Equilibrium state of cylindrical colloids with flat ends in nematic liquid crystals

S. Masoomeh Hashemi\textsuperscript{1,*} and Mohammad Reza Ejtehdi\textsuperscript{1,†}

\textsuperscript{1}Department of Physics, Sharif University of Technology, P.O. Box 11155-9161, Tehran, Iran

(Dated: October 7, 2014)

Abstract

A continuum theory is employed to numerically study equilibrium orientations and defect structures of circular cylindrical colloids with flat ends that are embedded in a uniform nematic medium. Considering homeotropic anchoring condition on the colloidal surfaces, we investigate several mesoscopic and nanoscopic colloidal particles of this geometry with different aspect ratios ranging from thin discotic to long rod-like colloids. We show that the equilibrium state of this colloidal geometry is sensitive to the two geometrical parameters: aspect ratio and length scale of the colloid. For large enough mesoscopic colloids there is a specific asymptotic equilibrium angle associated to each aspect ratio. Upon reducing the colloid sizes to nanoscales, the equilibrium angles follow a descending or ascending trend in such a way that the equilibrium angles for the colloids with the aspect ratios bigger than 1:1 (discotic colloids) go to a parallel alignment, whereas the equilibrium angles for the colloids with the aspect ratios 1:1 and smaller (rod-like colloids) tend toward a perpendicular alignment. The discrepancy between the equilibrium angles of mesoscopic and nanoscopic colloids originates from the significant differences between their defect structures. The possible defect structures related to mesoscopic and nanoscopic colloids of this geometry are also introduced.

PACS numbers: 61.30.Cz, 82.70.Dd, 61.30.Jf, 61.30.Gd

\textsuperscript{*}Electronic address: mhashemi@physics.sharif.edu
\textsuperscript{†}Electronic address: ejtehadi@sharif.edu

arXiv:1410.1145v1 [cond-mat.soft] 5 Oct 2014
I. INTRODUCTION

Since the recognition of a novel class of long range inter-colloidal interactions mediated by the elasticity of the nematic liquid crystal host [1], extensive research has been devoted to colloids in uniform nematic media. When colloids with definite boundary conditions are dispersed in liquid crystal media, localized regions of reduced molecular order (topological defect cores) are formed in some specific places near colloidal surfaces. These topological defect cores are accompanied by long-range slow-varying elastic interactions and are highly anisotropic even for the very symmetric geometries of spherical colloids. For an individual spherical colloid with homeotropic anchoring condition immersed in a uniform nematic, two types of topological defects are in general known: a dipolar defect (a hyperbolic hedgehog point defect), and a quadrupolar defect (a disclination ring with winding number -1/2 called the Saturn ring).

Introducing anisotropy to the shape of colloids dictates more complexity to defect structures and interactions of a liquid crystal colloidal system. Defect structures specifically depend on the geometry of the colloids. Therefore, by carefully choosing the geometry of the colloids one can be able to design defect structures with predetermined architecture in a liquid crystal colloidal system possibly resulting in exclusive optical properties for technological applications. Micro- and nano-scale colloidal particles with variety of geometrical shapes are fabricated and studied in nematic liquid crystals [2–9], but some crucial questions remained less answered. The most important questions are about the equilibrium orientation of an anisotropic colloid and the defect structures formed in the system. Spherocylindrical and elongated elliptical colloids are well studied in uniform nematic [3, 10–13]. In case of homeotropic anchoring conditions, both of these elongated colloids orient with their symmetry axes perpendicular to the far field nematic. The perpendicular orientation has been confirmed using experiments [12], a combination of Monte Carlo and molecular dynamics simulations [3] and a continuum theory [10, 11, 13]. In case of very thin discotic colloids with homeotropic anchoring a parallel alignment has been reported [2, 14, 15]. However, for more complex colloidal shapes the stable orientation is not always a perpendicular or parallel alignment. While an elongated triangular nano-prism aligns perpendicular to the far field nematic, a cube with homeotropic boundary condition has several energetically-equivalent stable orientations [16].
A number of parameters are thought to have controlling roles in the equilibrium state of cylindrical colloids with homeotropic anchoring condition in a uniform nematic. The free energy expressions for perpendicular and parallel alignments of an infinitely long cylindrical colloid corresponding to rigid [17], weak [18] and arbitrary [19, 20] anchoring strengths have been analytically carried out using a continuum theory. It has been shown that a dimensionless parameter, which is constructed from the colloid radius, liquid crystal elastic and anchoring constants, determines that the equilibrium state is either a parallel or a perpendicular orientation [19]. For finite-sized cylindrical colloids the shape of the two ends has a pronounced effect in their equilibrium state [4]. Although there are a number of studies discussing the equilibrium orientation and defect structures of cylindrical colloids with flat ends [4, 15, 16, 21, 22], there is not a clear precise answer to the question considering various aspect ratios (ratio of diameter to height), length scales and anchoring strengths. Micron-sized rod-like solid particles with the typical aspect ratio 1:5 restricted to strong homeotropic anchoring condition have been experimentally studied [4]. The stability of the reported dipolar and quadrupolar defect structures depend on the orientation of the colloid’s symmetry axis with respect to the far field uniform nematic. The dipolar defect structures are stable in a small angular interval around the parallel orientation, while the quadrupolar defect structures are stable within a wider angular interval around the perpendicular alignment.

Analytical description of liquid crystal colloidal systems has been being in fast development along with experimental, numerical and simulative studies. Analytical study on arbitrary shapes of colloids in liquid crystals has been developed mostly in analogy with the common methods and expressions of electrostatics. Different types of elastic multipoles specifically dipoles and quadrupoles are characterized based on the symmetries in the director field around the colloidal surface that have close connection with the colloidal shape and anchoring type [23, 24]. Using multipole expansion methods that are valid in regions without nonlinearities of the director field, pair and collective colloidal interactions are also discussed [23–27]. But analytical investigation of liquid colloidal systems considering the nonlinearity of the director field in close vicinity of the colloidal surface is not achieved yet. Numerical minimization methods can be used in order to study director fields in close vicinity of colloidal surfaces.

In this paper, using a finite element method for numerical minimization of the Lundau-
de Gennes free energy, we present a detailed study on circular cylindrical colloids with flat ends that are immersed in uniform nematic media. Homeotropic boundary conditions are imposed on the colloidal surfaces. We investigate the dependency of the equilibrium angles on the aspect ratio and length scale of the colloids in the range of intermediate and strong anchoring strengths. Therefore, we study several mesoscopic and nanoscopic colloidal particles with the same geometries but different aspect ratios ranging from thin discotic to long rod-like colloids. Some of the results are also compared with some previous experimental studies [4, 21]. The defect structures related to different length scales are also introduced.

II. MODEL

A. Geometry

We consider a cylindrical particle with circular cross section and flat ends embedded in a uniform field of nematic liquid crystal. The uniform nematic medium is modeled using a cubic box with fixed anchoring conditions in the $z$ direction at all the six walls of the cub. A schematic illustration of the studied system is shown in Fig. 1. To prohibit finite simulation box effects, the edge lengths of the cubic box ($L$) are taken to be nine times bigger than the longest length scale of the cylindrical colloid and the center of the colloid is considered at the center of the simulation box. By this procedure we have azimuthal symmetry in the system. Considering the geometrical symmetries of the system, the angular dependency of the free energy is only on the angle between the symmetry axis of the cylinder and the

FIG. 1: Schematic illustration of the studied system.
nematic direction ($\theta$). Therefore it is enough to consider the symmetry axis of the cylinder located in the $y - z$ plane and let it free to rotate around the $x$ axis. It is also sufficient to limit the investigation to the angular interval 0 to 90 degrees.

B. Free Energy Expression

The spatially varying orientations of nematic liquid crystal molecules in a colloidal system can be described using the symmetric traceless tensor order parameter $Q_{ij}$

$$Q_{ij} = S(n_i n_j - \frac{\delta_{ij}}{3})$$

where the director $\vec{n}$ represents the local average orientations of liquid crystal molecules and the scalar order parameter $S$ gives a scalar measure of the local degree of molecular orientational order along the director. To avoid dealing with singularities of the defect cores, instead of working with the director $\vec{n}$ in numerical minimization, we use the general form of the tensor order parameter with six components $Q_{xx}, Q_{yy}, Q_{zz}, Q_{xy}, Q_{xz}$ and $Q_{yz}$, in which $x, y$ and $z$ represent the Cartesian coordinates. The largest eigenvalue of the tensor order parameter gives the scalar order parameter and the principal eigenvector corresponding to this eigenvalue gives the director of the nematic field.

To obtain the equilibrium nematic field, we minimize the free energy of the system which is written, based on the Lundau-de Gennes model \cite{28}, in powers of the tensor order parameter and its derivatives. A summation over the Lundau-de Gennes free energy for the isotropic-nematic phase transition, $f_{IN}$, the elastic free energy for uniaxial nematic \cite{29}, $f_{el}$, and the surface energy for imposing a specific anchoring direction to the directors at the colloidal surfaces \cite{30}, $f_s$, yields a general expression for the free energy

$$F = \int_{\text{bulk}} dV \left( f_{IN} + f_{el} \right) + \int_{\text{col. sur.}} dA \ f_s,$$

The Landau-de Gennes free energy for isotropic-nematic phase transition is written in powers of the tensor order parameter as

$$f_{IN} = \frac{A(T)}{2} Q_{ij} Q_{ji} - \frac{B}{3} Q_{ij} Q_{jk} Q_{ki} + \frac{C}{4} (Q_{ij} Q_{ji})^2,$$

where $A$, $B$ and $C$ are material-dependent parameters and only $A(T)$ is taken to be temperature dependent.
The elastic energy for uniaxial nematic is constructed from the tensor order parameter derivatives in the form

\[ f_{\text{el}} = \frac{L_1}{2} \partial_k Q_{ij} \partial_k Q_{ij} + \frac{L_2}{2} \partial_k Q_{ik} \partial_j Q_{ij} + \frac{L_3}{2} Q_{ij} \partial_i Q_{kl} \partial_j Q_{kl} + \frac{L_4}{2} \partial_j Q_{ik} \partial_k Q_{ij}, \]

in which the elastic constants \(L_1, L_2, L_3\) and \(L_4\) are related to the Frank-Oseen elastic constants \(K_1, K_2, K_3\) and \(K_{24}\) (respectively denoting splay, twist, bend and saddle-splay elastic constants) by

\[ \begin{align*}
L_1 &= \frac{3K_2 + K_3 - K_1}{6S^2}, \\
L_2 &= \frac{K_1 - 2K_{24}}{S^2}, \\
L_3 &= \frac{K_3 - K_1}{2S^3}, \\
L_4 &= \frac{-K_2 + 2K_{24}}{S^2}.
\end{align*} \]

We adopt one elastic constant approximation by taking \(K_1 = K_2 = K_3 = 2K_{24}\) that sets \(L_2, L_3\) and \(L_4\) equal to zero.

The surface energy for preferential anchoring of the directors on the colloidal surfaces is

\[ f_s = \frac{W}{2} \left( Q_{ij} - Q_s^i \right) \left( Q_{ji} - Q_s^j \right) \]

where \(W\) is the anchoring constant and \(Q^s\) is referred to the preferred orientational anchoring of molecules at the colloidal surfaces. We assume homeotropic anchoring with \(Q^s = S(v_i v_j - \delta_{ij}/3)\) in which \(S\) is the bulk scalar order parameter and \(\vec{v}\) stands for the normal vector to the colloidal surfaces.

A combination of rescaling the parameters and changing the variables is a useful technique to modify the equations to the ones with more appropriate units and less material dependent parameters which are favorable to numerical calculations. We rescale the scalar order parameter as \(S = S_{eq} S_q\) and subsequently the tensor order parameter as \(Q = S_{eq} q\), where \(S_{eq} = (\frac{2}{3})^{3/2}B/C\) is the dimensionless rescaling parameter and \(q = S_q (n_i n_j - \delta_{ij}/3)\) is the rescaled tensor order parameter. The dimensionless free energy of the system becomes

\[ \frac{F}{f_0 R^3} = \int dV \left( \frac{\tau}{2} q_{ij} q_{ji} - \frac{\sqrt{6}}{4} q_{ij} q_{ik} q_{ki} + \frac{1}{4} (q_{ij} q_{ji})^2 + \frac{1}{2} \left( \frac{\xi}{R} \right)^2 \partial_k q_{ij} \partial_k q_{ij} \right) + \int \frac{dA}{R^2} \left( \frac{\eta}{R} \right) (q_{ij} - q_{ij}^s) (q_{ji} - q_{ji}^s), \]

(7)
where \( f_0 = CS_{eq}^4 \) and \( \hat{\partial} = R\partial \). The dimensionless free energy involves only three material dependent parameters: the dimensionless temperature \( \tau = A/CS_{eq}^2 \), the dimensionless elastic constant \( \xi/R = \sqrt{L_1/CR^2S_{eq}^2} \) and the dimensionless anchoring constant \( \eta/R = W/CRS_{eq}^2 \). The first order isotropic-nematic phase transition takes place at \( \tau = 1/8 \) and the isotropic phase is unstable for \( \tau < 0 \). We take the equilibrium scalar order parameter of the uniform bulk nematic equal to \( S_{eq} \), so we have \( \tau = (3\sqrt{6}/8)/12 \). In this study we adopt the same parameters and rescaling method as Ref. [31], so we have \( S_{eq} = 0.653 \) and we always take the elastic constant to be \( L_1 = 25 \times 10^{-12} \text{J/m} \). There are two accepted conventions for estimating the correlation length. One definition is taken from the rescaled elastic constant in the above mentioned procedure, \( \xi \), which is the same definition as introduced in Ref. [28]. The other definition comes from the correlation function definition [32]. Both definitions give similar estimates for the correlation length [33]. To estimate the limits of weak, intermediate and strong anchoring strengths, the dimensionless parameter

\[
w = WR/K_1
\]

provides a criterion for comparing the relative contributions of the surface energy to the elastic energy [28]. \( R \) is the colloid’s characteristic length which is taken, in this study, equal to the colloid radius. Note that \( w \ll 1 \) implies weak anchoring limit whereas \( w \gg 1 \) describes strong anchoring condition.

C. Numerical Minimization of the Free Energy

To numerically minimize the total free energy of the model system, we implement a finite element method in which the nematic bulk of the system is discretized into tetrahedral elements. To do this, we have used the 3D finite element mesh generator Gmsh [34]. To reduce the minimization time simultaneously with having sufficient accuracy near colloidal surfaces, much finer mesh resolution is applied on the colloidal surfaces than on the cubic box of the model. Starting from given initial conditions, the numerical minimization is carried out using a conjugate gradient (CG) method [35]. The angular dependency of the free energy is scanned in the angular interval \( 0 \leq \theta \leq 90 \) in steps of 5 degrees. The minimization process continues until the free energy differences of the subsequent director configurations drop below about 0.0001%. We have studied cylindrical colloids with rounded edges to
achieve more efficient numerical minimization as the same approach adopted in Ref. [16]. The radius of the rounded edges is assumed to be much smaller than the height (H) and radius (R) of the colloids and the liquid crystal correlation length.

III. RESULTS AND DISCUSSION

We use the term aspect ratio to refer to the ratio of diameter to height of the cylindrical colloids ($2R/H$). We will investigate the equilibrium orientations concomitantly with the defect structures for colloidal particles with dimensions from tens to a few hundreds of nanometers. Several colloidal particles with the mentioned geometries but different aspect ratios are considered. Hence our investigation includes various colloidal shapes from thin discotic to long rod-like cylindrical colloids.

The general topography of the director field for this colloidal geometry is consisted of a disclination loop with winding number $-1/2$ that is tightly folded/wrapped around the colloidal surface. The disclination loop may experience some abrupt bending or piecewise widening that is strongly dependent on some colloid-dependent parameters such as spatial orientation and length scale and some material-dependent parameters like anchoring and elastic constants.

The several types of defect structures we have observed for a mesoscopic colloid with strong homeotropic anchoring strength ($w = 75.05$), are depicted in Fig. 2. The relative stability of these defect structures is highly dependent on the spatial orientation of the colloids and can be generally indicated for all the range of aspect ratios we have studied here. For parallel alignment of the symmetry axis with respect to the far field nematic we have observed the three defect structures Fig. 2(a-c) among which the top-ring is the most stable structure (Fig. 2(a)). A hyperbolic point defect structure has been neither experimentally nor numerically reported for this colloidal geometry. The dipolar structure reported is a flat thin ring located at the top or bottom edge of the cylindrical colloid [4, 21] (Fig. 2(a)) which is called the top-ring structure in here. The three structures for parallel alignment are depicted in descending order of stability from the most to the least stable structures in Fig. 2(a-c). Thus the chair-like structure in Fig. 2(b) is the next stable structure with about 3.8% of free energy higher than the top-ring and the mid-ring-0 in Fig. 2(c) has the highest energy cost with about 16% of free energy higher than the top-ring. For perpendicular
FIG. 2: Defect structures of the mesoscopic cylindrical colloid with $R = 160\text{nm}$ and aspect ratio 1:1 for $W = 10^{-2}\text{J/m}^2$. Black dashed lines are 2D view of the director field in the $y-z$ plane. Topological defect cores are visualized by the isosurface $S_q = 0.5$ of the rescaled bulk scalar order parameter. (a-c) Defect structures for $\theta = 0$ in descending order of stability: (a) top-ring, (b) chair-like, (c) mid-ring-0. (d-f) Defect structures for $\theta = 90$ in descending order of stability: (a) chair-like, (b) boat-like, (c) mid-ring-90. The insets of (a) and(c) illustrate the director field across the defect cores of the corresponding defect lines.

alignment we have observed the three structures Fig. 2(d-f) that are depicted in descending order of stability. The free energy of the boat-like structure in Fig. 2(e) is about 1.1% and the mid-ring-90 in Fig. 2(f) is about 7.6% higher than the chair-like structure of Fig. 2(d). We have seen that the same order of stability as Fig. 2(a-c) and Fig. 2(d-f) is true for the defect structures of all the mesoscopic colloids studied here. The free energy difference between these structures depends on the aspect ratio and length scale of the colloids and also the anchoring strength. For oblique orientation of mesoscopic colloids from 0 to about 10 degrees the top-ring structure and from about 10 to 90 degrees the chair-like structure
are the most stable structures (will be shown later). In such liquid crystal colloidal system besides very high elastic energy cost of the disclination core, the sharp edges of the colloids also induce strong elastic deformations into the director field. Therefore it can be seen from the possible defect structures corresponding to each spatial orientation that superimposition of topological defect cores on the sharp edges of the colloid reduces the elastic energy cost resulting in more stable structures.

If we restrict the colloids of different aspect ratios to have equal surface values, the free energy of all the systems including a thin discotic or long rod-like colloid become comparable to each other and all the energy graphs can be simultaneously shown in one single plot. This procedure helps us present some general results that we have obtained for the mesoscopic colloids with the aspect ratios 8:1 to 1:6. The free energy graphs of these colloids with respect to $\theta$ for strong homeotropic anchoring with the anchoring constant $W = 10^{-2} J/m^2$ are illustrated in Fig. 3(a).

It can be seen from the energy graphs of Fig. 3(a), whatever aspect ratios the colloids have, the top-ring dipolar defect is the most stable structure within the angular interval from 0 to about 10 degrees. After a crossover around 10 degrees from the top-ring to the chair-like structure, the most stable structure from about 10 to 90 degrees is the chair-like quadrupolar structure. The same angular interval of stability for top-ring structure has been experimentally observed for microrods of typical aspect ratios 1:5 with strong homeotropic anchoring [4]. This is true for all the aspect ratios from 8:1 to 1:6 studied here. This interval of stability for top-ring defects is exclusive to the geometry we have considered whereas for elongated elliptical colloids the top-ring dipolar defect is stable within the wider angular interval from 0 up to about 40 degrees [13]. We have also observed the mid-ring-0 in a small angular interval around 0 degrees and the boat-like and mid-ring-90 in a small angular interval around 90 degrees.

Another general point that can be deduced from the energy graphs of Fig. 3 is existence of only one global minimum corresponding to each aspect ratio in the interval 0 to 90 degrees. It can be seen, Fig. 3, the equilibrium angle that is about 90 degrees for long rod-like colloids gradually decreases upon increasing the aspect ratio and ultimately reaches about 0 degrees for thin discotic colloids. The equilibrium angle for the aspect ratio 1:1 is $55 \pm 5$ degrees which increases to $85 \pm 5$ degrees for a long cylinder with the aspect ratio 1:6. The experimental study of Ref. [4] on rod-like colloids with average aspect ratio 1:5 shows
FIG. 3: (a) Total free energy of the cylindrical colloids with the aspect ratios from 8:1 to 1:6 as a function of $\theta$ for the homeotropic anchoring constant $W = 10^{-2} J/m^2$. Solid squares are related to the chair-like structures and open circles represent the top-ring structures. All the colloids have equal surface values with a colloid with the aspect ratio 1:2 and $R = 160$nm. (b) Equilibrium angles as a function of aspect ratio. The equilibrium defect structures for the aspect ratio 1:4 and 6:1 (as typical examples respectively for rod-like and discotic colloids) are shown in the insets of (b) in which black dashed lines are 2D view of the director field in the $y-z$ plane and topological defect cores are visualized by the isosurface $S_q = 0.5$. The numerical resolution is 5 degrees for the chair-like structures and 2 degrees for the top-ring structures.

the same interval of stability for a quadrupolar structure. We see that the quadrupolar chair-like structure is the stable structure for the aspect ratios 1:1 and smaller of Fig. 3(a). This is characteristic of this colloidal geometry with flat ends that there are different global
minimums corresponding to different aspect ratios. In contrast, for example, in case of prolate elliptical colloids with homeotropic anchoring condition, the equilibrium alignment in a uniform nematic is a perpendicular alignment that is irrespective to the aspect ratio of the colloids, the length scale of the colloids and the anchoring strength \[13\].

The colloidal geometry studied here exhibits an exclusive equilibrium behavior according to which the equilibrium angle not only depends on the aspect ratio but also is highly dependent on the length scale of the colloid. To clarify this point, we assume the material dependent parameters to be constant, i.e. \( L_1 = 25 \times 10^{-12} \text{J/m} \) and \( W = 5 \times 10^{-3} \text{J/m}^2 \), while the colloid radius to vary from mesoscale to nanoscale. We firstly carry out calculations for the aspect ratios 2:1 and 1:2 (as typical examples respectively for the discotic and rod-like colloids of this geometry). The energy graphs of Fig. 4 illustrate the energies around global minimums corresponding to each colloid radius. To make comparison easier, we show the energy graphs just around their global minimums and normalize them. The normalization of the energies is carried out using the maximum \( (F_{\text{max}}) \) and minimum \( (F_{\text{min}}) \) values of each energy graphs.

The Fig. 4(a) for aspect ratio 2:1 shows that for all mesoscopic colloids with \( R = 400, 320 \) and 240nm the equilibrium angle is \( 40 \pm 5 \) degrees. By reducing the colloid radius, the equilibrium angle gradually decreases and ultimately reaches \( 0 \pm 5 \) degree for \( R = 20 \text{nm} \). Fig. 4(b) shows strikingly different behavior for the aspect ratio 1:2 upon reducing the colloid size. In this case for all mesoscopic colloids with \( R = 200, 160 \) and 120nm the equilibrium angle is \( 65 \pm 5 \) degrees. In contrast to the previous case, for this aspect ratio by reducing the colloid radius the equilibrium angle increases, so that for \( R = 10 \text{nm} \) the equilibrium angle reaches \( 90 \pm 5 \) degrees. Therefore the equilibrium angles associated to different aspect ratios respond differently to changes in the colloid size.

The graphs of Fig. 5 illustrate the equilibrium angle of the aspect ratios 1:4, 1:2, 1:1, 2:1 and 4:1 as a function of the colloid radius. The Fig. 5 shows that for all the aspect ratios for the mesoscopic colloids, when the colloid radii exceed some specific values, the equilibrium angles reach some asymptotic values. Note that there is a specific asymptotic equilibrium angle corresponding to each aspect ratio. As the results of Fig. 5 show, the equilibrium behavior of this colloidal geometry is remarkably different when the size of the colloids reaches nanoscales. Based on the aspect ratios of the colloids, there are two types of limiting behaviors. By reducing the colloid radius to nanoscales, the equilibrium orientation
FIG. 4: Normalized free energy as a function of $\theta$ when the colloid radii change from mesoscale to nanoscale considering $W = 5 \times 10^{-3}$ J/m$^2$ for (a) the aspect ratio 2:1 and (b) the aspect ratio 1:2.

for the colloids with the aspect ratios bigger than 1:1 (discotic colloids) goes to a parallel alignment whereas the equilibrium orientation for the colloids with the aspect ratios 1:1 and smaller (rod-like colloids) tends toward a perpendicular alignment (Fig. 5).

Given colloid size changes from mesoscale to nanoscale have also pronounced effects on the defect structures. The equilibrium defect structures of the aspect ratio 1:1 for $R = 240$ nm and $R = 40$ nm are depicted in Fig. 6(a-d). The disclination cores of both cases are well-localized in a small distance away from the colloidal surface. Fig. 6(c) and (d) are another view of the disclination lines that better show the disclination core distance from different parts of the colloidal surface. We call those parts of the chair-like structure that lie on the sharp edges the E-parts and those parts that are elongated parallel to the symmetry axis the
FIG. 5: Equilibrium angles as a function of the colloid radius for the anchoring constant $W = 5 \times 10^{-3} \text{J/m}^2$. Small nanocolloids with $R = 10 \text{nm}$ ($w = 2.345$) to mesoscopic colloids with $R = 320 \text{nm}$ ($w = 75.04$) are considered. The numerical resolution for equilibrium angles is 5 degrees.

P-parts. Fig. 6(a) shows that the chair-like structure for $R = 240 \text{nm}$ is a thin line compared to the colloid size. But the chair-like structure for $R = 40 \text{nm}$ is consisted of a much thicker line relative to the colloid size for which the core size of its P-part is much wider than the E-part, Fig. 6(b). Therefore by reducing the colloid size not only the defect core size relative to the colloid size increases but also the thickness difference between the P-part and E-part of the defect line becomes more pronounced. This is true for the chair-like structure of any other aspect ratios.

As we mentioned before we have observed three possible defect structures related to each of the parallel and perpendicular alignments of mesoscopic colloids (Fig. 2(a-f)), while by going to the limiting state for nanoscopic colloids (mentioned in analyzing the results of Fig. 5) we have observed only one defect structure associated to each of these angles. For parallel alignment the defect structure is a Saturn ring that covers all the lateral surface of the cylinder, e.g. Fig. 7(a) and (d). For perpendicular alignment the defect structure is a ring located perpendicular to the far field nematic that is elongated parallel to the colloid symmetry axis and covers the flat ends of the colloid, e.g. Fig. 7(c) and (f). Thereby, we have only observed three defect structures for the limiting state of nanocolloids of this geometry, e.g. Fig. 7(a-c) or (d-f).
FIG. 6: Equilibrium defect structures around colloids with the aspect ratio 1:1 for (a,c) $R = 240\text{nm}$ and (b,d) $R = 40\text{nm}$ and $W = 5 \times 10^{-3}\text{J/m}^2$. Black dashed lines in (a) and (b) are 2D view of the director field in the $y-z$ plane. Topological defect cores are visualized by the isosurface $S_q = 0.5$.

To show the director field across the defect cores of the Fig. 7(a-c), as typical examples for director field around the nanoparticles, Fig. 8(a-c) are presented with the contour plot background of the rescaled scalar order parameter in the $y-z$ plane.

Therefore, discrepancy between the equilibrium angles of mesoscopic and nanoscopic colloids of this geometry also manifest itself in their corresponding defect structures. The defect structure associated to all the asymptotic equilibrium angles of the mesoscopic colloids proposed in the Fig. 5 is a chair-like structure. We see that in nanoscales the equilibrium defect structures for 0 and 90 degrees undergo a structural change. In this case the effect of sharp edges on the defect structures are vanished resulting in more stable structures than the chair-like structure existed for oblique orientations. Therefore for the two limiting equilibrium states of the nanocolloids of Fig. 5, it can be generally indicated that the equilibrium defect structure for rod-like colloids is typically the defect structure depicted in Fig. 7(c) and for discotic colloids is typically the structure depicted in Fig. 7(d).
FIG. 7: (a-c) Defect structures around a colloid with the aspect ratio 1:2 and $R = 10\text{nm}$ at 0, 45 and 90 degrees. (d-f) Defect structures around a colloid with the aspect ratio 2:1 and $R = 20\text{nm}$ at 0, 45 and 90 degrees for the anchoring constant $W = 5 \times 10^{-3}\text{J/m}^2$. Black dashed lines are 2D view of the director field in the $y-z$ plane. Topological defect cores are visualized by the isosurface $S_q = 0.5$. Based on the results of Fig. 5, snapshot (c) illustrates the equilibrium defect structure related to the aspect ratio 1:2 and (d) the equilibrium defect structure related to the aspect ratio 2:1.

IV. CONCLUSION

We studied equilibrium orientations and defect structures of cylindrical colloids with flat ends and circular cross section immersed in a uniform nematic liquid crystal. We used finite element method for numerical minimization of the Lundau-de Gennes free energy considering homeotropic anchoring energy on colloidal surfaces. We adopted a commonly used choice of parameters as Ref. [31]. We investigated thin discotic to long rod-like colloids of this geometry with length scales ranging form mesoscales to nanoscales. We have shown that
FIG. 8: Director field around a nanoparticle with with $R = 10\text{nm}$ and aspect ratio 1:2 for the three orientations (a) 0, (b) 45 and (c) 90 degrees and the anchoring constant $W = 5 \times 10^{-3}\text{J/m}^2$. Black dashed lines are 2D view of the director field in the $y-z$ plane. The colored background represents the contour plot of the rescaled scalar order parameter in the bulk.

the equilibrium state is sensitive to the two geometrical parameters: aspect ratio and length scale of the colloid.

For any given aspect ratio and size of the colloids there is one equilibrium angle (Fig. 3). For large enough mesoscopic colloids there is a specific asymptotic equilibrium angle associated to each aspect ratio, which is insensitive to further increasing the colloid size. We showed that while the asymptotic equilibrium angle of a discotic colloid with aspect ratio 4:1 is $25 \pm 5$ degrees, upon reducing the aspect ratio, the asymptotic equilibrium angle increases and ultimately reaches $80 \pm 5$ for a rod-like colloid with aspect ratio 1:4 (Fig. 5). Upon reducing the colloid sizes to nanoscales the equilibrium angles of the colloids follow a descending or ascending trend. The equilibrium angles for the colloids with the aspect ratios bigger than 1:1 (discotic colloids) go to a parallel alignment, whereas the equilibrium angle for the colloids with the aspect ratios 1:1 and smaller (rod-like colloids) tend toward a perpendicular alignment (Fig. 5).

Among the defect structures we have observed for a mesoscopic colloid there are two stable structures, a dipolar top-ring and a quadrupolar chair-like defect (Fig. 2), that their relative stability depends on the spatial orientation of the colloid (Fig. 3). The angular interval of stability we have obtained for these structures are in agreement with the experimental study of Ref. [4]. In mesoscales the sharp edges of the colloids play crucial role in the relative stability of the defect structures with respect to each other. The defect structure related to the asymptotic equilibrium angles of the mesoscopic colloids, presented in Fig. 5 is a chair-
like structure. We mentioned that by decreasing the colloid size the defect core size relative to the colloid size increases, so that in the limiting state for nanocolloids the equilibrium defect structures of 0 and 90 degrees undergo a structural change. This change of defect structure leads to parallel quadrupolar stable defect structure for discotic and perpendicular quadrupolar stable defect structure for rod-like nanocolloids. So the discrepancy between the equilibrium angle of mesoscopic and nanoscopic colloids originates from the significant differences between their defect structures.

We see that to what extent the geometrical parameters of this colloidal shape can play role in its equilibrium behavior. However an interesting open question remains about the pairwise interactions between these colloids for which the equilibrium configurations are also expected to be highly dependent on the aspect ratios and length scale of the colloids. The significance of this study becomes more clear wherever these colloids are exploited as building blocks of a colloidal crystal in which the equilibrium orientations of single colloids may impose specific orientations to the whole layers of the crystal.

V. ACKNOWLEDGMENT

We would like to thank Mohammad Reza Mozaffari for his valuable comments and also for development of the numerical minimization code. We would also like to thank Ivan Smalyukh for his encouraging remarks and fruitful discussions. MRE acknowledges the Center of Excellence in Complex Systems and Condensed Matter (CSCM) for partial support.

[1] P. Poulin, H. Stark, T. C. Lubensky, and D. A. Weitz, Science 275, 1770 (1997).
[2] C. F. Hayes, Mol. Cryst. Liq. Cryst. 36, 245 (1976).
[3] D. Andrienko, M. P. Allen, G. Skačej, and S. Žumer, Phys. Rev. E 65, 041702 (2002).
[4] U. Tkalec, M. Skarabot, and I. Musevic, Soft Matter 4, 2402 (2008).
[5] C. P. Lapointe, T. G. Mason, and I. I. Smalyukh, Science 326, 1083 (2009).
[6] A. Martinez, T. Lee, T. Asavei, H. Rubinsztein-Dunlop, and I. I. Smalyukh, Soft Matter 8, 2432 (2012).
[7] M. A. Gharbi, M. Cavallaro, G. Wu, D. A. Beller, R. D. Kamien, S. Yang, and K. J. Stebe, Liq. Cryst. 40, 1619 (2013).
[8] C. P. Lapointe, K. Mayoral, and T. G. Mason, Soft Matter 9, 7843 (2013).
[9] B. Senyuk, Q. Liu, S. He, R. D. Kamien, R. B. Kusner, T. C. Lubensky, and I. I. Smalyukh, Nature 493, 200 (2013).
[10] F. R. Hung, O. Guzmán, B. T. Gettelfinger, N. L. Abbott, and J. J. de Pablo, Phys. Rev. E 74, 011711 (2006).
[11] F. R. Hung, Phys. Rev. E 79, 021705 (2009).
[12] Q. Liu, B. Senyuk, J. Tang, T. Lee, J. Qian, S. He, and I. I. Smalyukh, Phys. Rev. Lett. 109, 088301 (2012).
[13] M. Tasinkevych, F. Mondiot, O. Mondain-Monval, and J. C. Loudet, Soft Matter 10, 2047 (2014).
[14] J. S. Evans, C. N. Beier, and I. I. Smalyukh, J. Appl. Phys. 110, (2011).
[15] J. B. Rovner, D. S. Borgnia, D. H. Reich, and R. L. Leheny, Phys. Rev. E 86, 041702 (2012).
[16] F. R. Hung and S. Bale, Mol. Simul. 35, 822 (2009).
[17] F. Brochard and P. de Gennes, J. Phys. France 31, 691 (1970).
[18] S. V. Burylov and Y. L. Raikher, Phys. Lett. A 149, 279 (1990).
[19] S. V. Burylov and Y. L. Raikher, Phys. Rev. E 50, 358 (1994).
[20] S. V. Burylov and A. N. Zakhlevnykh, Phys. Rev. E 88, 012511 (2013).
[21] H. Matthias and H.-S. Kitzerow, Mol. Cryst. Liq. Cryst. 508, 127 (2009).
[22] B. Senyuk, J. S. Evans, P. J. Ackerman, T. Lee, P. Manna, L. Vigderman, E. R. Zubarev, J. Lagemaat, and I. I. Smalyukh, Nano Lett. 12, 955 (2012).
[23] V. Pergamenshchik and V. Uzunova, Cond. Matter Phys. 93, 760 (2010).
[24] V. M. Pergamenshchik and V. A. Uzunova, Phys. Rev. E 83, 021701 (2011).
[25] S. Chernyshuk, B. Lev, and H. Yokoyama, JETP 93 (2001).
[26] B. I. Lev, S. B. Chernyshuk, P. M. Tomchuk, and H. Yokoyama, Phys. Rev. E 65, 021709 (2002).
[27] O. M. Tovkach, S. B. Chernyshuk, and B. I. Lev, Phys. Rev. E 86, 061703 (2012).
[28] P. G. de Gennes and J. Prost, The physics of liquid crystal (Oxford university press, 1995).
[29] S. Kralj and S. Žumer, Phys. Rev. A 45, 2461 (1992).
[30] M. Nobili and G. Durand, Phys. Rev. A 46, R6174 (1992).
[31] J. Fukuda, H. Stark, M. Yoneya, and H. Yokoyama, Phys. Rev. E 69, 041706 (2004).
[32] S. Chandrasekhar, Liquid Crystals (Cambridge University Press, 1992).
Based on the Ref. [32] the correlation length of our model is

\[ \xi = \sqrt{\frac{2}{3} \frac{L_1}{\partial^2 f_{IN}} \bigg|_{S_{eq}}} \].

For our choice of parameters, this definition gives \( \xi \approx 16.5\text{nm} \) and the definition \( \xi = \sqrt{\frac{L_1}{C S_{eq}^2}} \) gives \( \xi \approx 14\text{nm} \).

[34] C. Geuzaine and J.-F. Remacle, Int. J. Numer.Meth. Eng. 79, 1309 (2009), URL http://geuz.org/gmsh/

[35] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes* (Cambridge University Press, 1992), 2nd ed.