Available online at www.sciencedirect.com
SCIENCE DIRECT®
Colloids and Surfaces B: Biointerfaces 38 (2004) 143–147
COLLOIDS AND SURFACES B
www.elsevier.com/locate/colsurfb

Numerical investigation of liquid crystal colloids using a continuum description

Jun-ichi Fukuda[a,*], Makoto Yoneya[a], Hiroshi Yokoyama[a,b], Holger Stark[c]

[a] *Yokoyama Nano-structured Liquid Crystal Project, ERATO, Japan Science and Technology Agency, 5-9-9 Tokodai, Tsukuba 300-2635, Japan*
[b] *Nanotechnology Research Institute, AIST, 1-1-1 Umezono, Tsukuba 305-8568, Japan*
[c] *Fachbereich Physik, Universität Konstanz, D-78457 Konstanz, Germany*

Received 13 October 2003; accepted 2 February 2004
Available online 9 September 2004

Abstract

We investigate numerically the configuration of a nematic liquid crystal around two spherical particles. For the description of the orientational order of a nematic liquid crystal, we adopt a Landau–de Gennes continuum theory in terms of a second-rank tensor order parameter Q_{ij} together with the use of bispherical coordinates to describe the geometry of the system with two spherical particles. Above but close to the nematic–isotropic transition point, we observe capillary condensation of a nematic liquid crystal between the two particles under appropriate conditions. Below the transition point where liquid crystals possess nematic order, a point-like defect called a hyperbolic hedgehog appears close to a particle when strong normal anchoring is imposed. With the aid of an adaptive mesh refinement scheme to achieve sufficient numerical resolution to describe topological defects, we present our numerical results showing how the orientation profile of a nematic liquid crystal is distorted when the distance between two particles is small enough.

Keywords: Liquid crystal; Colloid; Bispherical coordinates; Capillary condensation; Hedgehog defect

1. Introduction

As a novel class of composite materials, colloidal dispersions in anisotropic host fluids such as liquid crystals have been attracting great interest in technology as well as in fundamental science [1–14]. Many of the fascinating properties of liquid crystal colloidal dispersions are attributed to the elastic distortion of the host liquid crystal arising from the anchoring of the mesogenic molecules on the surfaces of the dispersed particles or droplets. For instance, when the surface anchoring is strong enough to induce strong elastic deformation of a nematic liquid crystal, topological defects are formed close to the particles, which include a point-like defect referred to as a hyperbolic hedgehog [2,3], a Saturn ring that surrounds a particle as the name implies [4,8], and two surface defects known as boojums [3]. Topological defects have long been one of the important subjects of condensed matter physics and the formation of topological defects due to foreign inclusions provides an interesting problem concerning topological defects.

Another interesting, possibly more important, property of liquid crystal colloidal dispersions is that the elastic deformation of a liquid crystal can mediate interaction between particles immersed in it. This novel elastic-distortion-mediated interaction, which is of course absent in usual colloidal dispersions with isotropic host fluids, has been known to be responsible for various types of superstructures formed by dispersed particles in a nematic liquid crystal, such as linear chains [2,3,5,9], anisotropic clusters [1,4,5], and periodic lattices [11]. Cellular structures observed in a liquid crystal colloidal dispersion close to the nematic–isotropic transition point [7] might be attributed to interactions associated with paranematic ordering.

It is therefore quite important to elucidate the properties of the interaction between particles dispersed in a liquid crystal in order to understand what kinds of resultant superstructures

* Corresponding author. Present address: Nenotechnology Research Instituté, AIST, 1-1-1 Umezone, Tsukuba 305-8568, Japan.
Tel:+81 29 861 3248; fax:+81 29 861 5375.
E-mail address: fukuda.jun-ichi@aist.go.jp (J. Fukuda).

0927-7765/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfb.2004.02.019

are formed and under which conditions. There have been many theoretical studies to calculate the interaction potential between two particles in a liquid crystal [14–24], which have shown that it sensitively depends on the symmetry of the liquid crystal, the geometry of the particles, or the type of topological defects that the particles carry, and so forth. However, many of them assumed that the elastic deformation of the liquid crystal is weak enough and used a harmonic elastic energy in terms of the order parameter (e.g., distortion of the director from a uniform state in a nematic, and layer displacement in a smectic). Although such a treatment enables one to calculate analytic formulas for the interaction potential, the applicability of the resultant formulas is somewhat limited; they are usually valid when the inter-particle distance is much larger than the characteristic dimension of the particles. When the particles are close enough, the use of the harmonic energy is sometimes no longer valid, and detailed information on the profiles of a liquid crystal will be necessary to calculate the interaction potential. Then a full non-linear elastic energy has to be employed, which makes the analytic treatment almost impossible and therefore one has to resort to numerical calculations. So far as we know, there have been only a few studies [25–27] calculating the interaction between particles in a liquid crystal numerically without the assumption of the harmonic energy.

The aim of this article is to calculate the profiles of a liquid crystal around two particles as a first step towards the understanding of the interaction between particles mediated by the liquid crystal host. Instead of microscopic simulations such as molecular dynamics, we employ numerical simulations based on a continuum theory in terms of the orientational order parameter which is a second-rank tensor Q_{ij}. The advantage of using a continuum theory is that only a small number of parameters are sufficient for the specification and the control of the behavior of a liquid crystal. To describe the geometry of the system containing two particles, some of the previous similar studies based on a continuum theory [25,26] used unstructured triangular grids, while Grollau et al. [27] used regular square or cubic grids without taking any special care of the curvature of the particle surfaces. In this article we use bispherical coordinates [28,29] for the description of the geometry with two spherical particles of equal radii. One of the great advantages of using bispherical coordinates is that under a simple transformation, the region outside the two spherical particles can be mapped onto a rectangular region, which makes the implementation of the differential equations and the treatment of the boundary conditions at the particle surfaces much easier. After presenting the model in Section 2 we give some of our preliminary results in Section 3. In Section 3.1, we present the profiles of the orientational order when the temperature is above but close to the nematic–isotropic transition point. Under suitable conditions with small inter-particle distances, a nematic region is shown to appear between the particles even when an isotropic state is stable in the bulk. In Section 3.2, the configurations of a nematic liquid crystal around two particles carrying a hyperbolic hedgehog defect are shown. The presence of topological defects whose core size is much smaller than the size of the particles makes the numerical calculation quite difficult, but the use of an adaptive mesh refinement scheme enables us to avoid those difficulties as we have shown in previous papers dealing with systems containing one particle [30]. From our numerical results, we find that when the particles are close enough, the orientation profile around the particles is significantly different from the one when only one particle is present. We make a brief conclusion in Section 4.

2. Model

2.1. Free energy and the boundary conditions

To describe the orientational order of a nematic liquid crystal, we use a second-rank tensor order parameter Q_{ij} [31], which is symmetric ($Q_{ij} = Q_{ji}$) and traceless ($\mathrm{Tr}Q = Q_{ii} = 0$, where summation over repeated indices is implied). In an isotropic state $Q_{ij} = 0$ and in a uniaxial nematic oriented along the director $\boldsymbol{n}$, $Q_{ij} = Q(n_i n_j - (1/3)\delta_{ij})$, with Q being a scalar order parameter representing the strength of the nematic order. We note that the employment of Q_{ij} is consistent with the head-tail symmetry of a nematic ($\boldsymbol{n} \leftrightarrow -\boldsymbol{n}$) and that the core of a topological defect does not have to be treated as a singularity [30].

We write the free energy density of a liquid crystal in terms of Q_{ij} as $f\{Q_{ij}\} = (1/2)A\mathrm{Tr}Q^2 - (1/3)B\mathrm{Tr}Q^3 + (1/4)C(\mathrm{Tr}Q^2)^2 + (1/2)L_1\partial_k Q_{ij}\partial_k Q_{ij}$, where A, B and C are the coefficients in the Landau–de Gennes expansion and L_1 is the elastic constant associated with the distortion of the liquid crystal. Here we adopt a simple form of the elastic energy with one-constant approximation ($L_2 = 0$). After rescaling the order parameter as $Q_{ij} = s\bar{Q}_{ij}$ with $s = 2\sqrt{6}B/9C$, the free energy density is rewritten as

$$\bar{f} = \frac{f}{Cs^4} = \frac{1}{2}\tau\mathrm{Tr}\bar{Q}^2 - \frac{\sqrt{6}}{4}\mathrm{Tr}\bar{Q}^3 + \frac{1}{4}\mathrm{Tr}\bar{Q}^4 + \frac{1}{2}\xi_\mathrm{R}^2\partial_k\bar{Q}_{ij}\partial_k\bar{Q}_{ij}, \quad (1)$$

where $\tau \equiv A/Cs^2 = 27AC/8B^2$ is the reduced temperature and we define the nematic coherence length as $\xi_\mathrm{R} \equiv \sqrt{L_1/Cs^2} = \sqrt{27L_1C/8B^2}$. We notice that the nematic–isotropic transition point is $\tau = 1/8$. In what follows we omit the overline of $\bar{Q}_{ij}$ unless confusion occurs.

The equilibrium profile of the order parameter Q_{ij} is obtained by solving the Euler–Lagrange equation $\delta F/\delta Q_{ij} = 0$ with $F = \int d\boldsymbol{r} f\{Q_{ij}\}$ being the total free energy of the system. The Euler–Lagrange equation reads

$$\tau Q_{ij} - \frac{3\sqrt{6}}{4}Q_{ik}Q_{kj} + (\mathrm{Tr}Q^2)Q_{ij} - {\xi_\mathrm{R}}^2\nabla^2 Q_{ij} + \lambda\delta_{ij} = 0, \quad (2)$$

where λ is the Lagrange multiplier to ensure $\mathrm{Tr}Q = 0$.

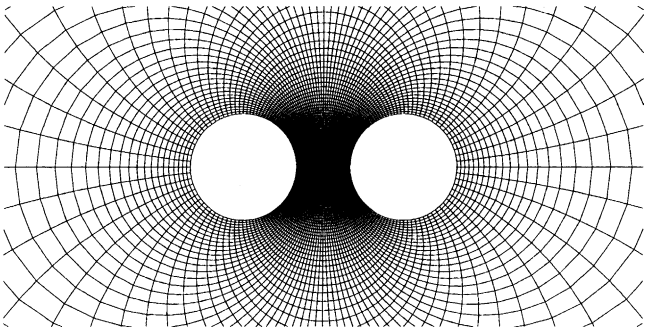

Fig. 1. Illustration of typical meshes in a real space.

We impose rigid normal anchoring at the particle surfaces so that the order parameter becomes $Q_{ij} = Q_s(\nu_i\nu_j - (1/3)\delta_{ij})$, where Q_s is some prescribed scalar order parameter at the surfaces and $\boldsymbol{\nu}$ is a unit vector normal to the particle surfaces. In the case of a liquid crystal above the nematic–isotropic transition point, we set $Q_{ij} = 0$ at infinity. Below the transition point, we assume uniform alignment of the nematic liquid crystal at infinity. The direction of the uniform alignment is taken along the z-direction and we impose $Q_{ij} = Q_{\text{bulk}}(e_i^z e_j^z - (1/3)\delta_{ij}) = Q_{\text{bulk}}(\delta_{iz}\delta_{jz} - (1/3)\delta_{ij})$, where Q_{bulk} is the scalar order parameter in the bulk and determined by the Euler–Lagrange Eq. (2).

2.2. Description of the geometry using bispherical coordinates

Bispherical coordinates [28,29] have proven to be useful and practical in the description of a system composed of two non-intersecting spheres. The relation between the bispherical coordinates (ξ, μ, ϕ) and the usual cylindrical coordinates (ρ, z, ϕ) is expressed as

$$\rho = \frac{a \sin\mu}{\cosh\xi - \cos\mu}, \quad z = \frac{a \sinh\xi}{\cosh\xi - \cos\mu}. \tag{3}$$

For the case of two spheres with equal radii R_0 whose centers are located at $z = \pm D/2$, $\rho = 0$ $(D > 2R_0)$, we set $a = \sqrt{(D/2)^2 - R_0^2}$. Then the surfaces of the two spheres are represented simply by $\xi = \xi_0 \equiv \cosh^{-1}(D/2R_0)$. The region outside the spheres is mapped to $-\xi_0 < \xi < \xi_0$ and $0 \le \mu \le \pi$ and $\xi = \mu = 0$ corresponds to infinity. In Fig. 1, we show typical meshes in a real space generated from equally spaced meshes in the (ξ, μ) space.

3. Results

3.1. Above and close to the nematic–isotropic transition

Fig. 2 shows typical profiles of the orientational order parameter just above the nematic–isotropic transition point $(\tau = 1/8 + 0)$. The distance between the centers of the particles is $D = 2.4R_0$, and the nematic coherence length is $\xi_R = 10^{-2}R_0$. The surface order parameter is set to

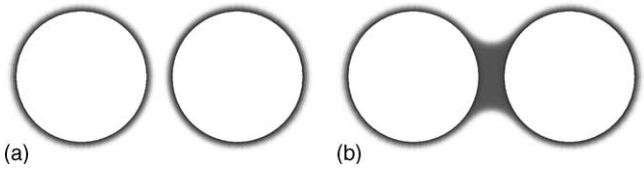

Fig. 2. Profiles of the orientational order of liquid crystals (gray-scale plots of $\mathrm{Tr}Q^2$). In the white regions the liquid crystals are in the isotropic state and in the black region they possess nematic order: (a) absence and (b) presence of a nematic capillary bridge, respectively.

$Q_s = 0.7$. In Fig. 2(a) two particles carry nematic coronas, which are almost uncorrelated, while Fig. 2(b) clearly shows capillary condensation of a nematic liquid crystal, or a "nematic capillary bridge". The capillary bridge can be at least metastable until D is as large as about $2.6R_0$. The comparison of the free energy of those two states can be carried out and the condition for the preference of the nematic capillary bridge can be determined. In the case of Fig. 2 with $D = 2.4R_0$, the presence of a nematic capillary bridge is energetically more favorable and the absence of a capillary bridge corresponds to a metastable state. Although the details of the analysis will be presented in a future article, we notice that the presence of a nematic capillary bridge leads to strong attraction between two particles. Intuitively, the strong attraction can be attributed to the increase in the interfacial area between the nematic and the isotropic phase (and therefore the increase in the free energy of a liquid crystal) with the increase of the inter-particle distance (when the temperature is higher than the transition point, the increase in the volume of the metastable nematic region also leads to the increase in the free energy). We notice that the strong attractive force due to the nematic capillary bridge close to the nematic–isotropic transition point has indeed been observed in recent experiments using an atomic force microscope [32].

3.2. Nematic state

As noted in the introduction, when a particle that imposes strong homeotropic anchoring is immersed in a uniformly aligned liquid crystal, a topological defect accompanies the particle to preserve the neutrality of the topological charges. When the particle is large enough compared to the size of the defect core, a point-like defect called a hyperbolic hedgehog is formed [2,3,14]. Particles carrying a hyperbolic hedgehog act as a dipole, which results in a chain-like superstructure of particles [2,3,5,9]. Due to the balance between the long-range attraction of the "dipoles" and the short-range repulsion due to the presence of a topological defect between the particles, two adjacent particles take a well-defined inter-particle distance, which stabilizes the chain-like structure.

In Fig. 3, we show several equilibrium profiles of the orientational order around two particles carrying a hedgehog in a nematic liquid crystal uniformly oriented along the horizontal direction. The distance between the center of the particles D is fixed to (a) $5.0R_0$, (b) $3.0R_0$, and (c) $2.28R_0$.

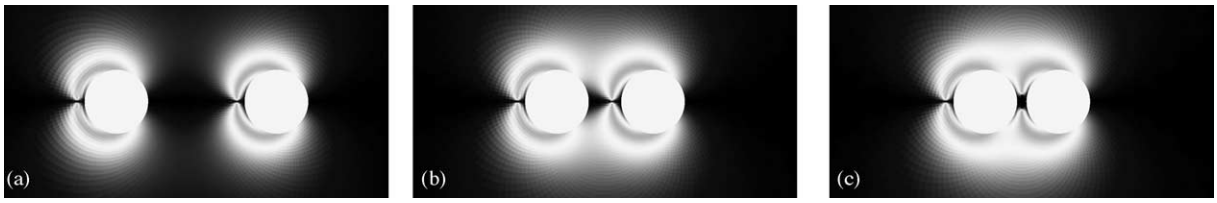

Fig. 3. The profiles of the orientational order of a nematic liquid crystal for (a) $D = 5.0R_0$, (b) $D = 3.0R_0$ and (c) $D = 2.28R_0$ (gray-scale plots of Q_{zz}^2, where the z-axis is along the horizontal direction).

The directions of the two "dipoles" are set parallel. This configuration is similar to a part of the chain-like structure observed experimentally. We have used the temperature $\tau = (3\sqrt{6} - 8)/12 < 0$, where an isotropic state becomes unstable and the scalar order parameter in the bulk is $Q_{\text{bulk}} = 1$. The scalar order parameter at the particle surface Q_{s} is set equal to Q_{bulk}. The nematic coherence length is taken as $\xi_{\text{R}} = 5 \times 10^{-3} R_0$. We notice that the grid spacings on the left-hand side of the left particle in real space are not small enough for the description of a topological defect as can be seen from Fig. 1, so we have used an adaptive mesh refinement scheme developed in our previous papers [30] to assign finer grids around the topological defects.

In Fig. 3(a) with $D = 5.0R_0$, the orientation profiles around each particle are almost independent of each other, while in Fig. 3(b) with smaller $D\,(3.0R_0)$, slight deformations of the orientation profiles from that around two isolated particles are found. When the inter-particle distance is sufficiently small (Fig. 3(c), with $D = 2.28R_0$), the hyperbolic hedgehog between two particles becomes unstable and opens up to a larger ring (we notice that a hyperbolic hedgehog is intrinsically made up of a small ring [30,33]). The resulting strong elastic deformations lead to a strong repulsion between the particles. The detailed analysis of the interaction energy between two particles in this case will be presented elsewhere.

4. Conclusion

By numerical simulations based on a continuum description, we have investigated the configuration of a liquid crystal around two spherical particles. The use of bispherical coordinates has proven to be an appropriate choice for the description of the geometry of the system containing two spherical particles. We have employed a Landau–de Gennes theory based on a tensor order parameter Q_{ij} to describe the orientational order of a nematic liquid crystal, which enables us to deal with a liquid crystal just above the nematic–isotropic transition point as well as deep in the nematic state where topological defects can occur. Above the nematic–isotropic transition point, we have observed a nematic capillary bridge, i.e., a condensed nematic region between the two particles, which forms under appropriate conditions when the inter-particle distance is small enough. We have also considered a situation where two particles are immersed in a uniformly aligned nematic liquid crystal and each particle carries a hyperbolic hedgehog defect. When the particles are far apart, their orientation profiles are almost independent of each other and similar to that around one isolated particle. As the inter-particle distance becomes smaller, strong elastic distortions from the long-distance profiles are observed. The hedgehog defect situated between the two particles eventually becomes unstable and opens up to form a larger ring. In this article we have restricted ourselves to the presentation of the configurations of a liquid crystal around two particles. The investigation of the interaction energy between two particles is possible and the results will be presented in future articles.

References

[1] P. Poulin, V.A. Raghunathan, P. Richetti, D. Roux, J. Phys. II (France) 4 (1994) 1557.
[2] P. Poulin, H. Stark, T.C. Lubensky, D.A. Weitz, Science 275 (1997) 1770.
[3] P. Poulin, D.A. Weitz, Phys. Rev. E 57 (1998) 626.
[4] O. Mondain-Monval, J.C. Dedieu, T. Gulik-Krzywicki, P. Poulin, Eur. Phys. J. B 12 (1999) 167.
[5] P. Poulin, N. Francès, O. Mondain-Monval, Phys. Rev. E 59 (1999) 4384.
[6] M. Zapotocky, L. Ramos, P. Poulin, T.C. Lubensky, D.A. Weitz, Science 283 (1999) 209;
L. Ramos, M. Zapotocky, T.C. Lubensky, D.A. Weitz, Phys. Rev. E 66 (2002) 031711.
[7] S.P. Meeker, W.C.K. Poon, J. Crain, E.M. Terentjev, Phys. Rev. E 61 (2000) R6083;
V.J. Anderson, E.M. Terentjev, S.P. Meeker, J. Crain, W.C.K. Poon, Eur. Phys. J. E 4 (2001) 11;
V.J. Anderson, E.M. Terentjev, Eur. Phys. J. E 4 (2001) 21.
[8] Y. Gu, N.L. Abbott, Phys. Rev. Lett. 85 (2000) 4719.
[9] J.C. Loudet, P. Barois, P. Poulin, Nature (London) 407 (2000) 611;
J.C. Loudet, P. Poulin, P. Barois, Europhys. Lett. 54 (2001) 175.
[10] J. Yamamoto, H. Tanaka, Nature (London) 409 (2001) 321.
[11] V.G. Nazarenko, A.B. Nych, B.I. Lev, Phys. Rev. Lett. 87 (2001) 075504.
[12] M. Mitov, C. Portet, C. Bourgerette, E. Snoeck, M. Verelst, Nat. Mater. 1 (2002) 229.
[13] T. Bellini, M. Caggioni, N.A. Clark, F. Mantegazza, A. Maritan, A. Pelizzola, Phys. Rev. Lett. 91 (2003) 085704.
[14] H. Stark, Phys. Rep. 351 (2001) 387 and references therein.
[15] S.L. Lopatnikov, V.A. Namiot, Zh. Eksp. Teor. Fiz. 25 (1978) 361;
S.L. Lopatnikov, V.A. Namiot, Sov. Phys. JETP 48 (1978) 180.
[16] S. Ramaswamy, R. Nityananda, V.A. Raghunathan, J. Prost, Mol. Cryst. Liq. Cryst. 288 (1996) 175.

[17] R.W. Ruhwandl, E.M. Terentjev, Phys. Rev. E 55 (1997) 2958.
[18] T.C. Lubensky, D. Pettey, N. Currier, H. Stark, Phys. Rev. E 57 (1998) 610.
[19] B.I. Lev, P.M. Tomchuk, Phys. Rev. E 59 (1999) 591;
B.I. Lev, S.B. Chernyshuk, P.M. Tomchuk, H. Yokoyama, Phys. Rev. E 65 (2002) 021709.
[20] M.S. Turner, P. Sens, Phys. Rev. E 55 (1997) 1275;
P. Sens, M.S. Turner, P. Pincus, Phys. Rev. E 55 (1997) 4394;
P. Sens, M.S. Turner, J. Phys II (France) 7 (1997) 1855;
M.S. Turner, P. Sens, Phys. Rev. E 57 (1998) 823.
[21] J. Fukuda, B.I. Lev, H. Yokoyama, Phys. Rev. E 65 (2002) 031710.
[22] J. Fukuda, B.I. Lev, K.M. Aoki, H. Yokoyama, Phys. Rev. E 66 (2002) 051711;
J. Fukuda, B.I. Lev, H. Yokoyama, J. Phys.: Condens. Matter 15 (2003) 3841.
[23] A. Borštnik, H. Stark, S. Žumer, Phys. Rev. E 60 (1999) 4210;
A. Borštnik, H. Stark, S. Žumer, Phys. Rev. E 61 (2000) 2831.
[24] P. Galatola, J.-B. Fournier, Phys. Rev. Lett. 86 (2001) 3915;
J.-B. Fournier, P. Galatola, Phys. Rev. E 65 (2002) 032702;
H. Stark, Phys. Rev. E 66 (2002) 041705;
P. Galatola, J.-B. Fournier, H. Stark, Phys. Rev. E 67 (2003) 031404.
[25] H. Stark, J. Stelzer, R. Bernhard, Eur. Phys. J. B 10 (1999) 515.
[26] P. Patrício, M. Tasinkevych, M.M. Telo da Gama, Eur. Phys. J. E 7 (2002) 117; M. Tasinkevych, N.M. Silvestre, P. Patrício, M.M. Telo da Gama, Eur. Phys. J. E 9 (2002) 341.
[27] S. Grollau, E.B. Kim, O. Guzmán, N.L. Abbott, J.J. de Pablo, J. Chem. Phys. 119 (2003) 2444.
[28] P.M. Morse, H. Feshbach, Methods of Theoretical Physics, McGraw-Hill, New York, 1953.
[29] J.-R. Roan, T. Kawakatsu, J. Chem. Phys. 116 (2002) 7283.
[30] J. Fukuda, H. Yokoyama, Eur. Phys. J. E 4 (2001) 389;
J. Fukuda, M. Yoneya, H. Yokoyama, Phys. Rev. E 65 (2002) 041709;
J. Fukuda, M. Yoneya, H. Yokoyama, Mol. Cryst. Liq. Cryst 413 (2004) 221;
J. Fukuda, H. Stark, M. Yoneya, H. Yokoyama, J. Phys.: Condens. Matter 16 (2004) S1957.
[31] P.G. de Gennes, J. Prost, The Physics of Liquid Crystals, second ed., Oxford University Press, Oxford, 1993.
[32] K. Kočevar, A. Borštnik, I. Muševič, S. Žumer, Phys. Rev. Lett. 86 (2001) 5914;
A. Borštnik Bračič, K. Kočevar, I. Muševič, S. Žumer, Phys. Rev. E 68 (2003) 011708.
[33] J. Fukuda, H. Yokoyama, Phys. Rev. E 66 (2002) 012703.