 0 \).

Next, we devise an appropriate form of the deviation of the electrostatic free energy \( \Delta f_E \). In the integrand of eqn (20), we note that \( D_x - iE_z \) is relatively large in the colloid interior compared to its value in the exterior. However, its interior value

![Fig. 2](image-url)  
**Fig. 2** (a) Phase diagram of the electric-field induced structure around a spherical particle with \( w = 0 \) in the \( A/A_t-u \) plane, where states with nematic caps or those with an isotropic ring appear between the isotropic and nematic phases. The other parameters are the same as in Fig. 1. (b) Patterns of the nematic order \( S \) in graduation and the director field \( n \) (short rods), where \( u \) is (A) 0.0280, (B) 0.0551, (C) 0.0800, and (D) 0.120 on the line of \( A = 1.18A_s \) in (a). (c) Cap volume \( V_{cap} \) divided by \( 4\pi R^3/3 \) vs. \( u \) for \( R = 30, 40, 50, \) and 60 at \( A = 1.18A_s \), which grows for \( u > u_{nc} \). (d) Expansion of the box region in (c), illustrating the discontinuous behavior of \( V_{cap}/(4\pi R^3/3) \).

![Fig. 3](image-url)  
**Fig. 3** (a) Threshold \( u_{nc} \) of the field strength parameter \( u \) in eqn (23) for cap formation vs. \( R^{-1} \), which is fitted by eqn (33). (b) Cap volume \( V_{cap}^{nc} \) at the transition \( u = u_{nc} \) in units of \( \xi_g^3 \) vs. \( R \) on a double logarithmic scale, where the slope is 1.75. Here, \( A = 1.18A_s \) and \( w = 0 \). Solid lines are eye guides.
is close to \(D_{\text{iso}} \sim \epsilon_0 e_{\text{iso}}^2\) in the isotropic case. Thus, we introduce the normalized difference,

\[
M = [(D_z - \epsilon E_z) - (D_{\text{iso}}^z - \epsilon_0 E_{\text{iso}}^z)]/\epsilon_0 E_z. \tag{35}
\]

Here, from eqn (29), \(D_z = \epsilon E_z\) is equal to \((\epsilon_0 - \epsilon)E_{\text{iso}}^z = 3\epsilon_0 e_{\text{iso}}^2\) in the colloidal interior and is zero in the exterior. We will display profiles of \(M(\rho, z)\) in Fig. 9. Then, we define

\[
\Delta f_{\text{el}} = -\epsilon_0 e_{\text{iso}}^2 M/8\pi. \tag{36}
\]

For a single particle, \(F_{\text{el}}\) in eqn (20) is rewritten as

\[
F_{\text{el}} = -\left(\frac{4V}{8\pi} + \frac{\alpha}{2}\epsilon_0 R^3\right)E_{\text{iso}}^2 + \int dr\Delta f_{\text{el}}(r). \tag{37}
\]

At fixed \(E_z\), we minimize the integral of the sum,

\[
\Delta f_{\text{tot}} = \Delta f_L + \Delta f_g + \Delta f_{\text{el}}, \tag{38}
\]

where we set \(\Delta f_{\text{tot}} = \Delta f_{\text{el}}\) in the colloidal interior.

In Fig. 5, we plot these free energy densities for the state (B) in Fig. 2. We notice the following. In (a), \(\Delta f_{\text{el}}\) is nonnegative and is of order \(f_{\text{tot}}\) in the cap region. In (b), \(\Delta f_{\text{el}}\) is peaked along the nematic–isotropic interface with relatively small magnitude. In (c), \(\Delta f_{\text{el}}\) is negative both in the cap region and the colloidal interior, which is the most important for the stability of caps. In (d), these free energy densities and \(\Delta f_{\text{tot}}\) are plotted along the \(z\) axis \((\rho = 0)\). We recognize that \(\Delta f_{\text{tot}}\) in eqn (38) is negative in the colloidal interior and the cap region.

We also consider the integrals \(\Delta f_k = \int dr\Delta f_k\) for \(k = L, g, \text{el}, \text{tot}\). In Fig. 6(a), we plot \(\Delta f_k\) vs. \(u\). Here, \(\Delta f_k \sim \sigma \sigma\) in terms of the surface area \(\sigma\) and the surface tension \(\sigma\) (see the sentences below eqn (9)). At the transition \(u = u_{\text{nec}}, \Delta f_{\text{tot}}\) is continuous, while the others are slightly discontinuous. In Fig. 6(b), we display the positive surface contribution \(\Delta f_{\text{el}}\) and the negative bulk contribution \(\Delta f_{\text{el}} + \Delta f_{\text{tot}}\) vs. \(u\), separately, for three \(R\). For \(u > u_{\text{nec}}\), we have \(\Delta F_L + \Delta F_{\text{el}} \sim -C_1 R^2(u - u_0)\) where \(C_1\) is a constant and \(u_{\text{nec}} > u_0\). The balance of this bulk free energy and the surface part \(\Delta F_{\text{el}} \sim C_2 R^2\) yields \(u_{\text{nec}} \sim u_0 \sim R^{-1}\), which is in accordance with eqn (33).

We also note that the \(R\) dependence of \(\Delta f_{\text{el}}\) should become weaker as the cap volume \(V_{\text{cap}}\) exceeds \(4\pi R^3/3\), because the electric field is weakened far from the particle (see Fig. 1). In

Fig. 4 Profiles of (a) \(S/S_t\), (b) \(-Q_1/S_t\), (c) \(Q_2/S_t\), and (d) \(Q_3/S_t\) around the nematic cap in state (B) in Fig. 2, where \(R = 60, A = 1.18A_0\), and \(u = 0.0551\). These are defined in eqn (4) and (26).

Fig. 5 Profiles of (a) \(\Delta f_L/\Delta f_{\text{tot}}\), (b) \(\Delta f_g/\Delta f_{\text{tot}}\), and (c) \(\Delta f_{\text{el}}/\Delta f_{\text{tot}}\) near the nematic cap in state (B) in Fig. 2. Projection of the colloidal particle on the \(\rho - z\) plane is also written (in red). (d) \(\Delta f_{\text{el}}/\Delta f_{\text{tot}}\) along the \(z\) axis \((\rho = 0)\) with \(k = L\) (Landau–de Gennes), \(g\) (gradient), \(e\) (electric), and tot (total). These are defined in eqn (34), (36) and (38).

Fig. 6 (a) Free energy contributions \(\Delta f_k\) divided by \(f_{\text{tot}}R^3\) vs. \(u\) around the transition for \(k = L\) (Landau–de Gennes), \(g\) (gradient), \(e\) (electric), and tot. At \(u = u_{\text{nec}}\), \(\Delta f_{\text{tot}}\) is continuous, while the others are discontinuous. (b) Surface part \(\Delta f_{\text{el}}\) and bulk part \(\Delta f_L + \Delta f_{\text{el}}\) divided by \(f_{\text{tot}}R^3\) vs. \(u\).
contrast, \( \Delta F_\text{el} \propto R^3 \) for any \( R \). This behavior of \( \Delta F_\text{el} \) limits the growth of the equilibrium cap size.

4 Cap structures for \( w \neq 0 \)

In this section, we examine the cap formation for \( w \neq 0 \) around a single particle. Without the applied electric field, it is known that a nematic wetting layer can appear on a planar wall and a sphere surface for \( w > 0 \) while the bulk region is in the isotropic phase. However, we are not aware of any discussions on the contact angle of a nematic domain on a solid wall surrounded by the isotropic phase.

Here, we introduce the normalized anchoring parameter,

\[
W = w/A_1 S_{oi}.
\]  

---

In the left panels of Fig. 7, we show the cap patterns just at \( u = u_{uc} \) for \( R = 60 \) and \( A = 1.18A_1 \), where nematic order appears as a wetting film for (A) \( W = 0.79 \) and as a detached domain for (B) \( W = -1.32 \). In (C), the cap volume \( V_{\text{cap}} \) is shown to increase with an increase in the field strength parameter \( u \). Remarkably, the transition is continuous for \( W = 0.79 \), while it is discontinuous for \( W = 0 \) and \(-1.32 \). Furthermore, in Fig. 8, well-developed caps are displayed for \( u = 0.0551 > u_{uc} \). In the contact region, the nematic cap wets the surface for \( W = 0.79 \) in (A) and (A'), but it is repelled for \( W = -1.32 \) in (B) and (B'). In (C), \( S(\rho, \rho) \) with \( z = \rho \) is given, whose surface value at \( \rho = R \) decreases with decreasing \( W \).

Thus, we recognize the following. Under an electric field with \( \varepsilon_1 > 0 \), the cap regions are attracted to the particle surface for \( W > 0 \) but are repelled from it for \( W < 0 \), where the homeotropic orientation along \( E_i \) is favored in the cap regions even for \( W < 0 \). For sufficiently large positive \( W \), nematic domains appear in the polar regions however small \( u \) is.

5 Effects of caps in experiments

We here investigate how the cap formation can be detected in three typical experiments, where the bulk region far from the suspended particles is in the isotropic phase. We assume that the colloidal density \( n_{co} = N_{co}/V \) is so small such that the colloidal volume fraction \( \phi \) satisfies

\[
\phi = (4\pi/3)R^3 n_{co} \ll 1.
\]  

Under this condition, we neglect the interactions among the particles and use the results so far for a single particle.

5.1 Dielectric constant

We calculate the effective dielectric constant \( \varepsilon_{\text{eff}} \) under a stationary electric field \( E_c \) applied between \( z = -H/2 \) and \( H/2 \). Since \( Hq/\Delta \) is the surface charge density, eqn (17) yields

\[
\varepsilon_{\text{eff}} = 4\pi Hq/\Delta E_c = (D_c)/E_c.
\]  

From eqn (18) we have \( F_{el} = -\varepsilon_0 \varepsilon_{\text{eff}} E_c^2/8\pi \). Using the dielectric constant \( \varepsilon \) without particles in eqn (19) and the function \( M(\rho, z) \) in eqn (35), we further obtain

\[
\varepsilon_{\text{eff}} = \varepsilon + \varepsilon_{\text{co}} \int_{\Delta} \text{d}M.
\]  

where \( \alpha \) is defined in eqn (30). Here, the integrals are only around one colloidal particle, which are well-defined because \( D_c \sim \varepsilon E_c \) and \( M \) vanish far from each particle.

In particular, we consider the case of \( W = 0 \). As \( u \to 0 \), we have \( D_c - \varepsilon E_c \equiv D_c - \varepsilon_0 E_c \equiv E_c^2 \) in the colloid exterior from eqn (C5) and \( D_c - \varepsilon_0 E_c \equiv 3\alpha e_0 E_c \) in the colloid interior. Thus,

\[
\varepsilon_{\text{eff}}^0 = \lim_{u \to 0} \varepsilon_{\text{eff}} = \varepsilon_0 + 3\varepsilon_0 e_0,
\]  

which is the dielectric constant of a normal isotropic liquid containing colloidal particles. We define \( \Delta_{\text{eff}} \) by
where \(\varepsilon_{\text{eff}} = \varepsilon + 3\phi\varepsilon_{\text{el}}(1 + \Delta_{\text{eff}})\). \hspace{1cm} (45)

In Fig. 9, \(M(\rho, z)\) is displayed for (a) \(u = 0.0280\), (b) 0.0551, and (c) 0.0800 for \(W = 0\), \(A = 1.18A_{t}\), and \(R = 60\) in the \(\rho-z\) plane, which correspond to (A), (B), and (C) in Fig. 2, respectively. Here, \(M\) grows with increasing \(u\), being nonvanishing around the particle and tending to zero far from it. In (d), we plot \(\Delta_{\text{eff}}\) vs. \(u\) for four values of \(R\). With increasing \(u\), \(\Delta_{\text{eff}}\) can be of order unity, but its growth is weaker than \(\nu_{\text{cap}}\). In fact, we roughly obtain \(\Delta_{\text{eff}} \sim R^{-1}(\nu_{\text{cap}})^{5/2}\).

### 5.2 Birefringence

Nematic liquid crystals become birefringent even for \(A > A_{t}\) with applied electric field.\(^{15,16,35,36}\) Let the dielectric tensor at optical frequency linearly depends on \(Q_{yy}\) as

\[
\varepsilon^{\text{op}}(r) = \varepsilon_{0}^{\text{op}}(r) + \varepsilon_{1}^{\text{op}}Q_{yy}(r),
\]

where \(\varepsilon_{0}^{\text{op}}\) and \(\varepsilon_{1}^{\text{op}}\) are constants. We assume that the particle radius \(R\) is much shorter than the laser light wavelength. Then, relevant in birefringence is the intrinsic part\(^{21,27}\) given by the space average,

\[
\langle \varepsilon_{yy}^{\text{op}} \rangle = \varepsilon_{0}^{\text{op}} + \frac{1}{2}\varepsilon_{1}^{\text{op}}Q_{yy}(r)\left(\delta_{yy} - \delta_{zz}\right),
\]

which follows from eqn (26) with \(Q_{yy} = Q_{zz}\). The difference between the \(zz\) and \(xx\) components is written as \(\langle \varepsilon_{zz}^{\text{op}} \rangle - \langle \varepsilon_{xx}^{\text{op}} \rangle = 3\varepsilon_{1}^{\text{op}}Q_{zz}/2\), which is detected as birefringence. On the other hand, the form dichroism (anisotropy in the absorption)\(^{21,27}\) is appreciable if \(R\) is on the order of the light wavelength.

The homogeneous part of \(Q_{yy}\) was measured without colloidal particles,\(^{35,36}\) where it is given by \(Q_{yy}^{h} = 2uS_{A}A_{t}/3A\) for \(u \ll 1\) from eqn (25). Thus, we write

\[
\langle Q_{yy} \rangle = Q_{yy}^{h} + \phi\Delta_{b},
\]

where the second term is the colloidal contribution with

\[
\Delta_{b} = \frac{1}{4\pi R^{3}}\int_{\text{vol}} d\mathbf{r} Q_{yy}(\mathbf{r}) - Q_{yy}^{h}.
\]

In Fig. 10, we plot \(\Delta_{b}\) for \(0 < u < 0.08\) and the combination \(\Delta_{b}(4\pi R^{3}/3)\nu_{\text{cap}}\) for \(0.03 < u < 0.08\). Here, \(\Delta_{b}\) increases strongly with the appearance of caps similarly to \(\Delta_{\text{eff}}\), while \(\Delta_{b}(4\pi R^{3}/3)\nu_{\text{cap}}\) decreases with increasing \(u\) and only weakly depends on \(R\). Thus, \(\langle Q_{yy} \rangle - Q_{yy}^{h} \approx 0.5\nu_{\text{el}}\nu_{\text{cap}}\).

#### 5.3 Depolarized light scattering

The depolarized light scattering can be detected from a nematic liquid even in the isotropic phase.\(^{29,38}\) Here, we show that it can be enhanced by nematic caps. We assume that there are many particles in the scattering region and their density \(n_{\text{co}}\) satisfies eqn (40) and

\[
V_{\text{scat}}n_{\text{co}} \gg 1,
\]

where \(V_{\text{scat}}\) is the experimental scattering volume. In the depolarized scattering, the initial and final light polarizations are along unit vectors \(\mathbf{g} = (g_{x}, g_{y}, g_{z})\) and \(\mathbf{f} = (f_{x}, f_{y}, f_{z})\), respectively, which are orthogonal as \(\mathbf{g} \cdot \mathbf{f} = g_{x}f_{x} + g_{y}f_{y} + g_{z}f_{z} = 0\). The depolarized scattering amplitude is proportional to the structure factor \(I_{\text{dik}}(\mathbf{q})\) of the following quantity,

\[
\mathcal{S}(r) = g_{x}f_{y}^{\text{op}}(r)/\varepsilon_{1}^{\text{op}} = g_{y}f_{x}Q_{yy}(r),
\]

where

\[
\Delta_{b}(4\pi R^{3}/3)S_{t}
\]

is plotted vs. \(u\) for \(R = 30, 40, 50,\) and 60, where \(W = 0\), and \(A = 1.18A_{t}\).
where $q$ is the scattering wave vector with $q = |q|$ larger than $V_{\text{scat}}^{-1/3}$. Then, some calculations give

$$I_{\text{scat}}(q) = n_\text{co} |q^2| + k_B T/2A + q^2,$$  \hspace{1cm} (52)

where $q^2 = \int_0^1 d\tau \mathcal{G}(\tau)s(q) \exp(iq \cdot r) \tau$ is the Fourier transform of $s(\tau)$ for a single particle. The second term in eqn (52) arises from the thermal orientation fluctuations in the isotropic phase.\textsuperscript{29,38}

From eqn (26) and (51) we have

$$s(\tau) = (2Q_1 + Q_2) \mathcal{G}_f F + (Q_1 + 2Q_2) \mathcal{G}_f G + Q_1 \mathcal{G}_f G + \mathcal{G}_f G.$$

where $g_f = g \cdot e_f = (g_x + g_y)/\rho$, $p = f \cdot e_f = (f_x + f_y)/\rho$, and $g_{xx}$ has been made of $g = g_{xx} + g_{yy} + g_{zz} = 0$.

For $q < \pi/R$, we may take the long wavelength limit. That is, for our geometry, we obtain

$$\lim_{q \to 0} s_f = \frac{3}{2} q^2 \int_0^1 d\tau \mathcal{G}(Q_2(\tau) - Q_2)^2 = 2\pi g_f R^3 \mathcal{A}_b,$$  \hspace{1cm} (54)

where $\mathcal{A}_b$ is defined by eqn (49) and we have used the relationships $[d(2Q_1 + Q_2) g_{\phi \phi}] [dQ_2] + [dQ_2] g_{\phi \phi}] [dQ_2]$ and $[dQ_2 \mathcal{G}_f G = 0$. It follows the depolarized scattering amplitude in the long wavelength limit,

$$\lim_{q \to 0} I_{\text{scat}}(q) = (2\pi g_f R^3 \mathcal{A}_b)^2 n_\text{co} + k_B T/2A.$$  \hspace{1cm} (55)

Here, $[4(\pi/3)^7/2] \sim S \nu_{\text{cap}}^2/2$ from Fig. 10(b). If $g = (1/\sqrt{2}, 1/\sqrt{2})$ and $f = (0, -1/\sqrt{2}, 1/\sqrt{2})$, we obtain $2\pi g_f R^3 \mathcal{A}_b \sim S \nu_{\text{cap}}^2$. We also set $k_B T/\mathcal{A} = D^2/2\xi$, where $\xi$ is the correlation length and $\xi$ is a molecular length. Thus, as $q \to 0$, the depolarized scattering from nematic caps exceeds that from the thermal fluctuations for

$$V_{\text{cap}}^2 n_\text{co} > \xi^2 \ell.$$  \hspace{1cm} (56)

With increasing $V_{\text{cap}}$, the above conditions can well be realized even for $\Phi < 1$ and $u \leq 1$.

6 Summary and remarks

Under an applied electric field, we have examined the formation of nematic caps around colloidal particles in a nematic liquid, which is in the isotropic phase in the bulk between parallel metal walls. Since the electric field is the strongest on the top and bottom of the particles, nematic caps appear locally even above the isotropic–nematic transition temperature. We summarize the main results as follows.

(i) In Section 2, we have explained Landau-de Gennes theory and the electrostatics around neutral particles in nematic liquids in the fixed potential conditions.

(ii) In Section 3, we have investigated the emergence of local nematic order around a single particle. This cap formation is controlled by a dimensionless field strength parameter $u$ in eqn (23). With increasing $u$, the transition takes place continuously or discontinuously depending on the anchoring parameter $w$ in eqn (2). This dependence is analogous to that in the nematic layer formation on a wall and around a colloid surface.\textsuperscript{42}

(iii) In Section 4, we have made some predictions on the effects of nematic caps in three kinds of experiments.

We make some remarks:

(1) Simulations have been performed on flexo- and order-electric effects in liquid crystals with homogeneous $E_f$.\textsuperscript{39,41} To explain such effects, we should further include the inhomogeneity of $E_f$. Also in analysis of electrophoresis in liquid crystals,\textsuperscript{42} inhomogeneous $E_f$ produced by charged particles should be accounted for.

(2) We should numerically study electric field effects with ferroelectric particles in nematogenic liquids,\textsuperscript{18-21} for which caps appear even without the applied field. We should also investigate the influence of doping on the Fredericksz transition.\textsuperscript{4}

(3) Stark et al.\textsuperscript{43} examined bridging of closely separated particles by nematic domains without the electric field. However, the applied electric field can induce bridging even for considerably large separation distances, on which we will report shortly.

(4) Colloid particles form strings in applied magnetic or electric field.\textsuperscript{44} It is of great interest how such particles assemble and aggregate in the liquid crystal solvent.

Appendix

A Numerical method

To efficiently calculate the equilibrium $\Phi$ and $Q_{ij}$, we treated the colloid surface to be diffuse.\textsuperscript{24,45,46} For one particle at the origin, we introduce the shape function $\theta(r) = (1 + \tanh((R - r)/d))/2$ with $d = \xi$, which tends to 1 within the particle and to 0 outside it. For this axisymmetric geometry, we sought the profiles in the 2D plane of $\rho = (x^2 + y^2)^{1/2}$ and $z$.

In the free energy $F$ in eqn (2) we replace the exterior integral $\int dr$ in the first term by $\int (dr(1 - \theta))$ and the second surface free energy by $-3dW[drQ_{ij}(\nabla \theta)/\nabla \theta]$ in this method. Using this $F$, we rewrite the equilibrium condition of $Q_{ij}$ as $h_{ij} = \delta \Phi/Q_{ij} = 0$, where $h_{ij}$ tends to the left hand side of eqn (21) in the liquid. Thus, with $\Phi$ held fixed, we integrated the relaxation equation,

$$\frac{\partial}{\partial t} Q_{ij} = -h_{ij}.$$  \hspace{1cm} (A1)

At long times, $Q_{ij}$ tends to be stationary with $h_{ij} = 0$ for each given $\Phi$. In this equation, we define $Q_{ij}$ in the whole cell, while we have $Q_{ij} \equiv 0$ within the colloid interior.\textsuperscript{44}

Next, we calculate $\Phi$ satisfying the Poisson equation, where the dielectric tensor is written as

$$\epsilon_{ij} = (1 - \theta)(\epsilon_0 + \epsilon_1 Q_{ij}) + \theta \epsilon_0 \delta_{ij}.$$  \hspace{1cm} (A2)

With $Q_{ij}$ held fixed, we integrated the diffusive equation,

$$\frac{\partial \Phi}{\partial t} = \nabla \epsilon_{ij} \nabla \Phi = \nabla \delta \nabla \Phi + \epsilon_1 \nabla (1 - \theta) Q_{ij} \nabla \Phi,$$  \hspace{1cm} (A3)

where $\delta \equiv (1 - \theta)\epsilon_0 + \theta \epsilon_0$ is the diagonal part. We impose the boundary condition (13) at $z = \pm H/2$ and assume $\partial \Phi/\partial \rho = 0$ on the side wall $\rho = (x^2 + y^2)^{1/2} = L$. We obtained the stationary solution of eqn (A3) at long times for each given $Q_{ij}$ using the
Crank-Nicolson method. We checked that the normal component of the induction \( \mathbf{D} \cdot \mathbf{v} \) behaves smoothly across the interface (being constant on the scale of \( d \)) in accordance with the assumption of no surface charges.

At each time step of the integration, we firstly calculated \( Q_{ij} \) as the stationary solution of eqn (A1). Secondly, substituting it in eqn (A3), we calculated \( \Phi \) as the stationary solution of eqn (A3). Repeating these procedures, we obtained the equilibrium \( Q_{ij} \) and \( \Phi \) at long times.

### B Renormalized dielectric constant

We calculate the fluctuation contribution \( \Delta \varepsilon \) to the dielectric constant in eqn (19) in homogeneous states without colloidal particles. It arises from the thermal fluctuations of the deviation \( \delta Q_{ij} = Q_{ij} - Q_{ij}^0 \). From eqn (43) it is written as

\[
\Delta \varepsilon = \varepsilon_1(\delta Q_{ij}\delta E_j)/E_z
\]

where \( \delta E_j = -\nabla_j \delta \Phi \) with \( \delta \Phi = \Phi + E_z z \) being the potential deviation. From eqn (12) we find the linear equation, \( \varepsilon_0 \nabla^2 \delta \Phi = \varepsilon_1 E_0 \nabla^2 Q_{ij} \). In the wave vector space, we rewrite eqn (B1) in the three-dimensional integral form \( \Delta \varepsilon_1 = -(\varepsilon_1^2/\varepsilon_0)|dH(q)/(2\pi)|^3 \). In the isotropic state in the limit \( E_z \to 0 \), we find

\[
H(q) = \left( \frac{\partial q}{\partial x} (Q_p(r + r_0)Q_{ij}(r_0))^2/2 \right) / (2(A + Kq^2))
\]

which the second line follows from the structure factors of \( Q_{ij} \) in the mean field theory.\footnote{Thus, \( H \propto q^{-2} \) for \( q \gg \xi^{-1} \) and the 3D integral \( |dH(q)| \) is divergent at large \( q \), where \( \xi = (\xi A)^{1/2} \). We need to introduce an upper-cut off wavenumber \( \Lambda \) larger than \( \xi^{-1} \) from the region \( q < \Lambda \), we obtain

\[
\Delta \varepsilon_1 = -(2\Lambda/\pi + \xi^{-1})k_B T \varepsilon_1^2/(6\pi^2 \varepsilon_0).
\]

which linearly depends on \( \Lambda \). The sum \( \varepsilon_0^R = \varepsilon_0 + \Delta \varepsilon_1 \) is the renormalized coefficient,\footnote{which is observable in the linear response experiments, so \( \varepsilon_0^R \) itself is insensitive to the choice of \( \Lambda \). From the term proportional to \( \xi^{-1} \) in eqn (B3), we find the singular temperature derivative \( \partial \varepsilon_0^R / \partial T \propto \xi \).

### C Equilibrium equations for a single particle in axisymmetric geometry

For a single colloidal particle placed at the origin, we substitute eqn (26) into (21) to obtain the equations of \( Q_1 \), \( Q_2 \) and \( Q_3 \) in the colloid exterior:

\[
\nabla Q_1 - B(Q_2^2 + Q_3^2 - J_3/3) + 2K(2Q_1 + Q_3)/\rho^2 = \varepsilon_1(2E_2\rho - E_3\rho^3)/24\pi,
\]

\[
\nabla Q_2 - B(Q_1^2 + Q_3^2 - J_3/3) = \varepsilon_1(2E_2\rho - E_3\rho^3)/24\pi.
\]

\[
[\nabla - B(Q_1 + Q_3) + K\rho^2]Q_3 = \varepsilon_1 E_2 E_3/8\pi.
\]

With \( \nabla_{\rho} = \partial / \partial \rho \) and \( \nabla_{\varphi} = \partial / \partial z \), \( \nabla \) is written as

\[
\nabla = A + CJ_2 - K(\nabla_{\varphi} + \rho^{-1}\nabla_{\rho} + \nabla_{\varphi}^2).
\]

We write \( E = E_1 \mathbf{e}_x + E_2 \mathbf{e}_y + E_3 \mathbf{e}_z \) with \( E_\rho = -\nabla_{\rho} \Phi \) and \( E_\varphi = -\nabla_{\varphi} \Phi \). We also set \( \mathbf{D} = D_1 \mathbf{e}_x + D_2 \mathbf{e}_y \). In the colloid exterior, we have

\[
D_1 = \varepsilon_0 E_{\rho} + \varepsilon_1(Q_1 E_{\rho} + Q_2 E_2),
\]

\[
D_2 = \varepsilon_0 E_{\rho} + \varepsilon_1(Q_2 E_{\rho} + Q_1 E_2).
\]

The Poisson equation is \( (\nabla_\rho + \rho^{-1})D_\rho + \nabla_\varphi D_\varphi = 0 \). From the boundary condition (22), we calculate the derivatives \( Q_\mu = \partial Q_{\mu}/\partial r \) at \( r = (\rho^2 + z^2)^{1/2} = R \)

\[
Q_1 = (3 \cos 2\theta - 1)W/6K,
\]

\[
Q_2 = -(3 \cos 2\theta + 1)W/6K,
\]

\[
Q_3 = -(\sin 2\theta)W/2K,
\]

where \( \cos \theta = z/r \) and \( \partial / \partial r = (\sin \theta)\nabla_{\rho} + (\cos \theta)\nabla_\varphi \).

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### References


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