Liquid crystal boojum-colloids

M Tasinkevych\textsuperscript{1,2}, N M Silvestre\textsuperscript{3} and M M Telo da Gama\textsuperscript{3}

\textsuperscript{1} Max-Planck-Institut für Intelligente Systeme, Heisenbergstrasse 3, 70569 Stuttgart, Germany
\textsuperscript{2} Institut für Theoretische und Angewandte Physik, Universität Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart, Germany
\textsuperscript{3} Centro de Física Teórica e Computacional and Faculdade de Ciências da Universidade de Lisboa, Av. Prof. Gama Pinto 2, 1649-003 Lisboa, Portugal

E-mail: miko@mf.mpg.de, nunos@cii.fc.ul.pt and margarid@cii.fc.ul.pt

\textit{New Journal of Physics} 14 (2012) 073030 (33pp)

Received 2 April 2012
Published 13 July 2012
Online at \url{http://www.njp.org/}
doi:10.1088/1367-2630/14/7/073030

Abstract. Colloidal particles dispersed in a liquid crystal (LC) lead to distortions of the director field. The distortions are responsible for long-range effective colloidal interactions whose asymptotic behaviour is well understood. The short-distance behaviour depends on the structure and dynamics of the topological defects nucleated near the colloidal particles and a full nonlinear theory is required to describe it. Spherical colloidal particles with strong planar degenerate anchoring nucleate a pair of antipodal surface topological defects, known as boojums. We use the Landau–de Gennes theory to resolve the mesoscopic structure of the boojum cores and to determine the pairwise colloidal interactions. We compare the results in three (3D) and two (2D) spatial dimensions for spherical and disc-like colloidal particles, respectively. The corresponding free energy functionals are minimized numerically using finite elements with adaptive meshes. Boojums are always point-like in 2D, but acquire a rather complex structure in 3D, which depends on the combination of the anchoring potential, the radius of the colloid, the temperature and the LC elastic anisotropy. We identify three types of defect cores in 3D that we call single, double and split-core boojums, and investigate the associated structural transitions. The split-core structure is favoured by low temperatures, strong anchoring and small twist to splay or bend ratios. For sufficiently strong anchoring potentials characterized by a well-defined uniaxial minimum, the split-core boojums are the only stable configuration. In the presence of two
colloidal particles, we observe substantial re-arrangements of the inner defects in both 3D and 2D. These re-arrangements lead to qualitative changes in the force-distance profile when compared to the asymptotic quadrupole–quadrupole interaction. In line with the experimental results, the presence of the defects prevents coalescence of the colloidal particles in 2D, but not in 3D systems.

Contents

1. Introduction 2
2. Three-dimensional systems 4
   2.1. Landau–de Gennes free energy functional 5
   2.2. Single spherical particle: three types of boojum cores 6
   2.3. Two spherical particles 15
3. Two-dimensional systems 21
   3.1. Free energy of smectic C films 21
   3.2. Single circular particle 23
   3.3. Two circular particles 25
4. Conclusions 27
Acknowledgments 29
Appendix. Numerics 29
References 31

1. Introduction

Controlling the self-assembly of colloidal particles is an important aspect of pure and applied colloid science. In this context, assembling novel structures in liquid crystal (LC) matrices has become a very active field of research as a result of important theoretical and experimental advances [1–3]. LCs are characterized by anisotropic mechanical and optical properties due to the long-range orientational molecular ordering. Consequently, in addition to the usual isotropic colloidal interactions, colloids in LCs interact through strongly anisotropic effective forces, and have been observed to self-assemble into ordered aggregates in two (2D) [4] and three (3D) spatial dimensions [5]. A distinctive feature of these systems is the presence of topological defects, the type of which determines the symmetry of the far-field director around an isolated colloidal particle, which in turn governs the asymptotic behaviour of the nematic-induced colloidal interactions [6]. The behaviour of the interactions at short distances is more complex since the defects can move when the colloidal particles are brought close together, rendering the description of the self-assembly of LC colloids a challenging theoretical problem.

Theoretical and simulation methods have been developed to study LCs on various scales. On the macroscopic scale, the long-range forces between colloidal particles can be calculated using the Frank–Oseen (FO) elastic free energy approach [6]. On the mesoscopic scale where nonlinear effects become important, a description based on the Landau–de Gennes (LdG) tensorial order-parameter theory is necessary [7]. This is the case when the interactions between the defects dominate, as revealed by the changes in their equilibrium structure when the distance between the particles decreases [8]. On the microscopic scale, presmectic ordering and density variations cannot be ignored and density functional approaches [9] or computer simulations are usually employed [10].
The anchoring at the surfaces of colloidal particles can be controlled, for instance, through the adsorption of surfactants or deposition of thin organic or inorganic films [11–14]. When the anchoring on a spherical colloid is planar, a tangential nematic director configuration is expected at the colloidal surface. At the FO level the boundary conditions are met by the creation of a pair of antipodal surface topological defects, called boojums [15, 16]. The boojums are aligned with the far-field director, ensuring that the far-field LC configuration is homogeneous as required by the global uniform boundary conditions [17].

Recently, experimental measurements of the effective forces between two spherical colloids with planar anchoring in a 3D nematic have been reported [13, 18, 19]. In the first of these studies [13], the authors have found that the forces at short distances deviate considerably from the asymptotic quadrupole–quadrupole ones and that the equilibrium configuration of a pair of particles corresponds to close contact, implying the absence of repulsion at short distances. By contrast, experimental results obtained for 2D disc-like inclusions in free-standing smectic C (smC) films [20, 21] revealed the presence of a short-distance repulsion which keeps the inclusions at a well-defined equilibrium separation larger than contact. Again, as in the 3D system of [13], the asymptotic quadrupole–quadrupole approximation for the pairwise force breaks down at short distances.

A recent theoretical study based on the numerical minimization of the 3D LdG free energy functional [22] is in line with the experimental results of [13] concerning the equilibrium configuration of two colloidal spheres and the absence of colloidal short-range repulsion. Theoretical analyses of the 2D FO model [20, 21], based on an ad hoc ansatz for a single-particle solution and the superposition approximation, have correctly described the configuration of two discs in an smC film at short distances, but have failed to provide a consistent mechanism for the short-range repulsion observed experimentally. A subsequent superposition analysis [23], based on the exact single-particle solution [24], has predicted the existence of two regimes as a function of the anchoring strength. For weak anchoring the inclusions coalesce, while for strong anchoring the effective interaction exhibits a well-defined minimum and a strong short-distance repulsion that prevents coalescence [23].

Although the 3D studies of [22] are in qualitative agreement with the experimental results of [13], the question of the structure of the boojum cores remains open. The authors of [22] could not resolve the structure of the defect cores because the meshes that have been used in the minimization of the LdG free energy functional were too coarse. In the 2D systems studied in [20, 21, 23], the theoretical results are far from satisfactory since the superposition approximation is not valid at short distances where the interaction between defects is expected.

Motivated by these open questions and by the experimental results which reveal a qualitative difference between 2D and 3D systems [13, 20, 21, 25], we address in this paper the structure of the boojum cores and the effective interactions between disc-like and spherical colloids in 2D and 3D, respectively. We concentrate on the mesoscale and present the results of a systematic numerical analysis of the LdG free energy functionals in 2D and 3D for colloidal particles characterized by a tangential (degenerate in 3D) anchoring. We use finite-element methods (FEM) with adaptive meshes in order to minimize the LdG functionals and obtain pairwise effective interactions at all distances. We find that the defects are point-like in 2D but acquire a rather complex structure in 3D. The structure depends on the combination of the anchoring potential, the particle radius, the temperature and the LC elastic anisotropy. More specifically, we identify defect core transitions between single-core, double-core and split-core structures. The split-core structure is favoured by increasing the anchoring strength or the
particle radius and by decreasing the temperature. The LC elastic anisotropy responsible for a preferred planar anchoring at the nematic–isotropic (NI) interface (twist elastic constant smaller than bend and splay) [26] also favours the split-core structure. Finally, the split-core structure is favoured by surface potentials characterized by a well-defined uniaxial minimum [27]. In 2D the boojums have a single-core point-like structure for strong enough surface potentials.

Defects similar to the split-core boojums have recently been reported on spherical colloids with strong planar anchoring in cholesteric LCs [28–30] and in nematics, with negative electric anisotropy, in the presence of strong electric fields [31], based on the LdG model. We note that in cholesterics the defect lines have a length comparable to the colloid radius and evolve into twisted disclination lines wrapped around the colloids as the pitch of the cholesteric decreases [29]. In the presence of two particles, the inner defect lines merge, forming strong defect bonds between the colloids [28] which may be responsible for the assembly of the 2D plates observed experimentally [32]. Although the split-core boojums in nematics reported here have more than a passing resemblance to the ‘handles’ [28] and ‘ansa’ [31] found in other systems, their size is controlled by the nematic bulk correlation length rather than by the colloid size and thus refined (adaptive) meshes are required to observe them.

This paper is organized as follows. In section 2, we discuss the 3D system. Firstly, we review the experimental results and define the LdG functional. Then we discuss the results for a single spherical colloid, focusing on the structures of the boojum core as a function of the anchoring strength, colloid size and temperature. We consider two types of LCs with different anisotropies. Finally, we consider the effective interaction between two colloidal particles and compare the results with the experimental measurements [13, 25]. In section 3 we turn our attention to 2D systems. We describe the appropriate LdG functional and calculate the interaction between colloidal discs, where a short-range repulsion is found in the strong anchoring regime. A comparison with the experimental results of [20, 21] for circular inclusions in smC films is carried out. In section 4, we discuss and compare our results in 2D and 3D. For completeness, the numerical techniques used throughout this paper are described in the appendix.

2. Three-dimensional systems

In the linear regime, the effective force between two colloidal particles can be computed within the one-elastic-constant approximation by using the electrostatic analogy [6]. For spherical colloids with degenerate tangential anchoring the leading asymptotic term in the multipole ansatz for the director field is given by a quadrupole term \( \propto r^{-5} \) [33], where \( r \) is the distance to the centre of the colloidal particle. The superposition approximation then leads to the quadrupolar effective interaction between two particles [1].

Smalyukh et al [13] measured the anisotropic interactions between two colloids with tangential anchoring by using laser tweezers. At (relatively) large distances \( d \) the radial dependence of the force was found to comply with the expected \( d^{-3} \) quadrupolar behaviour. However, the angular dependence of the force disagreed qualitatively with the quadrupolar one at all distances, indicating the importance of the nonlinear effects and a breakdown of the superposition approximation.

In what follows, we shall use the LdG theory to calculate the effective interactions between two colloids with tangential anchoring. Strong emphasis is placed on the short-distance behaviour and strong anchoring limit, where the nonlinear effects are expected to dominate.
The problem is challenging as the defect structure and dynamics are complex, both in the single-particle case as well as for interacting particles, as predicted a decade ago [8] in 2D and described recently in 3D [22]. In the following, we show that the colloidal interaction at short distances results not only from the re-arrangement of the defect positions, but also from structural changes of the defect cores.

2.1. Landau–de Gennes free energy functional

Within the LdG theory [34] nematic LCs are characterized by a traceless symmetric order-parameter tensor with components \( Q_{ij} \), which can be written as

\[
Q_{ij} = \frac{3}{2} Q (n_in_j - \frac{1}{3} \delta_{ij}) + \frac{1}{2} B (l_il_j - m_im_j),
\]

where \( n_i \) are the Cartesian components of the director field \( \mathbf{n} \), \( Q \) is the uniaxial order-parameter, which measures the degree of orientational order along the nematic director, and \( B \) is the biaxial order parameter, which measures the degree of orientational order along the directions perpendicular to \( \mathbf{n} \), characterized by the eigenvectors \( \mathbf{l} \) and \( \mathbf{m} \). The corresponding LdG free energy functional is

\[
F_{\text{LdG}} = \int_{\Omega} (f_b + f_{\text{el}}) \, d^3x + \int_{\partial\Omega} f_s \, ds
\]

with \( f_b \) and \( f_{\text{el}} \) being the bulk and elastic free energy densities, given by

\[
f_b = a \, \text{Tr} \, Q^2 - b \, \text{Tr} \, Q^3 + c \left( \text{Tr} \, Q^2 \right)^2,
\]

\[
f_{\text{el}} = \frac{L_1}{2} \delta_k Q_{ij} \delta_k Q_{ij} + \frac{L_2}{2} \delta_j Q_{ij} \delta_k Q_{ik},
\]

where \( a \) depends linearly on the temperature \( T \) and is usually written as \( a = a_0(T - T^*) \), with \( a_0 \) a material-dependent constant and \( T^* \) the supercooling temperature of the isotropic phase. \( b \) and \( c \) are positive (material-dependent) constants, and \( L_1 \) and \( L_2 \) are phenomenological parameters which can be related to the FO elastic constants. The first integral in equation (2) is taken over the 3D domain, \( \Omega \), occupied by nematic, whereas the second integral is over the surface \( \partial\Omega \) (in this case the surfaces of the colloidal particles) and accounts for non-rigid anchoring conditions.

Depending on the preferred orientation of the director (anchoring direction) with respect to the surface normal \( \nu \), the surface anchoring is: (i) homeotropic, when the anchoring direction is parallel to \( \nu \); (ii) planar, when the anchoring direction is orthogonal to \( \nu \); and (iii) tilted, when the angle between the anchoring direction and \( \nu \) is less than \( \pi/2 \) (and larger than zero). The last two cases can be classified further as monostable, multistable or degenerate (in some papers the term ‘random’ is used instead of ‘degenerate’), depending on whether the surface imposes one, a finite or an infinite number of equivalent anchoring directions [12], respectively. The simplest quadratic surface free energy density, \( f_s \), favouring monostable nematic ordering \( Q_s \), i.e. with a well-defined director, scalar and biaxial order-parameters was proposed by Nobili and Durand [35]:

\[
f_s = W \left( Q_{ij} - Q_s^{ij} \right)^2.
\]

When \( W > 0 \), \( f_s \) has a unique minimum at \( Q = Q_s \). In general, this is not necessary, the requirement being that the total free energy is bounded from below. In this paper, we consider
only planar degenerate anchoring described by a family of covariant surface potentials proposed by Fournier and Galatola [27]:

\[ f_s = W_1 \left( \tilde{Q}_{ij} - \tilde{Q}^\perp_{ij} \right)^2 + W_2 \left( \tilde{Q}_{ij}^2 - \frac{Q_b^2}{2} \right)^2, \]

where \( \tilde{Q}_{ij} = Q_{ij} + Q_b \tilde{b}_{ij} \), \( \tilde{Q}^\perp_{ij} = (\delta_{ik} - \nu_i \nu_k) \tilde{Q}_{ij} (\delta_{kj} - \nu_j \nu_l) \), \( W_1 \) is the anchoring strength favouring tangential orientation of the director \( \mathbf{n} \), and \( W_2 > 0 \) guarantees the existence of a minimum for the surface scalar order-parameter equal to its bulk value \( Q_b \). At a flat surface the nematic is uniform and uniaxial everywhere. In the original formulation [27], the surface scalar order-parameter is allowed to vary and the biaxiality at a flat surface increases with the difference between the surface and bulk scalar order-parameters. The quartic surface potential given by equation (6) may be viewed as the minimal biaxiality potential characterized by a well-defined degenerate planar minimum. The quadratic surface potential \((W_2 = 0)\) is the covariant version of equation (5) the minimum of which depends on the coupling to the bulk nematic. In section 2.2, we shall see that the quartic term \( W_2 \) has a profound effect on the structure of the topological defects, by controlling the coupling to the bulk nematic through the deviation of the surface and bulk scalar order-parameters. On the surface of spherical colloids point-like singularities with charge +1 split into pairs of point-like singularities with charge +\( \frac{1}{2} \) connected by disclination lines.

It is convenient to define the dimensionless temperature \( \tau = 24ac/b^2 \). At \( \tau < 1 \) the uniaxial nematic is stable and the degree of orientational order is given by

\[ Q_b = \frac{b}{8c} \left( 1 + \sqrt{1 - \frac{8\tau}{9}} \right). \]

The nematic becomes unstable at \( \tau > 9/8 \). At \( \tau = 1 \) both the nematic and the isotropic phases coexist. Typical values of the bulk parameters for 5CB are [36] \( a_0 = 0.044 \times 10^6 \) J (Km\(^{-3}\)), \( b = 0.816 \times 10^6 \) J m\(^{-3}\), and \( c = 0.45 \times 10^6 \) J m\(^{-3}\), \( L_1 = 6 \times 10^{-12} \) J m\(^{-1}\), \( T^* = 307 \) K. The spatial extension of inhomogeneous regions and the cores of topological defects are of the order of the bulk correlation length, which is given by \( \xi = 2\sqrt{2c (3L_1 + 2L_2)}/b \) at the NI transition [37].

We define the elastic constant anisotropy \( \eta \equiv L_2/L_1 \), and consider two cases: \( \eta = 2 \) with \( \xi \simeq 15 \) nm corresponding to 5CB, and \( \eta = -1/2 \) with \( \xi \simeq 8 \) nm. Note that stability requires \( \eta > -3/2 \) [38]. Depending on the LC material, \( L_2 \) is positive or negative, and its sign controls the molecular orientation at the NI interface, which is planar for \( \eta > 0 \) and homeotropic for \( \eta < 0 \) [26].

The LdG elastic constants \( L_1 \) and \( L_2 \) may be related to the FO elastic constants [39], \( K_1 = K_3 \) and \( K_2 \), through the uniaxial ansatz \( Q_{ij} = (3/2) Q_b (n_i n_j - \delta_{ij}/3) \), yielding \( K_1 = K_3 = 9Q_b^2(L_1 + L_2/2)/2 \) and \( K_2 = 9Q_b^2L_1/2 \). In general, \( K_1 \) and \( K_3 \) are different, but in most cases the difference is small and the elastic free energy density in equation (4) is deemed adequate.

2.2. Single spherical particle: three types of boojum cores

When spherical colloids with strong planar anchoring are dispersed in nematic LCs, a pair of topological surface defects, boojums, appears at the antipodes of the particles [15–17]. The understanding of the defect structure in terms of the order-parameter distribution in the cores is beyond mere topological arguments and has been the subject of investigation since the early
For infinitely strong anchoring and within the class of axially symmetric nematic configurations, hedgehog defects exhibit three different structures: the radial hedgehog, a small ring or loop disclination [41] and a third structure, a split-core defect, which was found to be metastable [42]. Phase and bifurcation diagrams indicate that the transition from the hedgehog to the ring structure is of first order, as predicted in [41]. Although several studies have addressed the structure of hedgehog defect cores [41–43], the structure of boojums has not been fully understood [44].

A homotopy classification of surface topological defects is given by Volovik [45]. According to this classification a point defect at the boundary of a nematic LC may be viewed as the combination of a bulk hedgehog and a surface boojum and is therefore characterized by two topological charges—the charge $N$ of the bulk hedgehog and the index $m$ of the projection $t = n - v(n \cdot v)$ of the director field onto the surface with normal $v$. The charges $N$ and $m$ are related to a continuous topological charge $\mathcal{A}$ defined as [46, 47]

$$\mathcal{A} = \frac{1}{4\pi} \int_{\sigma} \left( \frac{\partial n}{\partial \theta} \times \frac{\partial n}{\partial \phi} \right) d\theta d\phi,$$  

(8)

where $\sigma$ is a hemisphere surrounding the defect, and $\theta, \phi$ are arbitrary coordinates on $\sigma$. Evaluation of the integral in equation (8) gives an explicit relation between the continuous charge $\mathcal{A}$ and the charges $N$ and $m$ [46]

$$\mathcal{A} = \frac{m}{2}(n \cdot v - 1) + N,$$  

(9)

which provides a means of calculating $N$ since $m$ can be calculated independently [47]. If $\mathcal{A}$ is an integer the defects can detach from the surface and if $\mathcal{A} = 0$ they may vanish altogether. By contrast, for non-integer charges $\mathcal{A}$ the defects are ‘topologically’ bound to the surface. For instance, a single-core boojum, which is discussed below, has $\mathcal{A} = \frac{1}{2}$ and $N = 1$, i.e. the defect cannot vanish or detach itself from the surface.

In this section, we investigate the dependence of the boojum core structure on (i) the strengths of the anchoring potential, $W_1, W_2$; (ii) the reduced temperature $\tau$; and (iii) the colloidal radius $R$. We introduce the dimensionless anchoring strengths $w_i = W_i Q_b^2 R / K_2$ ($i = 1, 2$), and consider LCs with positive (e.g. 5CB) and negative elastic anisotropies. We pay particular attention to the nature and degree of the nematic order within the boojum cores. In agreement with [48], we find that the apparent singularities of the director field are replaced by uniaxial order-parameter distributions with negative scalar order-parameter, corresponding to oblate nematic order, surrounded by biaxial layers.

We shall show that on small colloids boojum cores are axially symmetric point-like with index $m = +1$. We call this structure single-core boojum. It is stable at high temperatures and relatively weak anchoring. In [44] a similar boojum core structure (named ‘fingered’ boojum) has been reported at a flat surface. On large colloids, at low temperatures and strong anchoring, the axial symmetry is broken and the boojum’s $+1$ point-like cores split into pairs of $+\frac{1}{2}$ point-like surface defects which are connected by disclination lines. A structure without a fully developed disclination line, the double-core boojum, is also found. The detailed structure of the boojums as well as the transitions between the different configurations depend in detail on the colloid and the LC parameters as we shall discuss below.

We start by describing the three stable configurations of boojum cores, namely single-, double- and split-core boojums. The cores differ both in their surface and bulk
Figure 1. Three types of boojum core structures: (a) single-core, (b) double-core and (c) split-core configurations. The transitions between different configurations are driven by decreasing temperature $\tau$: (a) $\tau \simeq -0.3$, (b) $\tau \simeq -0.7$ and (c) $\tau \simeq -3.2$, at fixed anchoring strengths, $w_1 \simeq 37$, $w_2 = 0$, the radius of the colloidal particle, $R = 0.1\mu m \simeq 6.6\xi$, and the elastic constant anisotropy, $\eta = 2$. The scale bars represent the nematic correlation length $\xi$ at the NI transition. In the upper panels and in the lower panel of (c), the iso-surface of the scalar order-parameter corresponding to $Q = 0.3Q_b$ is shown. In the lower panel of (b) the proto-ring of the double-core boojum is represented by the iso-surfaces $Q = 0.4Q_b$ and $Q = 0.2Q_b$. The lower panels depict the colour-coded biaxiality parameter equation (10) in the plane $z = R$. The biaxiality parameter in the plane $y = 0$ is also shown for the single-core boojum, in the lower panel of (a). The short lines on the surface of the colloidal particle represent the eigenvector of $Q$ corresponding to the largest eigenvalue. This eigenvector corresponds to the nematic director only in the case of prolate nematic order. See the main text for further details.

Typical core configurations are illustrated in the lower panels of figure 1 where the degree of biaxiality defined as

$$\beta^2 = 1 - 6\frac{(\text{Tr} \: Q^2)^2}{(\text{Tr} \: Q^2)^3}$$

is shown by a colour map. $\beta = 0$ characterizes the uniaxial nematic, while $\beta = 1$ corresponds to the maximal biaxiality nematic state. $\beta = 1$ is obtained when one (and only one) eigenvalue of $Q$ vanishes. Note that in the isotropic phase all of the eigenvalues of $Q$ vanish [42]. Figure 1 illustrates the effect of $\tau$ on the structure of boojums at $\eta = 2$ and strong quadratic ($w_2 = 0$) surface potentials. As $\tau$ decreases the boojum core transforms from the single to the double core and then to the split-core structure with the accompanying disclination half-ring. The core
Figure 2. Eigenvalues of the tensor order-parameter $Q_{ij}$ on the $z$-axis for the three types of boojum cores: (a) single-core, (b) double-core and (c) split-core configurations, respectively. The model parameters are as in figure 1. The far-field director is oriented along the $z$-axis.

Figure 3. Structure of the double-core boojum represented by the iso-surface $\det Q = 0$, and the colour-coded biaxial parameter equation (10) in the plane $z = R$. (a) The model parameters are the same as in figure 1(b); (b) $\tau \simeq 0.16$, $R \simeq 9.3\xi$.

is fairly large close to the NI transition and shrinks as the temperature decreases. A description of the boojum core configurations in terms of the eigenvalues of $Q$ along the $z$-axis (the direction of the far-field director) is illustrated in figure 2, where the eigenvalues $\lambda_i$, $i = 1, 2, 3$, are plotted as functions of the distance $z$ to the colloidal surface at fixed $x = y = 0$ (the $x, y$ coordinates of the centre of the colloidal particle).

Single-core boojums are uniaxial along the $z$-axis, as revealed by the two degenerate eigenvalues. The scalar order-parameter vanishes at $z/\xi \simeq 0.5$ above the colloidal surface, where the three eigenvalues vanish and the system is isotropic. Below this point the scalar order-parameter is negative, since the principal (non-degenerate) eigenvalue is negative and the nematic order is oblate. Above $z/\xi \simeq 0.5$ the scalar order-parameter is positive, indicating that the nematic becomes prolate.

By contrast, double-core boojums are biaxial along the $z$-axis. The surface of maximal biaxiality intersects the $z$-axis at three distinct points (see figures 2(b) and 3) separating regions of low nematic oblate and prolate order.

Split-core boojums are also biaxial along the $z$-axis. The surface of maximal biaxiality intersects the $z$-axis at two distinct points, $z/\xi \simeq 0.49$ and $z/\xi \simeq 0.63$, which delimit the region of oblate nematic order. In the outer region, $z/\xi > 1$, two of the eigenvalues are degenerate and
the nematic is uniaxial. As \( z \) decreases the two negative eigenvalues depart from each other, implying nonzero biaxiality. One eigenvalue remains negative. The other two exchange their places at a point that can be identified with the centre of the boojum core. At this point the nematic is uniaxial with \( Q_b < 0 \). All such points form a 3D curve that is surrounded by the surface of maximal biaxiality (\( \det Q = 0 \)). This surface encloses the region with oblate uniaxial order (\( Q_b < 0 \)).

In all cases, the boojum cores are non-singular and biaxial over extended regions, with linear dimensions of the order of the bulk correlation length, \( \sim \xi \). We proceed to describe in detail the structure of the three types of boojum cores.

Single-core boojums are characterized by an axially symmetric distribution of the order-parameter \( Q \). Consequently, \( \beta = 0 \) on the \( z \)-axis, where two eigenvalues are degenerate, as shown in figure 2(a). The iso-surface \( \det Q = 0 \) is a distorted hemisphere that is biaxial (\( \beta = 1 \)) everywhere (see figure 1(a)) except at the intersection point with the \( z \)-axis, \( z/\xi \simeq 0.5 \), where the fluid is isotropic. At \( z = 0 \), the location of the putative surface point defect, the scalar order-parameter is negative, i.e. the molecules are perpendicular to the director (oblate nematic order).

In double-core boojums the axial symmetry is broken. As a result the system becomes biaxial along the \( z \)-axis (figures 1(b) and 2(b)). The most prominent feature of this structure, however, is the appearance of a proto-ring resembling the fully developed half-ring disclination of the split-core boojum. The proto-ring is formed in a region, of the order of \( \xi \), of low nematic order (the scalar order-parameter is \( \leq 0.5 Q_b \)) and is depicted in figure 1(b) by the iso-surface \( Q = 0.2 Q_b \). The double-core structure shares a number of features with the split-core boojum. Its innermost core is a half-ring starting and ending on the colloidal surface, with very low biaxiality, \( \beta \simeq 0 \), and negative scalar order-parameter. Further inspection of the eigenvalues of \( Q \) reveals that the iso-surface \( \det Q = 0 \) (\( \beta = 1 \)) is a hemisphere with a handle at the top; see figure 3. This iso-surface intersects the colloidal surface in a single closed loop. In the hole, below the handle, the biaxiality is vanishingly small and the scalar order-parameter is positive, i.e. the nematic is prolate uniaxial.

Finally, the split-core boojum is characterized by a \( \frac{1}{2} \) disclination half-ring connected to the colloidal surface. The inner core of the ring has zero biaxiality and oblate nematic order. This region is surrounded by the iso-surface \( \det Q = 0 \), forming a half-torus, see figures 1(c) and 2(c), which intersects the colloidal surface in two distinct closed loops. The nematic is prolate uniaxial everywhere except in a region of order \( \sim \xi \) in the core of the half-ring.

The three types of boojums are topologically equivalent, in the sense that any of them can be transformed smoothly into any other. The split and double-core boojums result from the breaking of the axial symmetry of the single core, which splits on the colloidal surface. This splitting is complete in the split-core boojum in the sense that it is accompanied by the splitting of the \( \det Q = 0 \) surface, and is only partial in the double-core boojum. In the following subsections, we address the question: how does the stability of these structures depend on the colloidal and LC parameters?

2.2.1. Strength of the anchoring potential. Here we report on the effects of the quadratic (\( w_1 \)) and quartic (\( w_2 \)) surface potentials, equation (6). When the anchoring strengths \( w_1 \) and \( w_2 \) are large the split-core structure is favoured for all \( R, \tau \) and \( \eta \). When \( w_2 = 0 \) and \( w_1 \) is large the split (double) core boojum is found for large colloids and low temperatures in LCs with \( \eta > 0 \) (\( \eta < 0 \)). At flat surfaces the quartic potential induces uniform uniaxial nematic profiles [27]. On
Figure 4. Elastic-free energy (excess over the uniform nematic free energy $F^{(1)}$ minus the surface free energy $F_s$) as a function of the dimensionless quadratic anchoring strength, $w \equiv w_1$, ($w_2 = 0$), at several reduced temperatures $\tau$. The inset shows the elastic (full line) excess (dashed line) and surface (dash-dotted line) free energies as functions of $w$. The lower panel depicts the configurations of (1) the single-core boojum for $w \simeq 3.7$, and (2) the split-core boojum for $w \simeq 37$, $\tau \simeq -1.6$. The black lines on the surface of the colloidal particles represent the eigenvectors corresponding to the largest eigenvalue of $Q$. The isosurfaces $Q = 0.3Q_b$ are also shown. The LC anisotropy $\eta = 2$ and the radius of the colloid $R/\xi \simeq 6.6$.

spherical colloids, in the strong anchoring regime, this potential stabilizes the split-core boojums where the biaxial regions are reduced. By contrast, in systems with quadratic surface potentials, $w_2 = 0$, the minimum is determined by the coupling of the surface to the bulk nematic [27]. In this case, the stability of the boojum cores depends in detail on $W_1$, $R$, $\tau$ and $\eta$.

We start by investigating the quadratic surface potential, $w_2 = 0$. In figure 4, we plot the elastic free energy $F^{(1)} - F_s$, where $F^{(1)} \equiv F_{\text{LdG}} - F_b(Q_b)\Omega$ is the excess (over the uniform uniaxial nematic) free energy and $F_s$ is the surface free energy, as a function of the dimensionless anchoring strength, $w \equiv w_1$, for several values of $\tau$ from just below the NI transition ($\tau \simeq 0.97$) to deep in the bulk nematic ($\tau \simeq -1.6$). We set $\eta = 2$ and $R \simeq 6.6\xi$.

Two regimes are observed. In the strong anchoring regime, $w \gg 1$, the elastic free energy exhibits a plateau that starts with the nucleation of the boojums at opposite poles of the colloidal particle. The inset shows that in this regime the excess, $F^{(1)}$, and the elastic, $F^{(1)} - F_s$, free energies approach each other asymptotically, since the surface free energy $F_s$ decreases as $w^{-1}$.
In the weak anchoring regime, \( w \lesssim 1 \), the surface free energy increases linearly with \( w \) and dominates over the elastic term, which increases as \( w^2 \). This behaviour is in line with that of homeotropic anchoring, where the elastic free energy was found to increase with \( w^2 \) for weak anchoring and to saturate in the strong anchoring regime [49].

Figures 4(1) and (2) illustrate how the structure of the boojum cores changes with increasing quadratic surface potential at low temperatures. As the anchoring strength increases, the competition between elastic and anchoring energies leads to conflicting director orientations at the poles of the colloidal particle where the regions of reduced uniaxial and increased biaxial order develop. Inspection of the director configurations confirms that the system starts by developing a single-core point-like surface defect; see figure 4(1). The projection \( t \) of the director field onto the surface of the particle is characterized by an index \( m = +1 \). In this regime of small \( w \), the surface director field has a finite normal component as seen in figure 4(1).

Deep in the strong anchoring regime the normal component of the surface director vanishes, see figure 4(2), and the region of reduced uniaxial nematic order opens into a half-ring attached to the colloidal surface, which resembles a \( \frac{1}{2} \) disclination line defect.

For the quadratic surface potential \( (w_2 = 0) \) structural transitions driven by the anchoring strength are observed at low temperatures only. The boojum core structure diagram is shown in figure 5 by circles. The single core is stable at weak anchoring \( w \lesssim 6 \), the double core is stable in a narrow range of anchoring strengths, \( 6 \lesssim w \lesssim 15 \), while the split core is stable at strong anchoring \( w \gtrsim 15 \). At high temperatures \( (\tau = 0.16, 0.97, \text{not shown in figure 5}) \), the quadratic anchoring potential does not stabilize the double or split-core boojums. Only the single-core structure is observed in the range of anchoring strengths 0.00037 \( \lesssim w \lesssim 370 \).
We now proceed to analyse the quartic potential equation (6) and assume for simplicity \( w = w_1 = w_2 \). As the strength \( w \) of the anchoring potential increases, the sequence of single, double and split-core structures is observed at all temperatures. Two cases corresponding to \( \tau \simeq 0.16 \) (squares) and \( \tau \simeq 0.97 \) (diamonds) are shown in the core structure diagram of figure 5. At high temperature the single core is stable for \( w \lesssim 4.9 \), whereas the split core is stable for \( w \gtrsim 5.5 \). The double core is stable for intermediate anchoring strengths \( w \). The transition between the core structures occurs at lower values of \( w \) as \( \tau \) decreases. When compared with the quadratic potential, at the same temperature and colloidal radius, the transitions occur at lower \( w \).

In summary, at a fixed colloidal size and temperature, a strong quartic potential stabilizes the split core structure. A strong quadratic potential stabilizes the split-core boojums for LCs with positive elastic anisotropy, but for LCs with negative elastic anisotropy the split-core boojums are not observed. Here only two systems with \( \eta = 2 \) and \( \eta = -1/2 \) were investigated. Presumably, there exists a threshold value of \( \eta \) above which quadratic surface potentials stabilize the split-core structure. The double-core structure is stable over a limited range of anchoring strengths for both types of surface potential.

2.2.2. Temperature. In the previous section, we found evidence that temperature plays a major role in the stability of the boojum cores. Here we consider temperature to be the control parameter of the structural boojum core transitions.

We start by investigating a colloidal particle with a quadratic surface potential, \( w_2 = 0 \). We consider reduced temperatures in the range \(-3.24 \lesssim \tau \lesssim 1 \) and set \( R = 0.1 \mu \text{m} \), which is \( \simeq 6.6 \xi \) for LCs with positive elastic anisotropy \( \eta = 2 \) and \( \simeq 12.4 \xi \) for LCs with \( \eta = -1/2 \), since the bulk correlation length \( \xi \) depends on \( \eta \).

A quadratic potential (\( w_2 = 0 \)) with \( w_1 \simeq 37 \) stabilizes the split-core structure at low temperatures only in LCs with positive elastic anisotropy, \( \eta = 2 \). The core structure diagram is depicted in figure 6 by circles. For \( \tau \lesssim -1.12 \) the split-core structure is stable, while at high temperatures \( \tau \gtrsim -0.27 \) the boojum has a single core. The transition between these structures seems to occur continuously through the intermediate double-core structure, which is observed in the range \(-1.12 \lesssim \tau \lesssim -0.27 \). The surface splitting of the split-core structure increases slowly as the temperature decreases and saturates at a value close to \( \xi \).

The split-core structure was not observed in LCs with negative anisotropy, \( \eta = -1/2 \). Recalling that \( \eta > 0 \) corresponds to \( K_1 = K_3 > K_2 \), while \( \eta < 0 \) describes \( K_1 = K_3 < K_2 \), we find that unfavourable twist distortions are responsible for the suppression of the split-core structures in LCs with \( \eta = -1/2 \). Twist deformations vanish when the azimuthal component of the director field, \( n_\phi \), vanishes [50], which is the case with single-core boojums. By contrast, for double and split-core boojums \( n_\phi \) acquires a nonzero value that increases from the double to the split-core structures. As twist distortions are energetically unfavourable in LCs with \( \eta < 0 \), the split-core boojum becomes unstable with respect to the double-core structure. This is in line with the twist transition reported in hyperbolic hedgehog defect cores (see figures 4 and 5 of [50]) on colloids with homeotropic anchoring, and in general, with the effect of elastic anisotropy on the structure of distortions around topological defects in 2D [51].

For a quartic potential with \( w_1 = w_2 \simeq 37 \) the split-core is stable for both types of LCs, at all temperatures. The core splitting increases with temperature up to \( 2.8 \xi \) for \( \eta = 2 \) and \( 4.9 \xi \) for \( \eta = -1/2 \), close to the NI coexistence temperature (see figure 6, diamonds and squares, respectively). The quartic term in the surface potential is quite effective in stabilizing the
split-core structure, even when twist distortions are unfavourable ($\eta = -1/2$). In fact, the split core is not only stabilized, but its splitting is larger than that observed in systems with $\eta > 0$. We note that the boojum size is proportional to the splitting parameter shown in figure 6, which decreases as the temperature decreases.

In summary, strong quadratic potentials and low temperatures favour split-core boojums for LCs with positive elastic anisotropy. When $\eta < 0$ the double-core structure is stable. Strong quartic potentials favour split-core boojums, which are the only stable structures, regardless of the LC anisotropy.

2.2.3. Particle radius. Finally, we investigate the effect of the colloidal radius $R$ on the structural transitions of the boojum cores. For this purpose we consider colloids with sizes in the range $0.05 \mu m \leq R \leq 0.5 \mu m$.

Boojum core transitions driven by the colloidal size, for quadratic (circles) and quartic (diamonds) potentials, are illustrated in figure 7. For LCs with $\eta = 2$, the quadratic potential stabilizes the split-core boojum on large colloids, $R/\xi \gtrsim 10$, the single-core boojum on small colloids, $R/\xi \lesssim 8$, and the double-core boojum at intermediate colloid sizes. By contrast, for LCs with $\eta = -1/2$ and the same quadratic potential, the split-core is not observed and the single–double-core transition occurs at $R/\xi \simeq 45$ (not shown). This behaviour is similar to that described in previous sections for quadratic potentials. The suppression of twist distortions destabilizes the split-core boojum.

For a quartic potential with $w_1 = w_2$ the split core is stable for both types of elastic anisotropy in the entire range of colloidal sizes. The size of the half-ring, given by the core splitting on the colloidal surface, increases with $R$ and saturates at $\simeq 6\xi$ for $\eta = 2$ and at $\lesssim 10\xi$ for $\eta = -1/2$. Again, the quartic surface potential equation (6) stabilizes split-core boojums in LCs with negative elastic anisotropy.
Figure 7. Defect core transitions driven by the colloidal size, for quadratic (circles) and quartic (diamonds) potentials with \( w \simeq 37 \), at \( \tau \simeq 0.16 \). For quadratic potentials, single-core boojums are stable for small and spilt-core boojums are stable for large colloidal sizes, \( R \). The LC anisotropy \( \eta = 2 \). For the quartic potential, the split-core structure is stable over the entire range of \( R \). The solid lines are a guide to the eye.

We end this section by noting that although it may be difficult to observe the reported boojum core structures using standard optical methods, their influence on the effective interaction between colloidal particles at short distances is significant, as will be discussed in section 2.3. The far-field nematic configuration, however, is not affected by the mesoscopic structure of the boojum cores.

2.3. Two spherical particles

In this section, we calculate the two-body effective interaction potential \( F^{(2)}(d, \theta) \) [52] for colloids with a quadratic surface potential, equation (6). For the definitions of \( d \) and \( \theta \), see figure 8. The interaction free energy, \( F^{(2)} \), is defined as the excess (over the free energy of the uniform nematic) free energy \( F_2 \equiv F_{\text{LdG}} - f_b(Q_b)\Omega \) over the (excess) free energy of two independent particles,

\[
F_2(d, \theta) = 2F^{(1)} + F^{(2)}(d, \theta),
\]

i.e. \( F^{(1)} \) is the excess free energy of a single colloidal particle. By definition, \( F^{(2)} \) tends to zero as \( d \to \infty \).

In particular, we shall demonstrate how the nonlinear effects become dominant, leading to a qualitative change of the effective interaction, e.g. the potential \( F^{(2)}(d, \theta = 0) \) changes from repulsive at large \( d \) to strongly attractive at moderate to short distances. As we shall see, this is driven by the complex behaviour of the interaction between the topological defects that results in a re-arrangement of their structure at short distances. Analogous changes in the effective interaction have been reported experimentally [13] and confirmed within LdG theory [22] where it is shown that the axial symmetry of the location of the boojum pairs is continuously broken, resulting in an effective colloidal attraction.

New Journal of Physics 14 (2012) 073030 (http://www.njp.org/)
Figure 8. Schematic representation of two interacting boojum colloids. The far-field director is parallel to the $z$-axis. For large $d$, pairs of boojums are aligned parallel to the far-field director.

Here we shall re-examine the effective colloidal interaction based on the results of the previous section where we have shown that the axial symmetry of the boojum cores may be broken at the level of a single colloidal particle. In what follows, we use the notation set in figure 8. The far-field director is aligned with the $z$-axis. Due to the spherical symmetry of the colloids, $F^{(2)}$ depends on the colloidal separation $d$ and on the polar angle $\theta$ only. We consider colloidal particles of equal size, and set $R = 0.1\mu m$, $\eta = 2$, $\tau \simeq 0.16$, and the other model parameters corresponding to the LdG parametrization of 5CB, described in section 2.1. For this set of parameters, the boojum cores exhibit a single-core configuration over the entire range of anchoring strengths $w \equiv w_1$.

In figure 9, we plot $F^{(2)}(d)$ in the weak anchoring regime. In this regime, the interaction is repulsive when the inter-colloidal vector is either parallel or perpendicular to the far-field director, $\theta = 0$ or $\pi/2$, and is attractive at intermediate colloidal orientations, as expected for quadrupole–quadrupole interactions.

The character of the effective interaction changes significantly in the strong anchoring regime, as shown in figure 10. For oblique, $\theta = \pi/4$, and perpendicular, $\theta = \pi/2$, orientations of the colloidal pair the interaction remains qualitatively the same: attractive when the colloids are at an oblique angle with the far-field director and purely repulsive when the colloids are perpendicular to it. However, at $\theta = 0$ the effective interaction is no longer purely repulsive. At short distances, $d \lesssim 3R$, the particles start attracting each other. This change results from a symmetry break of the boojum-pair configuration as shown in the insets of figure 10. At large distances the boojums are located at the poles of the particles (see inset (3) in figure 10) and aligned parallel to the far-field director, as in isolated particles. As the separation between the colloids decreases, the repulsion of the inner defects increases. The change from repulsive to attractive colloidal interaction is driven by a change in the position of the inner defects; see inset (2) in figure 10. This mechanism for attractive colloidal interactions—re-arrangement of the inner defects with quadrupolar symmetry—was reported almost 10 years ago for 2D colloids with homeotropic anchoring [8]. We note that although in the single-particle configuration the boojums are single cores, the inner boojums undergo a transition to split cores as the distance between the colloidal particles decreases; see figure 10(2). The symmetry break in the

New Journal of Physics 14 (2012) 073030 (http://www.njp.org/)
Figure 9. Effective interaction potential $F^{(2)}(d)$ for several values of $\theta$. The surface potential is quadratic, equation (6), and the anchoring strength $w \equiv w_1 \simeq 0.37$. Elastic anisotropy $\eta = 2$, the radius of the particles $R \simeq 6.6 \xi$ and reduced temperature $\tau \simeq 0.16$.

Figure 10. Effective interaction potential $F^{(3)}(d)$ for several values of $\theta$. The anchoring strength $w \simeq 37$. Elastic anisotropy $\eta = 2$, the radius of the particles $R \simeq 6.6 \xi$ and reduced temperature $\tau \simeq 0.16$. The insets depict the boojum configurations for several distances $d$ and $\theta = 0$. In the attractive range, $2R \lesssim d \lesssim 3R$, the inner boojums are $\frac{1}{2}$ disclination rings represented by the iso-surface of the scalar order-parameter $\tilde{Q} = 0.3Q_b$.

Position of the inner boojums’ is accompanied by a symmetry break of the inner boojums’ core structure, which changes from the axially symmetric single core to the asymmetric split-core configuration. For even smaller separations, colloidal particles are strongly bound by sharing their inner boojums that ‘lock in’ to form a double-bond defect between the particles; see figure 10(1). A similar configuration was reported in [28] for spherical colloids in cholesterics.
Figure 11. Effective interaction potential as a function of the distance \(d\) between two spherical colloidal particles, aligned with the far-field director, \(\theta = 0\). The surface anchoring potential is quadratic, equation (6). Elastic anisotropy \(\eta = 2\), the radius of the particles \(R \approx 6.6\xi\), and reduced temperature \(\tau \approx 0.16\). The anchoring strength \(w\) varies in the range \([0.4, 37]\). The inset depicts the height of the free energy barrier as a function of \(w\), exhibiting quadratic behaviour \(w^2\) in the weak anchoring regime.

The global minimum of \(F^{(2)}(d, \theta)\) corresponds to close contact, \(d = 2R\), at an oblique angle \(\theta\) close to \(\pi/4\). This is in line with the experimental results of [13, 17] where boojum colloids were reported to coalesce. In section 3, we show that this is not the case for boojum colloids in 2D (discs).

The effect of the anchoring strength \(w\) is trivial for colloidal orientations \(\theta = \pi/4, \pi/2\), and thus we focus on \(\theta = 0\). In figure 11, we plot \(F^{(2)}(d, \theta = 0)\) for several values of anchoring strength \(w\). The dependence of the free energy barrier on the anchoring strength is illustrated in the inset. The barrier height is weakly discontinuous at \(w = w^* \approx 0.7\) delimiting two types of behaviour. For strong anchoring, \(w > w^*\), the free energy at distances close to the free energy maximum, \(d^*\), is a smooth function of \(d\). This implies that as the colloidal separation decreases the boojums rearrange smoothly, driving the change from repulsive to attractive interactions. For weak anchoring, \(w < w^*\), the nematic order at the poles of the particles is suppressed, but there are no defects. The system behaves almost linearly in this regime, i.e. \(Q \propto w\), and the resulting free energy \(\propto w^2\). The effective interaction is repulsive at all \(d\), as expected for two quadrupoles oriented at \(\theta = 0\).

We conclude that the interaction between colloids aligned with the far-field director changes from repulsive to attractive at short distances as a result of the re-arrangement of the positions and of the core configurations of the inner boojums.

We proceed to give a detailed description of the angular dependence of the effective force acting on the colloids. The measurement of this force was reported in [13]. While Brownian motion was found to dominate the dynamics for \(d > 6R\), at shorter distances \((d \lesssim 4R)\) a nematic mediated force, of the order of the elastic constant \(K\), was reported. As the elastic force is dominant only at small distances, strong deviations from the asymptotic quadrupolar interaction were observed. For instance, the orientation \(\theta\) corresponding to the strongest attraction was
found to depend on the distance between colloidal particles, while the quadrupolar attraction is maximal at $\theta \approx 49^\circ$, for any $d$. Additionally, an attraction for $0^\circ < \theta < 70^\circ$ and repulsion for $75^\circ < \theta < 90^\circ$ were reported, while quadrupoles repel at $\theta = 0$. Finally, the radial dependence of the force (at fixed $\theta = 30^\circ$) deviates systematically from the quadrupolar power law $\propto d^{-6}$ for $d \lesssim 3R$. These results suggest that nonlinear effects dominate and that the superposition approximation does not hold in the range of distances that were investigated.

We have calculated the absolute value $F$ of the elastic force, $\mathbf{F} = F_r \mathbf{e}_r + F_\theta \mathbf{e}_\theta$, as well as its radial and polar components $F_r = -\partial F_{\text{el}} / \partial d$ and $F_\theta = -(1/d) \partial F_{\text{el}} / \partial \theta$ by numerical differentiation. In figure 12, the magnitude of the force is plotted as a function of the relative orientation, $\theta$, for several values of $d$. We note that as the distance between the particles increases the magnitude of the force decreases and its structure as a function of $\theta$ decreases.

In figure 12 the angular dependence of the force, at separation $d = 4R$, resembles that of the quadrupolar force \[53\] with principal maxima at $\theta = 0$ and $\theta = \pi$. In addition, the force exhibits three secondary maxima at intermediate values of $\theta$ in line with the angular dependence of the quadrupole–quadrupole force \[13, 53\]. As the distance between the colloids decreases the angular dependence of the force changes quite rapidly and quite drastically. Just below $d = 3R$ the maximum at $\theta = \pi$ becomes a minimum (the force weakens) and the difference between the secondary maxima at intermediate values of $\theta$ becomes more pronounced. A similar angular dependence of the force was reported in \[13\] at colloidal separations $3R \lesssim d \lesssim 4R$. However, our theoretical results appear to be more sensitive to the inter–colloidal separation and predict different angular behaviours at colloidal separations $d = 3R$ and $d = 4R$ at $\theta = 0$. At this orientation the experiments report a local minimum for colloidal separations in the range $3R \lesssim d \lesssim 4R$ \[13\].

In an attempt to rationalize the discrepancies between the theoretical and the experimental results, we have plotted the radial and polar components of the force as a function of $\theta$ in figures 13 and 14. The radial component of the force is found to be two orders of magnitude larger than the polar component, and thus dominates the behaviour of the total force. This is in sharp contrast with the measured force, which is characterized by a radial component that differs significantly from the total force at short distances, around $\theta = 0$ (see figure 4 of \[13\]).

\[\text{Figure 12. Absolute value of the pairwise force as a function of } \theta, \text{ for several values of } d. \eta = 2, R \approx 6.6\xi, \tau \approx 0.16 \text{ and } w \approx 37.\]
Figure 13. The radial component of the force between two colloidal particles as a function of $\theta$, for several values of $d$. The model parameters are the same as in figure 12.

Figure 14. The polar component of the force between two colloidal particles as a function of the colloidal orientation, $\theta$, at several values of the particles separation $d$. The model parameters are the same as in figure 12.

particularly the inset (c) where the radial component of the force at $d = 3R$ appears to vanish at $\theta = 0).$ The results for the polar component of the force plotted in figure 14 reveal that the angular dependence changes abruptly at $\theta = 0$, in contrast to the behaviour of the force at $\theta = \pi/4$ and $\pi/2$. This is related to the head-on interaction of the inner boojums and the associated discontinuity of $F_\theta$ at $\theta = 0$. This probably has an impact on the accuracy of the experimental results as the colloidal configuration at $\theta = 0$ is unstable, rendering the force measurement, at this orientation, difficult. In addition, it is known [18] that the use of optical tweezers may substantially alter the nematic configuration around trapped colloids. Finally, the colloidal particles used in the experiment are one order of magnitude larger than the colloids used in our calculations. One or more of these effects may account for the discrepancies between
the theoretical and the experimental results. We have also calculated the force for colloidal particles five times larger and found no significant differences compared to the behaviour shown in figures 13 and 14. This discrepancy is somewhat surprising and will be further investigated in future work.

3. Two-dimensional systems

Dispersed colloidal particles in smC films are realized either as 2D inclusions (discs) of a lower order phase (isotropic, nematic or cholesteric) or as smectic islands with a larger number of layers than the surroundings [2, 21]. Planar boundary conditions at the 2D inclusions may lead to the nucleation of a pair of surface defects [21, 54]. At longer distances the interaction between these discs is of quadrupolar type, and deviates from it at short distances. In contrast to the observations in 3D systems, where the spherical colloids with planar anchoring coalesce [17], discs in smC films maintain a well-defined separation $d_{eq} \simeq 2.7R$, where $R$ is the disc radius.

The distortions in smC films due to an isolated disc with planar anchoring, as well as the asymptotic effective pair interaction, have been described using the electrostatic analogy and the superposition approximation. In the simplest approach [20] the distortions around one disc are modelled by the superposition of three solutions to the Laplace equation corresponding to one topological defect with charge $+1$ in the centre of the disc and two $-\frac{1}{2}$ surface defects. Then by using the superposition approximation a quadrupole–quadrupole effective interaction is obtained. However, this solution does not satisfy the boundary conditions at the disc boundary, and the superposition approximation fails to describe the repulsion observed experimentally at small distances [20]. A related approach [23], based on the exact solution for the $c$-director (defined below) around a disc with arbitrary anchoring strength [24], reveals that the repulsion appears simultaneously with the nucleation of the defects. Nevertheless, neither approach describes the nonlinear effects responsible for the re-orientation of the defects at short distances.

In what follows, we shall use the Landau description of smC films in order to calculate the interaction between two discs with planar anchoring. We will show that the short-distance colloidal interactions result from the re-arrangement of the defect positions, as in other 2D and 3D systems with quadrupolar symmetry [8, 22].

3.1. Free energy of smectic C films

In smC phases the LC molecules are organized into 2D layers with the local average molecular orientation $n$ at a characteristic angle $\phi$ with respect to the layer normal $\nu$. When layer deformations are negligible there are no variations of $\phi$ in the direction of $\nu$, $\nabla \cdot \phi = 0$. In this case, the relevant order-parameter is the in-plane projection of the director $n$. This is an ordinary (variable-length) 2D vector field $c$ (figure 15).

The simplest mesoscopic model for smC films is obtained by expanding the free energy in terms of the invariants of the order-parameter $c$ and its derivatives $\partial_i c_j$ [55]. The free energy is then written as $F = l \int_{\Omega} (f_b + f_e) \, d^2x$, where $l$ is the thickness of the film, and the bulk and elastic free energy densities are, at lowest order,

$$f_b = -\frac{a(T)}{2} |c|^2 + \frac{b}{4} |c|^4,$$

$$f_e = \frac{K}{2} \left( (\nabla \cdot c)^2 + (\nabla \times c)^2 \right).$$

New Journal of Physics 14 (2012) 073030 (http://www.njp.org/)
Figure 15. Schematic representation of an smC. $n$ is the normal to the layers, $\mathbf{n}$ is the average local molecular orientation and $\mathbf{c}$ is the in-plane projection of $\mathbf{n}$.

where, for simplicity, we use the one-elastic constant approximation ($\tilde{K}_1 = \tilde{K}_3 = \tilde{K}$). Note that $\tilde{a}(T)$ is a linear function of temperature $T$ and $\tilde{b}$ is a constant.

Dimensionless free energy densities (the free energy $F$ has the units of volume) are defined through the rescaling $\tilde{\mathbf{c}} = \sqrt{\tilde{b}/(2\tilde{a})}\mathbf{c}$ and $\tilde{F} = (\tilde{b}/\tilde{a}^2)F$,

$$\tilde{f}_b = |\tilde{\mathbf{c}}|^2 \left(|\tilde{\mathbf{c}}|^2 - 1\right),$$

$$\tilde{f}_e = \tilde{\xi}^2 \left((\nabla \cdot \tilde{\mathbf{c}})^2 + (\nabla \times \tilde{\mathbf{c}})^2\right),$$

where $\tilde{\xi} = \sqrt{b\tilde{K}/\tilde{a}(T)^2}$ is the correlation length. Equation (14) predicts nonzero values for the bulk scalar order-parameter $|\tilde{\mathbf{c}}_b| = 1/\sqrt{2}$ at all temperatures. Topological defects correspond to regions of reduced orientational order $|\tilde{\mathbf{c}}| \to 0$, and their topological charge is defined by the winding number of the vector field $\tilde{\mathbf{c}}$ [34].

Due to the vector nature of the $\mathbf{c}$ director, it is possible to distinguish clockwise, anticlockwise or mixed planar anchoring on discs in smC films [51]. The orientation that is realized results from the interplay of the anchoring potential, the $\mathbf{c}$ director field in the vicinity of the disc and the LC properties. We consider mixed planar anchoring that favours the nucleation of boojum pairs [23], the 2D counterpart of the 3D boojums investigated in section 2.2. We use a surface potential of the Rapini–Papoular form [56], which is the 2D version of the quadratic surface potential, equation (6),

$$F_s = l \int_{\partial\Omega} \frac{W}{2} \left(\frac{\mathbf{c} \cdot \nu}{|\mathbf{c}_b|}\right)^2 d\ell,$$

where $W$ is the anchoring strength, and $\nu$ is the normal to the surface $\partial\Omega$ of the disc. We note that in 2D quartic terms do not change the surface potential qualitatively and will not be considered.
Rescaling the variables yields
\[ \tilde{F}_s = l \int_{\Omega} \frac{w \hat{\xi}^2}{2R} \left( \frac{\hat{c} \cdot \nu}{|\hat{c}|} \right)^2 \, dl, \]  
\[ \tag{17} \]
where we introduced the dimensionless anchoring strength \( w = WR/\tilde{K} \). For notational simplicity, we will drop the tildes on the variables in the following discussion.

### 3.2. Single circular particle

In this section, we consider a single disc in an smC film. Mixed planar anchoring is enforced by fixing the far-field \( \mathbf{c} \)-director parallel to the \( y \)-axis. We start by reviewing the results of the FO elastic theory, where the \( \mathbf{c} \)-director is a unit vector \( \mathbf{c} = (\cos \Phi, \sin \Phi) \). The analytic solution for the orientational field, \( \Phi \), at arbitrary anchoring strength \( w \) is written as \[ \Phi(r, \varphi) = -\arctan \left[ \frac{(R/r)^2 p(w) \sin 2\varphi}{1 - (R/r)^2 p(w) \cos 2\varphi} \right], \]  
\[ \tag{18} \]
where \( r, \varphi \) are the polar coordinates, and \( p(w) = (2/w)(\sqrt{1 + (w/2)^2} - 1) \). The corresponding free energy is \( F_{\text{FO}} = \pi l \tilde{K} (-\log(1 - p^2) + (w/2)(1 - p)) \). The solution, equation (18), describes non-singular surface defects with a core size \( r_c = (8R/w^2)(\sqrt{1 + w^2}/4 - 1) \) \[24\], which for strong anchoring behaves as \( r_c \approx 4R/w \). For any finite \( w \) the elastic free energy is also regular, with the leading large \( w \) behaviour \( F(w \gg 1) \approx \pi \tilde{K} \ln(w) \). Singular topological defects appear only in the limit \( w \to \infty \). In the strong anchoring regime \( w \to \infty \) the exact solution, equation (18), may be approximated by the sum of a finite number of solutions \( \Phi_i \) of the Laplace equation, where \( \Phi_i \) represents a point singularity (or topological defect) of winding number \( q_i \) \[1\]. The number of these topological defects, their locations and winding numbers are chosen to comply with the boundary conditions. The behaviour of the \( \mathbf{c} \)-director near the boojums suggests that they are \(-\frac{1}{2}\) topological defects. Since the disc with rigid planar anchoring accounts for a +1 virtual defect in its centre, a naive guess suggests that \( \Phi \) is the sum of three point singularities, \((-\frac{1}{2}) + (+1) + (-\frac{1}{2})\) \[20\]. The two \((-\frac{1}{2})\) singularities are located on opposite poles of the disc oriented along the far-field \( \mathbf{c} \)-director. A more careful analysis reveals that this guess violates the boundary condition at the disc surface, and additional virtual defects must be taken into account. The asymptotic \( w \to \infty \) behaviour of the solution, equation (18), indicates that the correct approximation is given by the triplet \((-1) + (+2) + (-1)\), where the (+2) virtual defect is in the centre of the disc and the two \((-1)\) surface defects may be thought of as the sum of two \((-\frac{1}{2})\) defects, one of which is virtual and the other real \[58\].

In figure 16, we compare the excess free energy \( F^{(1)} \), the surface free energy \( F_s \) and the elastic free energy \( F^{(1)} - F_s \), obtained by numerical minimization of the Landau free energy (equations (14), (15) and (17)) with the analytical solutions, equation (18), of the FO theory. Details of the numerical method may be found in the appendix. In the weak anchoring regime the agreement is excellent but it breaks down in the strong anchoring regime. Inspection of figure 16 reveals that the discrepancies result from differences in the surface free energy. Indeed, the FO free energy breaks down in the strong anchoring regime and ultimately diverges as \( \sim \log(w) \). In the weak anchoring regime, \( w \ll 1 \), the excess free energy is dominated by the surface term which is linear in \( w \), while the elastic free energy is quadratic, \( w^2 \), as in 3D systems; see figure 4.
Figure 16. Elastic free energy $F^{(1)} - F_s$, excess (over the uniform system) free energy $F^{(1)}$, and surface free energy $F_s$ as a function of the anchoring strength $w = WR/\bar{K}$. Points are the results of the Landau free energy (equations (14), (15) and (17)). Dashed lines are the analytical solution, equation (18). The radius of the disc is $R = 100\bar{\xi}$.

Figure 17. Equilibrium c-director configurations for anchoring strengths, (a) $w = 0.1$, (b) $w = 1$, (c) $w = 10$ and (d) $w = 100$. The greyscale map corresponds to the light intensity $\propto \sin^2 2\Phi$ as seen in experiments under cross-polarizers. The radius of the disk is $R = 100\bar{\xi}$.

Figure 17 illustrates the equilibrium c-director configurations. The greyscale map corresponds to the optical transmittance, $I/I_0 \propto \sin^2 (2\Phi)$, as seen in experiments under cross-polarizers. As the anchoring strength increases the disc-induced distortions, seen as bright
fringes, increase. For \( w > 10 \) a pair of topological defects nucleates at opposite poles of the disc (see figures 17(c) and (d)). In order to quantify the spatial extension of the boojums, we follow [43] and introduce an effective core radius as follows:

\[
\chi = \left[ \frac{1}{\pi} \int_{\Omega} d^2 x \left( 1 - \frac{|\mathbf{c}|}{|\mathbf{c}_b|} \right) \right]^{1/2},
\]

where the integral is over the region with one boojum. \( \chi \) as a function of the anchoring strength \( w \) is plotted in figure 18. We distinguish three regimes. As the anchoring increases, the LC molecules align along the preferred surface orientation, creating small regions of low orientational order. At intermediate anchoring strength, \( 1 \lesssim w \lesssim 10 \), \( \chi \propto \log(w) \). Finally, in the nucleation regime, \( w \gtrsim 10 \), the effective radius increases slowly with \( w \), and saturates at \( \simeq 7/4\xi \).

In contrast to the 3D case, the 2D boojums are always point-like and never split. This is a direct consequence of the topological constraint that forbids half-integer defects in smC films. In 3D nematics, however, half-integer ring disclinations are not only topologically allowed, but also energetically favourable [41, 42, 59–61].

### 3.3. Two circular particles

We proceed to analyse the pairwise effective interaction between discs with planar anchoring in smC films. The discs ‘decorated’ by boojums interact as 2D quadrupoles [8]

\[
F_{\text{quad}}(d, \theta) \approx \frac{1 - 2 \sin^2(2\theta)}{d^4}.
\]

This interaction is repulsive for \(-\pi/8 < \theta - m\pi/2 < \pi/8\) and attractive for \(\pi/8 < \theta - m\pi/2 < 3\pi/8\), with \(m = 0, 1, 2, \ldots\). At longer distances the single-particle distribution of the \(\mathbf{c}\)-director is only slightly perturbed by the presence of the other particle. As the separation decreases the perturbation increases and nonlinear effects take over, changing the character of the interaction. The threshold distance \(d^*\) where the nonlinear regime sets in strongly depends on the anchoring strength.

Figure 18. Effective radius \( \chi \), equation (19), of the 2D boojum core as a function of the anchoring strength \( w = W R/\bar{K} \).
The Landau free energy, equations (14), (15) and (17), is minimized numerically. Details may be found in the appendix. In figures 19 and 20, we plot the interaction free energy $F^{(2)}(d) = F + F_s - F_0 - 2F^{(1)}$ as a function of the discs separation, $d$, for anchoring strengths $w = 0.1, 1.0, 10$ and 100. $F + F_s - F_0$ contains the contributions to the free energy from the distortions of the c-director, $F_0 = F(c_b)$ is the free energy of the uniform bulk system, and $F^{(1)}$ is the free energy of an isolated disc. At weak anchoring, $w = 0.1$, $F^{(2)}$ is always repulsive for perpendicular $\theta = \pi/2$ or parallel $\theta = 0$ orientations, and attractive for oblique orientations.

When the anchoring strength increases, regions of reduced order develop around the poles of the discs, leading to an increase of the elastic free energy, see figure 16. This also results in an increase of the interaction strength at short distances, as seen in figure 19 for $w = 1.0$ and figure 20 for $w = 10$. After the nucleation of topological defects the effective interaction changes drastically as shown in figure 20, $w = 100$, at separations $d \lesssim 4R$. In this regime, the repulsion becomes even stronger for orientations $\theta = 0, \pi/2$, but at $\theta = \pi/4$ the free energy develops a well-defined local minimum at $d \simeq 2.4R$, followed by a repulsion for $d < 2.4R$. The

Figure 19. Interaction potential $F^{(2)}(d)$ for several values of $\theta$, anchoring strengths $w = 0.1, 1.0$ and disc radius $R = 100\xi$.

Figure 20. The same as figure 19, but for anchoring strengths $w = 10$ and 100.
latter prevents the discs from coalescing in line with the experimental observations in 2D [21, 54] in contrast to 3D boojum colloids, where no such repulsion is observed.

For strong anchoring and $\theta = 0$, $F^{(2)}(d)$ changes from repulsive to attractive, with a discontinuous slope, at $d \simeq 2.45R$, see figure 20, $w = 10$. A similar behaviour is observed for $w = 100$ at $d \simeq 2.10R$, not shown in figure 20. Figure 21 illustrates the equilibrium e-director configurations for discs oriented along the far-field e-director, $\theta = 0$, at separations (a) $d = 3.0R$ and (b) $d = 2.05R$, $R = 100\bar{\xi}$. (c) Close-up of the configuration between discs for the parameters of (b). The greyscale map corresponds to the light intensity $\propto \sin^2 2\Phi$ as seen in experiments under cross-polarizers.

4. Conclusions

We carried out a detailed study of the effective colloidal interactions for particles dispersed in a nematic (3D) or in an smC film (2D). In both cases, planar (degenerate in 3D) anchoring is imposed on the surfaces of the colloids. Within the FO formalism in the strong anchoring regime, the boundary conditions are met by the creation of a pair of antipodal surface defects, boojums [16]. For an isolated particle the vector connecting two boojums aligns itself
with the far-field director, as required by the global boundary conditions [17]. The resulting director field has quadrupolar symmetry, and the ensuing effective colloidal interactions exhibit quadrupole–quadrupole asymptotic behaviour [13, 20, 21, 25], in both 2D and 3D. However, at short distances, where the superposition approximation fails and the nonlinear effects dominate, the experimental results report significant deviations from this quadrupolar behaviour. The most important of these is the crossover from a repulsive to an attractive interaction at some threshold distance for particles aligned along the far-field director, $\theta = 0$. The threshold distance is $\simeq 3R$ in 3D, see figure 10, and $\simeq 2.5R$ in 2D, see figure 20. This crossover is driven by the configurational reorientation of the inner boojums as the distance between the particles decreases.

We have shown that the short-range colloidal interactions in 3D result not only from the re-arrangement of the defect positions, as predicted in 2D a decade ago [8] and described recently in 3D [22], but also from changes in the structure of the boojum cores. The description of the structural transitions between boojum cores is a challenging theoretical problem as distinct structures, characterized by tensor order-parameters that vary in regions of the order of the bulk correlation length, have similar free energies. Their stability results from a delicate balance of various contributions and structural transitions may be driven by the anchoring strength, the temperature or the colloid radius. We have concentrated on the mesoscale and addressed the structure and dynamics of the boojums and the resulting colloidal interactions based on the LdG free energy in 3D and 2D, for spherically symmetric colloids. We have used finite elements methods with adaptive meshes in order to resolve the structure of the defect cores and establish the nature of the short-distance effective colloidal interactions. We found that the defects are point-like in 2D, but acquire a rather complex structure in 3D, which depends on the combination of the anchoring potential, the colloid radius, the temperature and the LC elastic anisotropy. In addition, we have found defect-core transitions between (i) single-core, (ii) double-core and (iii) split-core structures of the boojum pairs.

Single-core boojums are uniaxial along the $z$-axis (see figures 1(a) and 2(a)). The scalar order-parameter vanishes at one point above the colloidal surface, where the system is isotropic. Below this point the scalar order-parameter is negative and the nematic order is oblate. Above that point the scalar order-parameter is positive, indicating that the nematic order is prolate. By contrast, double-core boojums are biaxial along the $z$-axis (see figures 1(b) and 2(b)). The surface of maximal biaxiality intersects the $z$-axis at three distinct points separating regions of low nematic oblate and prolate order. Split-core boojums are also biaxial along the $z$-axis. The surface of maximal biaxiality intersects the $z$-axis at two distinct points that delimit the region of oblate nematic order (figures 1(c) and 2(c)). As a general conclusion we find that on small colloids boojum cores are axially symmetric (see figure 7), point-like with index +1 (the index referring to the charge of the projected director field on the surface), which are stable at high temperatures (see figure 6) and relatively weak anchoring (see figure 5). On large colloids at low temperatures and strong anchoring, the axial symmetry is broken and the boojum $+1$ point-like cores split into a pair of $+\frac{1}{2}$ point-like surface defects, connected by a disclination line (see figure 1(c)). A structure without a fully developed disclination line, the double-core boojum, was also found (see figures 1(b) and 3). The detailed structure of the cores as well as the transitions between the different configurations depend in detail on the colloid and LC parameters. We stress that the details of the core structure do not affect the far-field configuration, i.e. on a spherical surface surrounding the boojum cores, the order-parameter distribution resembles that of a point boojum. Their effect, however, on the short-distance interaction may be significant.
Indeed, we have shown that the short-distance attraction at $\theta = 0$, which results from the reorientation of the inner boojums, as the distance between the colloids decreases, corresponds to a structural change from single-core to split-core for the inner boojums pair.

We have shown how the nonlinear effects become dominant, both in 2D and 3D, leading to a qualitative change of the effective colloidal interaction, namely, the crossover from the long-distance quadrupole–quadrupole repulsion for a range of orientations around $\theta = 0$, to an attraction at moderate to small distances; see figures 10 and 20. This results from the complex dynamics of the topological defects that rearrange their position at short distances in both 2D and 3D. This attraction, along the far-field direction, agrees with experimental observations [13, 20, 21, 25] and with earlier calculations [22] where it is shown that the axial symmetry of the boojum pairs is broken when repulsion changes into attraction. The mechanism for attractive colloidal interactions—driven by the re-arrangement of defects with quadrupolar symmetry—was reported in 2D for homeotropic anchoring nearly a decade ago [8].

We emphasize an important difference between the 2D and 3D effective pair interaction potentials. In 3D the global minimum occurs at contact $d = 2R$ at an oblique angle with the far-field director. In 2D the optimal orientation of two inclusions is also oblique, but there is a free energy barrier $\simeq 0.51\bar{K}$ keeping the particles apart. This distinction is in line with experimental observations in 2D and 3D [13, 20, 21, 25].

Finally, we have calculated the force between boojum colloids in 3D; see figure 12. We found that as the distance decreases the angular dependence of the force changes rapidly and quite drastically. Just below $d = 3R$ the maximum at $\theta = \pi$ becomes a minimum and the difference between the secondary maxima at intermediate values of $\theta$ becomes more pronounced. This angular dependence was actually observed in [13] at larger colloidal separations, $3R \leq d \leq 4R$. The theoretical results appear to be too sensitive to the inter-colloidal distance when compared with the experimentally measured forces.

Acknowledgments

We acknowledge partial financial support from the FCT-DAAD Transnational Cooperation Scheme under grant no. 50108964, FCT grants PEstOE/FIS/UI0618/2011, PTDC/FIS/098254/2008 and PTDC/BPD/50327/2007 (NMS), and FP7 IRSES Marie-Curie grant PIRSES-GA-2010-269181.

Appendix. Numerics

In this section, we discuss briefly how the scheme for numerical minimization of the free energy functionals is implemented. In order to discretize the continuum models we resort to an FEM [62] with adaptive meshes. For 3D systems the nematic and the colloidal particles of radius $R$ are confined in a cubic box of linear size $30 \times R$. For smC films the system is confined in a $10R \times 10R$ square box.

A.1. Meshing

The surfaces of the spherical colloidal particles are discretized using the open source GNU Triangulated Surface Library [63]. The library uses a recursive subdivision algorithm in order to triangulate the surface of a unit sphere. Starting from the icosahedron as the first approximation,
the next levels of refinement are constructed by subdividing each triangle into four smaller triangles. We have used the sixth refinement level corresponding to a surface mesh with 20480 triangles.

In the next step, the domain $\Omega$ accessible to the nematic is triangulated. For 3D systems the triangulation is carried out using the *Quality Tetrahedral Mesh Generator*, TetGen [64], library. TetGen generates boundary conforming Delaunay [65] meshes of 3D domains with a piecewise linear boundary. The boundary can also be specified as a surface mesh, which is the case with the triangulated surfaces of the spherical particles. TetGen supports an isotropic size conforming triangulation, i.e. the resulting elements conform to a given local size map. For 2D systems the corresponding domains are triangulated using INRIA’s *BL2D* software [66]. The *BL2D* package supports the creation of anisotropic meshes, where the triangulation process is governed by specifying a metric map.

### A.2. Minimization

We use linear elements in both 2D and 3D, i.e. the values of the nematic field $\mathbf{Q}_i$ are specified only at the vertices $\mathbf{x}_i$ of the mesh and a linear interpolation is used in order to determine the values of $\mathbf{Q}(\mathbf{x})$ at some other point $\mathbf{x}$ of $\Omega$. Due to the discretization the volume and surface integrals in 3D are replaced by sums of integrals over tetrahedral and triangular elements, respectively, and in 2D by sums of integrals over triangular and line elements (the discretized perimeters of the colloids). Each integral is evaluated numerically using generalized Gaussian cubature rules for multiple integrals [67]. For integration over tetrahedra a fully symmetric cubature rule with 11 points, which is exact for polynomials of degree 4, is used [67, 68]. For integration over triangles a fully symmetric quadrature rule with seven points, which is exact for polynomials of degree 5 [69], is used. Finally, one-dimensional integrals are evaluated using the five-point Gauss–Legendre quadrature, which is exact for polynomials of degree 9.

During the minimization the values of the tensor order-parameter $\mathbf{Q}$ at the vertices of the bounding box are kept fixed, equal to the values of the uniaxial bulk nematic. The values of $\mathbf{Q}_i$ at all other vertices are obtained by numerical minimization. We used INRIA’s *MIQN3* [70] optimization routine. The routine implements a limited-memory quasi-Newton technique (limited memory Broyden–Fletcher–Goldfarb–Shannon method) of Nocedal [71].

### A.3. Adaptive mesh refinement

The systems are characterized by two widely different length scales. One is given by the nematic correlation length and the other by the radius of the colloids. Therefore, we resort to adaptive re-meshing techniques in order to obtain a sufficiently good approximation for the ‘exact’ solution in a reasonable amount of time and with the finite computing resources in hand. The main objective of the adaptive refinement is to construct a mesh which meets the given interpolation error tolerance for a minimal number of elements. Such meshes are called optimally efficient [72]. Let $f$ be one of the components of the exact solution $Q_{ij}$ to our problem, and $f^1$ its linear interpolation on some mesh. It can be shown that the interpolation error associated with some element $E_k$ (either a tetrahedron or a triangle) satisfies the following inequality [73]:

$$
\max_{x \in E_k} |f(x) - f^1(x)| \leq \max_{x \in E_k} |x_a \mathcal{H}_{ab}(\mathbf{x}_0)x_b|,
$$

(A.1)
where $x_0$ is some vertex of the element $E_k$, $x$ is the position within element $E_k$ measured relative to $x_0$, and $\mathcal{H}_{\alpha\beta}(x_0) \equiv \frac{\partial^2 f}{\partial x_\alpha \partial x_\beta}|_{x_0}$ is the Hessian of the exact solution $f$ evaluated at the vertex $x_0$. If we define the absolute value of the 2D Hessian $|\mathcal{H}|$ as

$$|\mathcal{H}| = \mathcal{O} \begin{pmatrix} |\lambda_1| & 0 \\ 0 & |\lambda_2| \end{pmatrix} \mathcal{O},$$

where $\mathcal{O}$ is an orthogonal matrix that diagonalizes $\mathcal{H}$, then the estimate for the interpolation error on the element $E_k$ can be written in a simpler form

$$\max_{x \in E_k} |f(x) - f^1(x)| \leq h_k^2 \max(\lambda_1, \lambda_2).$$

$h_k$ is the diameter (the length of the longest edge) of the element $E_k$. It is straightforward to write down similar expressions for the 3D case. Therefore, if the sizes of the elements are chosen such that $h_k^2 \max(\lambda_1, \lambda_2) \simeq \text{const}$ for all the elements, then the resulting interpolation error will be approximately equally distributed among all the elements.

As was mentioned above, the BL2D package supports anisotropic meshes. The triangulation is governed by specifying a metric map $\mathcal{M}$, and the resulting mesh is characterized by edges of unit length according to the metric $\mathcal{M}$ [73]. We assume that the required metric is proportional to the Hessian, $\mathcal{M} \propto |\mathcal{H}|$. In order to estimate $\mathcal{H}$ at some vertex $x_0$ we use the weak definition of the Hessian [73]

$$\mathcal{H}_{\alpha\beta}(x_0) = -\frac{\int \frac{\partial f}{\partial x_\alpha} \frac{\partial \phi^0}{\partial x_\beta} \, d^dr}{\int \phi^0 \, d^dr},$$

where the integral is over the elements which share the vertex $x_0$, and $\phi^0$ is the piecewise linear hat-function associated with vertex $x_0$: $\phi^0 = 1$ at $x_0$ and $\phi^0 = 0$ at any other vertex. We use linear interpolation in order to obtain $\mathcal{H}$ at any other point $x$ of the element.

TetGen implements an isotropic mesh refinement strategy which is based on a maximum local element volume constraint. The constraints on the volume of elements are obtained by applying the equidistributing principle, where the nodes of the mesh are chosen such that for each element $E_k$ the following condition holds:

$$\int_{E_k} \sqrt{\det \mathcal{H}} \, d^dr = \text{const}. \quad (A.2)$$

In [72], it is shown that an optimally efficient 2D triangulation which minimizes the interpolation error fulfills asymptotically the equidistributing principle (A.2). We assume that the same is valid in the 3D triangulation.

References

[1] Stark H 2001 Phys. Rep. 351 387
[2] Bohley C and Stannarius R 2008 Soft Matter 4 683
[3] Tasinkevych M and Andrienko D 2010 Condens. Matter Phys. 13 33603
[4] Muševeci I, Škarabot M, Tkalec U, Ravnik M and Žumer S 2006 Science 313 954
[5] Ravnik M, Alexander G P, Yeomans J M and Žumer S 2011 Proc. Natl Acad. Sci. USA 108 5188
[6] Lubensky T C, Petley D, Currier N and Stark H 1998 Phys. Rev. E 57 610
[7] Ravnik M and Žumer S 2009 Liq. Cryst. 36 1201
[8] Tasinkevych M, Silvestre N M, Patricio P and da Gama M M T 2002 Eur. Phys. J. E 9 341

New Journal of Physics 14 (2012) 073030 (http://www.njp.org/)
[52] Tasinkevych M and Andrienko D 2006 Eur. Phys. J. E 21 277
[53] Ruhwandl R W and Terentjev E M 1997 Phys. Rev. E 55 2958
[54] Cluzeau P, Joly G, Nguyen H T and Dolganov V K 2002 JETP Lett. 75 482
[55] Silvestre N M, Patricio P and da Gama M M T 2006 Phys. Rev. E 74 021706
[56] Papoular M and Rapini A 1969 Solid State Commun. 7 1639
[57] Burylov S V and Raikher Y L 1990 Phys. Lett. A 149 279
[58] Fukuda J-I 2007 Eur. Phys. J. E 24 91
[59] Mori H and Nakanishi H 1988 J. Phys. Soc. Japan 57 1281
[60] Sonnet A, Kilian A and Hess S 1995 Phys. Rev. E 52 718
[61] Rosso R and Virga E G 1996 J. Phys. A: Math. Gen. 29 4247
[62] Wait R and Mitchell A R 1985 Finite Element Analysis and Applications (New York: Interscience (Wiley-Interscience))
[63] The Gnu Triangulated Surface Library 2006 http://gts.sourceforge.net
[64] Si H 2011 Tetgen: A Quality Tetrahedral Mesh Generator and a 3d Delaunay Triangulator http://wias-berlin.de/software/tetgen/
[65] Delaunay B N 1934 Bull. Acad. Sci. USSR VII 6 793
[66] Laug P 2003 Bl2d-v2: Isotropic or Anisotropic 2d Mesher http://www-roc.inria.fr/who/Patrick.Laug/logiciels/bl2d-v1/eng.htm
[67] Cools R 2003 J. Complexity 19 445
[68] Keast P 1986 Comput. Methods Appl. Mech. Eng. 55 339
[69] Stroud A H 1971 Approximate Calculation of Multiple Integrals (Englewood Cliffs, NJ: Prentice-Hall)
[70] Gilbert J C and Lemaréchal C 1989 Math. Program. 45 407 (https://who.rocq.inria.fr/Jean-Charles.Gilbert/modulopt/optimization-routines/m1qn3/m1qn3.html)
[71] Nocedal J 1980 Math. Comput. 35 773
[72] D’Azevedo E F 1991 SIAM J. Sci. Stat. Comput. 12 755
[73] George P-L and Borouchaki H 1998 Delaunay Triangulation and Meshing: Application to Finite Elements (Paris: Editions HERMES)