Spontaneous sense inversion in helical mesophases

H. H. Wensink

Laboratoire de Physique des Solides, Université Paris-Sud & CNRS, UMR 8502 - 91405 Orsay, France

received 14 April 2014; accepted in final form 7 July 2014
published online 22 July 2014

PACS 61.30.Cz - Molecular and microscopic models and theories of liquid crystal structure
PACS 64.70.M- - Transitions in liquid crystals
PACS 82.70.Dd - Colloids

Abstract – We investigate the pitch sensitivity of chiral nematic phases of helicoidal patchy cylinders as a generic model for chiral (bio-)polymers and helix-shaped colloidal rods. The behaviour of the macroscopic helical pitch is studied from microscopic principles by invoking a simple density functional theory generalised to accommodate weakly twisted director fields. Upon changing the degree of alignment along the local helicoidal director we find that chiral nematic phases exhibit a sudden sense inversion whereby the helical symmetry changes from left- to right-handed and vice versa. Since the local alignment is governed by thermodynamic variables such as density, temperature or the amplitude of an external directional field, such pitch sense inversions can be expected in systems of helical mesogens of both thermotropic and lyotropic origin. We show that the spontaneous change of helical symmetry is a direct consequence of an antagonistic effective torque between helical particles with a certain prescribed internal helicity. The results may help opening up new routes towards precise control of the helical handedness of chiral assemblies by a judicious choice of external control parameters.

Over the past decades considerable research activity has been directed to understanding the chiral mesostructure of liquid crystals composed of elongated molecules or colloidal particles. Examples of systems which form chiral nematic phases (also referred to as cholesteric phases) include a range of synthetic helical polymers such as polyisocyanates [1,2] and polysilanes [3]. In addition, there are numerous helical bio-polymers that self-assemble into chiral nematic phases, such as DNA [4,5], rod-like fd-virus [6], polypeptides [7,8], chiral micelles [9], polysaccharides [10], microfibrillar cellulose derivatives [11] and chitin [12]. The intrinsic length scale associated with the helical organisation of the director field, referred to as the cholesteric pitch, depends strongly on the particle concentration, temperature and solvent properties such as the ionic strength. The sensitivity of the pitch with respect to these individual factors has been the subject of a considerable body of experimental research [4,13–22].

The subtle interplay between the molecular features that render the particle interactions chiral and the mesostructure of the chiral nematic phase is far from understood and remains an outstanding problem in liquid crystal physics [23]. Many biomacromolecules owe their chiral shape to some spatially non-uniform distribution of charges or surface groups residing on the molecule, a prominent example being the double-helix backbone of the DNA phosphate groups. A natural route to understanding self-organisation of these complex biomolecules is to put forward coarse-grained descriptions invoking an effective chiral shape determined by electrostatic and steric effects pertaining to the intrinsic molecular conformation. Common examples are the bent-core or banana-shaped molecules [24,25] whose broken particle symmetry alone can be shown responsible for stabilising chiral nematics. Other helical bio-polymers or microfibrillar aggregates can be represented by effective chiral shapes such as a threaded cylinder [24,26], a twisted rod [12,27] or a semi-flexible helical object [28].

Despite recent progress in the simulation domain [29,30] a common theoretical framework capable of rationalising the pitch trends of chiral nematic materials starting from the microscopic properties of the constituents remains elusive. In this paper we endeavour to make a first step in this direction by considering a semi-analytical density functional treatment of chiral nematic assemblies starting from a generic helical segment model. To establish a microscopic understanding of the subtle connection between micro- and macrochirality we start by deriving the effective chiral potential between two slender helical objects as a generic model for chiral nanoparticles with arbitrary
internal helicity. Next, the implications of such chiral potentials on the structure and symmetry of a chiral nematic phase will be addressed using statistical mechanical theory. Our chiral potential has a simple pseudo-scalar form similar to the ones derived from more explicit electrostatic models in which chiral interactions are mediated through helically arranged local dipoles [31]. Owing to its tractable form the pseudo-scalar chiral potential is routinely invoked similar to the ones derived from more explicit electrostatic ory. Our chiral potential has a simple pseudo-scalar form with respect to the helical properties of the constituents as well as the thermodynamic state of the system.

The magnitude and symmetry of the pitch turn out to be sensitive to not only the microscopic pitch but also the degree of alignment along the helical director field. The latter, in turn, can be steered by the density (lyotropic), temperature (thermotropics) or by some directional external field. To illustrate the concept, we show that a helix with fixed internal pitch may self-assemble into both right- and left-handed chiral phases whose handedness may spontaneously switch depending on the thermodynamic state of the system. Such pitch inversions have been found in various experimental observations [38,39] but a sound statistical mechanical underpinning of these phenomena is lacking mainly because the construction of generic, predictive models is strongly impeded by the complicated physico-chemical nature of many thermotropic liquid crystals.

Model. – Let us consider a pair of strongly elongated helices each described by a linear array of rigidly linked soft segments with a radially symmetric interaction potential \( u_c(r) \) wrapped around a cylindrical backbone (see fig. 1). In the continuum limit the potential \( U_h \) between two helices with length \( \ell \) depending on the centre-of-mass distance \( r_{12} \) and solid orientation angles \( \Omega_i \) formally reads:

\[
U_h = \int_{-\ell/2}^{\ell/2} dt_1 \int_{-\ell/2}^{\ell/2} dt_2 u_h(|r_{12} + s_1 - s_2|),
\]

where \( s_i(t_i, \Omega_i) \) denotes the local segment position of rod \( i \) parameterized by \( t_i \). A helix of diameter \( \delta \) can be defined by invoking a molecular orthonormal basis \( \{\hat{u}_i, \hat{v}_i, \hat{w}_i\} \) \( i = 1, 2 \) in terms of the longitudinal orientation vector \( \hat{u} \) and auxiliary unit vectors \( \hat{v} = \hat{u}_1 \times \hat{u}_2/|\hat{u}_1 \times \hat{u}_2| \) and \( \hat{w} = \hat{u}_1 \times \hat{v} \). The contour vector of helix \( i = 1, 2 \) then takes on the form 

\[
s_i = r_i + \frac{t_i}{2} \hat{u}_i + \frac{\delta}{2} \{\cos(q t_i + \psi_i) \hat{v} + \sin(q t_i + \psi_i) \hat{w}_i\}, \tag{2}
\]

with \( q = 2\pi/p \) the internal helical pitch such that \( q > 0 \) corresponds to a right-handed (R) helix and \( q < 0 \) to a left-handed (L) one. Since a helical object is not invariant with respect to rotations about its longitudinal axis \( \hat{u} \), the pair potential must explicitly depend on a set of (internal) azimuthal angles \( 0 \leq \psi_i \leq 2\pi \). To derive a simple expression for the chiral potential associated with the rather intractable form eq. (1) we follow the procedure outlined in an earlier paper [40]. First, we focus on strongly elongated helices and expand \( U_h \) for small width-to-length ratio \( \delta/\ell \ll 1 \). The leading-order term is of \( O(\delta/\ell)^2 \) and embodies all chiral contributions for slender helices. The next step is to mitigate the multi-angular dependency of \( U_h \) by constructing an angle-averaged chiral potential \( U_c \) obtained by preaveraging over the internal azimuthal angles. To this end we impose the Helmholtz free energy of the angle-averaged potential to be equal to that of the full angle-dependent potential [41]. Setting the thermal energy \( k_B T \) to unity we may write the potential of mean force in the following way:

\[
U_c = -\ln \langle \exp[-U_h] \rangle_\psi = \langle U_h \rangle_\psi - \frac{1}{2} \langle U_h^2 \rangle_\psi + \cdots, \tag{3}
\]

where the brackets denote a double integral over the internal angles \( \langle \cdot \rangle_\psi = (2\pi)^{-2} \int_0^{2\pi} d\psi_1 d\psi_2 \). The last term can be identified with the strength of the azimuthal fluctuations and is obtained by expanding the free energy up to quadratic order in \( U_h \). It can be readily shown that the simple average yields zero \( \langle U_h \rangle_\psi = 0 \) so that only the quadratic fluctuation term survives. This is consistent with the notion that the azimuthal helix-helix correlations play a key role in stabilising chiral nematic order, as discussed in [42]. Physical justification of the expansion above relies on the observation that in most experimental systems the twist deformation of the director field is weak (typical pitch length \( \gg \ell \)). As a result, the chiral contribution to \( U_h \) which is the only part responsible for the formation of a helical director field is generally much smaller than the thermal energy. The integrations over the azimuthal angles are trivial and all contributions invariant under a parity transformation \( r_{12} \rightarrow -r_{12} \) are non-chiral and may be discarded. Combining all relevant contributions leads us to the following compact expression.
for the chiral potential between two strongly elongated helices with $\delta / \ell \ll 1$:

$$U_c(r_{12}; \mathbf{u}_1, \mathbf{u}_2) \simeq \frac{1}{4} \left( \frac{\delta}{\ell} \right)^2 \mathcal{F}(r_{12}, q)(\mathbf{u}_1 \times \mathbf{u}_2 : \ell^{-1} \mathbf{r}_{12}).$$

(4)

The term between brackets is a chiral pseudo-scalar which changes sign under a parity transformation and is routinely imposed to describe chiral interactions [31]. We show that this form naturally emerges as the leading-order chiral potential for slender helical objects. Most importantly, however, our prefactor provides direct access to the microscopic helical pitch via

$$\mathcal{F}(r_{12}, q) = \langle u_1'(r_{12}) \cos q \ell t_1 \rangle \langle u_2'(r_{12}) \sin q \ell t_1 \rangle,$$

(5)

in terms of the double contour average $\langle \cdot \rangle = \int_0^1 dt_1 dt_2$, intersegment force $u_1'(x) = - \partial u_1(x)/\partial x$ and linear segment distance $r_{12}^2 = \ell^{-2} r_{12}^2 + \frac{1}{4}(t_1 \mathbf{u}_1 - t_2 \mathbf{u}_2)^2$. In order to appeal to both lyotropic and thermotropic assemblies of helical building blocks we may consider two different segment potentials. First, a (repulsive) Yukawa segment potential $u_s(r) = u_0 \exp(-\kappa r)/r$, with $\kappa$ an inverse electrostatic screening length, provides a relevant description of charge-stabilised colloidal helices whose self-assembly properties are governed mainly by particle concentration.

To make a connection to thermotropic systems, we consider a van der Waals (vdW) form $u_s(r) = -u_0 r^{-6}$ in which case the system temperature rather than concentration constitutes the chief thermodynamic control parameter owing to the long-ranged attractive interparticle forces. The amplitudes $u_0 > 0$ pertain to various electrophysical properties (surface charge, dielectric constant etc.) of the individual helices which we do not need to not specify here.

Irrespective of the nature of the segment potential, the chiral potential exhibits an intricate angular dependence (fig. 2). Results are shown for a particular interhelix distance of 0.1f but the overall features do not change qualitatively for different values, provided the distance remains larger than the core diameter $\delta$. In particular, the amplitude and direction of the effective torque that each helix experiences depends sensitively on its local orientational freedom. Since the latter is tuned primarily by density or temperature we expect a highly non-trivial response of the chiral nematic symmetry upon variation of these quantities. Two observations in fig. 2 hint at a subtle relationship between the helical properties of the individual particles and those of the macroscopic phase. First, for $q = 4$ the sign of the effective torque $\tau \sim -\partial U_c/\partial \gamma_{\mathbf{u}_1, \mathbf{u}_2}$ at small mutual angle $\gamma_{\mathbf{u}_1, \mathbf{u}_2}$ is opposite to that of the other helices shown. This implies that helices may stabilise a helix sense with opposite symmetry in the asymptotic limit of strong alignment (viz. very large concentrations) [37].

A second, more implicit, observation is that for certain values of $q$, the local and global minima correspond to opposite torque directions. The consequence is that the symmetry of the effective microscopic torque experienced by each helix due to correlations with its neighbours depends crucially on the degree of local alignment along the helical director.

**Oseen-Staley theory**. To scrutinise the effect of these subtleties on the macroscale we invoke a simple Oseen-type theory appropriately generalised for weakly helical director fields with pitch $k \ll \ell^{-1}$ [43,44]. The Helmholtz free energy density $F$ per unit volume $V$ depends on the one-particle orientational distribution $f(\mathbf{u})$ and reads up to quadratic order in $k$:

$$\frac{F}{V} = \rho \int d\mathbf{u} f(\mathbf{u}) \left[ \ln[\rho V f(\mathbf{u})] - 1 \right] + \sum_{n=0}^{\infty} K_n(-k)^n/n!,$$

with $\rho$ the particle number density and $V$ the immaterial thermal volume of a helix. Equation (6) reflects a balance between the ideal mixing and (local) orientational entropy and the excess free energy accounting for helix-helix interactions on the second virial level.

The kernels are given by the following angular averages [44]:

$$K_n[f] = \frac{\pi^2}{2} \int d\mathbf{u}_1 \int d\mathbf{u}_2 [\partial_0 f(\mathbf{u}_1) f(\mathbf{u}_2)] M_n(\mathbf{u}_1, \mathbf{u}_2),$$

(7)

in terms of the derivatives $\partial_0 = 1$, and

$$\partial_1 = u_{2\perp} \partial_{u_2}, \quad \partial_2 = u_{1\perp} \partial_{u_1} u_{2\perp} \partial_{u_2},$$

(8)

acting on $f$ with $(||, \perp)$ denoting the vector component along and transverse to the pitch direction. The reference term, $K_0$ is associated with an untwisted nematic system, whereas $K_1$ embodies an effective torque field emerging
from the chiral potential. $K_2$ represent a twist elastic energy counteracting the helical deformation of the director field. The kernels eq. (7) are entirely microscopic and are given by higher-order spatial averages of the Mayer function of the helical pair potential

$$M_n = -\int \, \dd r_{12} r_{12}^{-\gamma} (e^{-U_h} - 1). \tag{9}$$

If we assume the helix envelope to consist of a cylindrical hard inner core of diameter $\delta$, then

$$M_0 = 2\delta^2 |\sin \gamma|, \tag{10}$$

identical to the excluded volume $v_{ex}$ of the cylinder-shaped helical envelope. The soft potential can be subsumed into an effective, angle-dependent diameter $\delta = \epsilon(\gamma)\delta$. The orientation-dependent prefactor reads

$$\epsilon(\gamma) = 1 + \int_1^\infty \dd x (1 - \exp[-u_s(x) \cos^2(\gamma)]), \tag{11}$$

which reduces to unity for strictly hard rods ($u_s = 0$). The cosine term reflects the intrinsic tendency of the attractive helix pairs to align and the repulsive ones to adopt a perpendicular configuration [45]. Similar arguments can be applied to the twist elastic constant in which case the kernel is represented by some higher-dimensional excluded volume

$$M_2 = \frac{1}{6} \epsilon^4 \delta |\sin \gamma| (u_{11}^2 + u_{22}^2). \tag{12}$$

The symmetry of $M_1$ dictates that the torque-field constant $K_1$ depend only on the pseudo-scalar contribution to the helix potential (eq. (4)). Recalling that $U_c \ll 1$ and adopting a simple van der Waals ansatz one arrives at a tractable form

$$M_1 \simeq \int_{v_{ex}} \, \dd r_{12} r_{12}^\gamma U_c (r_{12}, \hat{u}_1, \hat{u}_2), \tag{13}$$

where the spatial integral runs over the space complementary to the excluded volume $v_{ex}$ of the helix envelope.

**Pitch inversion.** – Most helically organised assemblies known in experiment possess a pitch length much larger than the molecular size. It is therefore reasonable to suppose that the local nematic order is only marginally affected by the twisted director field. In this situation the local orientational distribution of the main helix axis $f(\hat{u})$ can be established from a formal minimisation of the nematic free energy (eq. (6), setting $k = 0$) so that

$$f(\hat{u}) = \mathcal{N} \exp \left( -c \int \dd \hat{u} \epsilon(\gamma)|\sin \gamma|f(\hat{u}) \right), \tag{14}$$

where the constant $\mathcal{N}$ ensures normalisation and $c = \rho \ell^2 \delta$ defines a dimensionless concentration measure. From $f^*$ one can extract the nematic order parameter along the local director $\hat{n}$ via $S = \int \dd \hat{u} f(\hat{u})P_2(\hat{u} \cdot \hat{n})$ (with

![Fig. 3: (Colour on-line) (a) Pitch length $p_\ell$ in arbitrary units vs. concentration for a system of helical Yukawa rods with $\kappa l = 20$ and $\delta / \ell = 0.02$ for different values of the internal pitch $q \ell$. (b) Same result plotted against the local nematic order parameter $S$. A pitch sense inversion (right-handed ↔ left-handed) occurs for $q \ell = 4$ and $q \ell = 7$.](image)

$P_2(x) = \frac{3}{2} x^2 - \frac{1}{2}$ a Legendre polynomial). The ratio of the microscopic constants $K_1$ define the equilibrium pitch

$$k = K_1[f]/K_2[f]. \tag{15}$$

This result naturally follows from the extremum condition $\partial F / \partial k = 0$ and reflects a balance between the torque-field and twist elastic contributions to the free energy. In keeping with the internal pitch we identify $k > 0$ with a right-handed (R) helical director field and $k < 0$ with a left-handed (L) one. With this, we have established the desired connection between thermodynamic variables (concentration or temperature) and pitch $k$ for helical particles with arbitrary internal pitch $q$.

To illustrate the pitch sensitivity of chiral nematic assemblies we now focus exclusively on lyotropic chiral nematics composed of Yukawa helices for which the concentration $c$ constitutes the main thermodynamic parameter. The results in fig. 3 show the variation of the pitch length with $c$ for different values of the internal pitch $q$. The pitch has been normalised to its value corresponding to the chiral nematic phase at coexistence with the isotropic phase ($c = 6.28$ setting $u_0 = 1$) to avoid having to make an explicit reference to the physico-chemical helix details that go into $u_0$ [40].

The helices corresponding to fig. 3 all possess a right-handed symmetry and one would naively expect the chiral nematic phase to adopt the same symmetry. Figure 3 shows that this is indeed the case for $q \ell = 3$ and $q \ell = 6$, where the helical sense remains right-handed (R) throughout the probed concentration range, but not for $q \ell = 4$ and $q \ell = 7$. In the latter cases a more complicated scenario is
found in which a R-chiral nematic phase transforms into a L-phase upon increasing c. The critical value at which the sense inversion occurs is found to be $c \approx 17.6$ for the weakly coiled ($q\ell = 4$) and $c \approx 11.4$ for the strongly coiled ones ($q\ell = 7$). The transition from R to L is continuous and must be associated with a diverging pitch length $p_c \propto |c - c^*|^{-1}$ at the inversion point $c^*$ where the system becomes nematic. For $c < c^*$ the pitch strongly decreases upon lowering c and a distinct unwinding of the helical director field occurs close to the transition towards the isotropic phase. Symmetry prescribes the same sequence of pitch changes to occur for left-handed helices with the sense changing R $\rightarrow$ L upon dilution. Independently of q the chiral nematic phase becomes more strongly coiled upon increasing concentration and the pitch length attains a simple proportionality $p_c \propto 1/c$ in the asymptotic concentration limit [46]. Note that the inversion phenomena are consistent with the low-k expansion of the free energy (eq. (6)) since the nematic twist $k$ becomes arbitrarily weak upon approaching the inversion point from either direction.

Equation (4) presents a schematic overview of the interrelation between microscopic and nematic chirality. We can infer that pitch inversions upon change of local nematic alignment only occur in certain q intervals while absent in others. The pitch amplitude (fig. 4(b)) depends sensitively on q with the pronounced extremum around $|q\ell| \approx 3$ revealing an optimal “twisting strength” for moderately coiled nanohelices [40]. As alluded to in fig. 2, the sense inversion is imbedded in the intricate dependence of the chiral potential on the microscopic twist angle $\gamma$.

A prerequisite for the pitch inversion is the presence of an antagonistic effect in the azimuthally averaged interhelix potential represented by minima located at opposite sign of the angle $\gamma$ between the main helix axes. The ratio at which these minima are sampled depends crucially on the degree of nematic alignment around the local director and a change of nematic order (by varying particle concentration or temperature) allows the helix pairs to preferentially adopt either a positive or negative twist which then proliferates towards the formation of a left- or right-handed director field.

In view of the similarity between the scenarios depicted in fig. 2 one can envisage an analogous pitch inversion for attractive van der Waals segment potentials. This situation would correspond to thermotropic helical assemblies where a change of temperature $k_BT/\mu_0$ (at fixed pressure) provides the main driving force for liquid crystal order.

The present model could therefore also be used to model thermotropic systems of coiled molecules in which a similar complex interplay between micro- and macrochirality can be expected by variation of temperature.

**Conclusion.** – We propose a course-grained helical segment model to study chiral self-organisation in lyotropic or thermotropic assemblies of helical mesogens. From the general pair potential we extract an algebraic chiral potential similar to the pseudo-scalar form [31] widely used to describe long-ranged chiral dispersion forces. Whereas the pseudo-scalar model potential usually requires an unknown adjustable prefactor, our algebraic form provides explicit reference to the molecular helicity. By combining the potential with a simple Onsager-Straley theory we study the pitch as a function of the magnitude and sense of the pitch as well as the thermodynamic state. The helical handedness is not a priori dictated by the symmetry of the individual helices but depends sensitively on the precise value of the internal pitch and the thermodynamic state of the system. We map out the precise conditions under which right-handed helices generate left-handed chiral phases and vice versa. The antagonistic effect of helical interactions is consistent with experimental observations in M13 virus systems [47] and various types of DNA [5,29] where left-handed chiral nematic phases are formed from right-handed helical polyelectrolyte conformations. Small variations in the shape of the helical coil, induced by, e.g., a change of temperature, may lead to a sense inversion of the helical director. Such inversions have been found in thermotropic (solvent free) polypeptides [38], cellulose derivatives [39], and in mixtures of right-handed cholesterol chloride and left-handed cholesterol myristate [48].

The present model could be interpreted as a benchmark for complex biomacromolecules such as DNA and f/d which are characterised by a helical distribution of charged surface groups. Other lyotropic chiral nematic systems, such as cellulose and chitin microfibers in solution could also be conceived as charged rods with a twisted
charge distribution [12]. A more accurate description of the pitch sensitivity, particularly for DNA systems, could be achieved by taking into account the steric contributions associated with the helical backbone of the chains as well as the influence of chain flexibility. This could open up a route towards understanding the unusual behaviour of the pitch vs. particle and salt concentration as encountered in DNA [5,15,49] using simple coarse-grained models.

Last but not least, in view of their intricate interplay between micro- and macrochirality assemblies of helical particles could be exploited for photonic applications as well as the design of opto-electronic switching devices with improved performance and controllability [50].

REFERENCES

[1] Aharoni S. M., Macromolecules, 12 (1979) 94.
[2] Sato T., Sato Y., Umemura Y., Teramoto A., Nagamura Y., Wagner J., Weng D., Okamoto Y., Hatada K. and Green M. M., Macromolecules, 26 (1993) 4551.
[3] Watanabe J., Kame H. and Fujiki M., Polym. J., 33 (2001) 495.
[4] Robinson C., Tetrahedron, 13 (1961) 219.
[5] Livolant F. and Leforestier A., Prog. Polym. Sci., 21 (1996) 1115.
[6] Dogic Z. and Fraden S., Curr. Opin. Colloid Interface Sci., 11 (2006) 47.
[7] Uematsu I. and Uematsu Y., Adv. Polym. Sci., 59 (1984) 37.
[8] DuPré D. B. and Samulski E. T., in Liquid Crystals: the Fourth State of Matter, edited by Saeva F. D. (Dekker, New York) 1979.
[9] Hiltrop K., in Chirality in Liquid Crystals, edited by Kitzerow H. S. and Bahr C. (Springer-Verlag, New York) 2001.
[10] Sato T. and Teramoto A., Adv. Polym. Sci., 126 (1996) 85.
[11] Werbowyj R. S. and Gray D. G., Mol. Cryst. Liq. Cryst., 34 (1976) 97.
[12] Revol J.-F. and Marchessault R. H., Int. J. Biol. Macromol., 15 (1993) 329.
[13] van Winkle D. H., Davidson M. W., Chen W. X. and Rill R. L., Macromolecules, 23 (1990) 4140.
[14] Yevdokimov Y. M., Skuridin S. G. and Salyanov V. I., Liq. Cryst., 3 (1988) 1443.
[15] Stanley C. B., Hong H. and Strey H. H., Biophys. J., 89 (2006) 2552.
[16] Dogic Z. and Fraden S., Langmuir, 16 (2000) 7820.
[17] Grelet E. and Fraden S., Phys. Rev. Lett., 90 (2003) 198302.
[18] DuPré D. B. and Duke R. W., J. Chem. Phys., 63 (1975) 143.
[19] Yoshida K., Teramoto A., Nakamura N. and Sato T., Macromolecules, 36 (2003) 2108.
[20] Dong X. M. and Gray D. G., Langmuir, 13 (1997) 2404.
[21] Miller A. F. and Donald A. M., Biomacromolecules, 4 (2003) 510.
[22] Dong X. M., Kimura T., Revol J. F. and Gray D. G., Langmuir, 12 (1996) 2076.
[23] de Gennes P. G. and Prost J., The Physics of Liquid Crystals (Clarendon Press, Oxford) 1993.
[24] Straley J. P., Phys. Rev. A, 8 (1973) 2181.
[25] Jäkli A., Bailey C. and Harden J., in Thermotropic Liquid Crystals, edited by Ramamurthi A. (Springer, Netherlands) 2007, p. 59.
[26] Kimura H., Hosino M. and Nakano H., J. Phys. Soc. Jpn., 51 (1982) 1584.
[27] Orts W. J., Godbout L., Marchessault R. H. and Revol J.-F., Macromolecules, 31 (1998) 5717.
[28] Pelcovits R. A., Liq. Cryst., 21 (1996) 361.
[29] Tombolato F. and Ferrari A., J. Chem. Phys., 122 (2005) 054908.
[30] Frezza E., Ferrari A., Kolli H. B., Giacometti A. and Cinacchi G., J. Chem. Phys., 138 (2013) 164906.
[31] Goossens W. J. A., Mol. Cryst. Liq. Cryst., 12 (1971) 237.
[32] Berardi R., Kuball H., Memmer R. and Zannoni C., J. Chem. Soc., Faraday Trans., 94 (1998) 1229.
[33] van der Meer B. W., Vertogen G., Dekker A. J. and Ypma J. G. J., J. Chem. Phys., 65 (1976) 3935.
[34] Lin-Liu Y. R., Shih Y. M. and Woo C. W., Phys. Rev. A, 15 (1977) 2530.
[35] Onsager L., Ann. N. Y. Acad. Sci., 51 (1949) 627.
[36] Varga S. and Jackson G., Mol. Phys., 104 (2006) 3681.
[37] Wensink H. H. and Jackson G., J. Chem. Phys., 130 (2009) 234911.
[38] Watanabe J. and Nagase T., Macromolecules, 21 (1988) 171.
[39] Yamagishi T., Fukushima T., Miyamoto T., Ichizuka T. and Watanabe J., Liq. Cryst., 7 (1990) 155.
[40] Wensink H. H. and Jackson G., J. Phys.: Condens. Matter, 23 (2011) 194107.
[41] Israelachvili J. N., Intermolecular and Surface Forces (Academic Press, London) 1991.
[42] Harris A. B., Kamien R. D. and Lubensky T. C., Rev. Mod. Phys., 71 (1999) 1745.
[43] Straley J. P., Phys. Rev. A, 14 (1976) 1835.
[44] Allen M. P., Evans G. T., Frenkel D. and Mulder B. M., Adv. Chem. Phys., 86 (1993) 1.
[45] Stroobants A., Lekkerkerker H. N. W. and Oudijk T., Macromolecules, 19 (1986) 2232.
[46] Odlum T., J. Phys. Chem., 91 (1987) 6060.
[47] Tombolato F., Ferrari A. and Grellet E., Phys. Rev. Lett., 96 (2006) 258302.
[48] Sackmann E., Meiboom S., Snyder L. C., Meixner A. E. and Dieltz R. E., J. Am. Chem. Soc., 90 (1968) 3567.
[49] Zanchetta G., Giavazzi F., Nakata M., Buscaglia M., Cerbino R., Clark N. A. and Bellini T., Proc. Natl. Acad. Sci. U.S.A., 107 (2010) 17497.
[50] Kopf V., Zhang Z. and Genack A., Prog. Quantum Electron., 27 (2003) 369.