Cholesteric order in systems of helical Yukawa rods

H H Wensink\(^1\) and G Jackson

Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, UK

E-mail: wensink@thphy.uni-duesseldorf.de

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Abstract
We consider the interaction potential between two chiral rod-like colloids which consist of a thin cylindrical backbone decorated with a helical charge distribution on the cylinder surface. For sufficiently slender helical rods a simple scaling expression is derived which relates the chiral ‘twisting’ potential to the microscopic properties of the particles, such as the internal helical pitch, charge density and electrostatic screening parameter. To predict the behaviour of the macroscopic cholesteric pitch of the fluid bulk phase we invoke a simple second-virial theory generalized to treat anisotropic states with weakly twisted director fields. It is shown that, while particles with weakly coiled helices always form a cholesteric phase whose helical sense is commensurate with that of the internal helix, more strongly coiled rods lead to the formation of a cholesteric state of opposite sense. The correlation between the helical symmetry at the microscopic and macroscopic scale is found to be very sensitive to the pitch of the Yukawa helix. Mixing helical particles of sufficiently disparate length and internal pitch may give rise to a demixing of the uniform cholesteric phase into two fractions with a different macroscopic pitch. Our findings could be relevant to the interpretation of experimental observations in systems of cellulose and chitin microfibres, DNA and fd virus rods.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
In contrast to a nematic phase, where the nematic director (direction of preferential orientational order) is homogeneous throughout the system, the cholesteric (chiral nematic) phase is characterized by a helical arrangement of the director field along a common pitch axis. As a result, the cholesteric phase possesses an additional mesoscopic length scale, commonly referred to as the ‘cholesteric pitch’, which characterizes the distance along the pitch axis over which the local director makes a full turn\(^1\). The behaviour of the pitch as a function of density, temperature and solvent conditions is of great fundamental and practical importance as the unique rheological, electrical and optical properties of cholesteric materials are determined in large part by the topology of the nematic director field\(^1,2\).

\(^1\) Present address: Institute for Theoretical Physics: Soft Matter, Heinrich-Heine-University-Düsseldorf, Universitätsstraße 1, D-40225, Düsseldorf, Germany.

A considerable research effort has been devoted to studying chirality in lyotropic liquid crystals comprising colloidal particles or stiff polymers immersed in a solvent. In addition to a number of synthetic helical polymers such as polyisocyanates\(^3,4\) and polysilanes\(^5\) which form cholesteric phases in organic solvents, there is a large class of helical bio-polymers which have long been known to form cholesteric phases in water. Examples are DNA\(^6,7\), the rod-like fd virus\(^8\), polypeptides\(^9,10\), chiral micelles\(^11\), polysaccharides\(^12\), microfibrillar cellulose (and its derivatives)\(^13\) and chitin\(^14\). In these systems, the cholesteric pitch exhibits a marked dependence on the particle concentration, and temperature as well as, for example, the ionic strength which has been the subject of extensive experimental research\(^6,15–24\).

The sensitivity of the properties of cholesteric phases on the nature of the electrostatic interactions is perhaps not that surprising as the relative stability of achiral nematic and smectic liquid crystalline phases formed by thermotropic liquid crystals are well known to be affected by the disposition.
of polar groups on the molecule [1] (for example, see the studies on the effect of varying the position and orientation of dipoles on the molecular core on the stability of the various mesophases [25–29]).

Understanding the connection between the molecular interactions responsible for chirality at the microscopic scale and the structure of the (macroscopic) bulk cholesteric phase has been a long-standing challenge in the physics of liquid crystals [1]. The chiral nature of most biomacromolecules originates from a spatially non-uniform electrostatic distribution of charges on the molecule. The most prominent example is the double-helix backbone structure adopted by the phosphate groups in DNA which gives rise to right-handed superstructures in the anisotropic phase. Combining the electrostatic interactions with the intrinsic conformation of the particle allows for a coarse-grained description in terms of particles with an effective shape which generates chiral nematic order at the macroscopic scale. Examples are bent-core [30] or banana-shaped molecules [31] where the mesogen shape is primarily responsible for chirality [32]. Many other helical bio-polymers and microfibrillar assemblies of chiral molecules (such as cellulose) can be mapped onto effective chiral objects such as athreaded cylinder [32–34], twisted rod [14, 35] or semi-flexible helix [36].

The development of a microscopic theory for the cholesteric phase is a serious challenge owing to the complexity of the underlying chiral interaction and the anisotropic nature of the phase [37]. Coarse-grained model potentials aimed at capturing the essentials of the complex molecular nature of the surface electrostatics of such macromolecules have been devised mainly to treat DNA [38–43]. A more general electrostatic model potential for chiral interactions was proposed much earlier by Goossens [44] based on a spatial arrangement of dipole–dipole and dipole–quadrupole interactions which can be cast as a multipole expansion in terms of tractable pseudo-scalar potentials [45]. This type of electrostatic description of the chiral interaction can be combined with a Maier–Saupe mean-field treatment [46–51], or with a bare hard-core model and treated within the seminal theory of Onsager [52–54].

A drawback of the Goossens potential is that its simple form precludes an explicit connection with the underlying microscopic (electrostatic) interactions involved. As a consequence, the potential is unsuitable for studying the sensitivity of the cholesteric pitch of charged rod-like colloids where the strength of the chiral interactions depends strongly on the configuration of the surface charges and the electrostatic screening (namely salt concentration). In this paper, we propose a simple but explicit model for long-ranged chiral interactions based on an impenetrable cylindrical rod decorated with a helical distribution of charges located on the rod surface. The local interactions between the charged helix segments is represented by a simple Yukawa potential in line with the Debye–Hückel approximation appropriate for weakly charged poly-electrolytes [55]. A subsequent analysis of the chiral potential between a pair of rods comprising helical Yukawa segments leads to a simple general expression which relates the intrinsic twisting potential to the electrostatic screening, charge density and internal pitch of the helical particles. The overall form of the chiral Yukawa potential resembles the one proposed by Goossens [44], albeit with a longer-ranged decay with respect to the interparticle distance. The most important difference, however, is that the amplitude of the chiral Yukawa potential can then be linked to the helix configuration and the local electrostatic potential. By mapping a chiral charge distribution onto a simple Yukawa helix the present model can be conceived as a simple prototype model to explain the cholesteric organization in aqueous solutions of cellulose [35, 56] or chitin microfibers [14]. Likewise, the α-helical structure of polypeptide molecules [34] can also be interpreted as a coiled rod on a coarse-grained level.

In the second part of this analysis, the potential is employed within a simple Onsager second-virial theory (see Onsager’s original paper [52] and the reviews in [57, 58] for a detailed description of the theory for achiral nematic phases) to predict the behaviour of the macroscopic cholesteric pitch of Yukawa helices. The sensitivity of the equilibrium pitch of the cholesteric phase with respect to the helix configuration and amplitude of the electrostatic interactions is scrutinized in detail. The implications of mixing two helical species with different lengths and/or internal pitches on the isotropic–cholesteric phase behaviour are also considered.

The theoretical description is found to be consistent with experimental findings and correctly captures the response of the cholesteric pitch to the variation of the particle concentration and salt content. The theory also unveils the subtle relationship between the internal conformation (e.g. internal pitch) of the helical rod and the handedness of the cholesteric phase. The delicate relationship between the helical symmetry of the macroscopic cholesteric state and the internal helicity of the rod is consistent with experimental observations in aqueous suspensions of filamentous virus systems such as fd [59] and M13 [60] and with numerical calculations based on a more chemically explicit poly-electrolyte site model [60].

This paper is structured as follows: in section 2 we introduce the helical Yukawa model and derive a general expression for the chiral potential imparted by the helical charge distribution. The effect of the various features of the potential on the cholesteric pitch is analysed in detail in section 3 where we focus first on monodisperse systems of identical helical particles followed by a treatment of binary mixtures of Yukawa helices differing in length and/or internal pitch. Finally, section 4 is devoted to a discussion and some concluding remarks.

2. Chiral interaction between Yukawa helices

In this study we aim to quantify the chiral or twisting potential of a pair of colloidal rods with a helical charge distribution starting from a continuum electrostatic model based on a screened Coulombic (or Yukawa) potential. Within a linearized Poisson–Boltzmann theory the electrostatic interaction $U(r)$ between two charged point particles with equal charge $±Ze$ in a dielectric medium with a relative permittivity $\varepsilon_r(\varepsilon_0)$ being the
value in vacuum) is given by \[55\]
\[\beta U_N(r) = Z^2 \lambda_B \frac{\exp[-\kappa r]}{r} \]
(1)
where \(\beta = 1/(k_BT)\) with \(T\) the temperature and \(\lambda_B\) the Boltzmann constant, \(r\) is the distance between the particles, \(\lambda_B = e^2/(4\pi\varepsilon_0 k_B T)\) is the Bjerrum length (\(\lambda_B = 0.7\) nm for water at \(T = 298\) K) and \(\kappa\) is the Debye screening constant \(\kappa = \sqrt{4\pi\lambda_B(Z\rho + 2c_i)}\) which characterizes the extent of the electric double layer surrounding each particle. Here, \(\rho = N/V\) is the particle density and \(c_i\) refers to the concentration of added monovalent salt.

Equation (1) can be generalized in a straightforward manner to describe the interaction between two helical macroions in three spatial dimensions by assuming that the total pair potential can be written as a summation over Yukawa sites residing on the helices (see figure 1). In the limit of an infinite number of sites per unit length, the electrostatic potential of helical rods of variable lengths \(L_1\) and \(L_2\), and common diameter \(D\) at centre-of-mass positions \([r_1, r_2]\) and with orientational unit vectors \([\hat{u}_i, \hat{u}_j]\) and azimuthal angles \([\psi_i, \psi_j]\) (describing the helix orientation perpendicular to the pitch direction \(\hat{u}_i\)) are then given by a double contour integral over the longitudinal (pitch) axes of the helices:

\[\beta U_N(\Delta r, \hat{u}_i, \hat{u}_j, \psi_i, \psi_j) = \frac{1}{Z_i Z_j \lambda_B} \int_{-1}^{1} dt_1 \int_{-1}^{1} dt_2 \frac{\exp[-\kappa|\hat{r}_2 - \hat{r}_1|]}{|\hat{r}_2 - \hat{r}_1|^2} \]
(2)
where \(\Delta r = r_2 - r_1\) is the distance vector between the centres-of-masses of the helices and \(Z_i\) is the total number of charges on species \(i\).

In order to describe the segment position \(\hat{r}_i\) along the contour of helix \(i\) it is expedient to introduce a particle-based Cartesian frame spanned by three orthogonal unit vectors \([\hat{u}_i, \hat{v}_i, \hat{w}_i]\) \((i = 1, 2)\), where \(\hat{w}_1 = \hat{u}_1 \times \hat{u}_2/|\hat{u}_1 \times \hat{u}_2|\) and \(\hat{w}_2 = \hat{u}_2 \times \hat{u}_1\). Within this frame the segment positions can be parametrized in terms of dimensionless contour variables \(t_i\) \((-1 \leq t_i \leq 1\) in the following way:

\[\hat{r}_i = r_i + \frac{L_i}{2} \hat{u}_i + \frac{D}{2} \left[ \cos(k_1 t_i + \psi_i) \hat{v}_i + \sin(k_1 t_i + \psi_i) \hat{w}_i \right] \]
(3)
where \(k_1 = \pi L_1/p_{int}^{(i)}\) is the helical wavenumber of the particle and \(p_{int}^{(i)}\) the internal pitch, which corresponds to the distance along the longitudinal rod axis over which the helix makes a full turn. With this convention \(k_1 > 0\) corresponds to a right-handed helix and \(k_1 < 0\) to a left-handed one.

In this development we focus on the general case of a binary mixture of helical species with a different internal pitch (in terms of sign and/or magnitude), i.e. \(k_1 \neq k_2\). Since a helix is not invariant with respect to rotations about the longitudinal pitch axis \(\hat{u}_i\), there must be an additional orientational unit vector \(\hat{e}_i \perp \hat{u}_i\) to account for its azimuthal orientation with respect to \(\hat{u}_i\). The interaction potential equation (2) must therefore depend on a set of internal azimuthal angles \(\psi_i\) \((0 \leq \psi_i \leq 2\pi)\), defined such that \(\cos \psi_i = \hat{w}_i \cdot \hat{e}_i\).

An expression for the norm of the segment–segment distance can be obtained from equation (3), which can subsequently be used in equation (2) to establish the full electrostatic potential. This potential can, however, be greatly simplified in the case of sufficiently slender helical particles \((D/L_1 \ll 1)\) by Taylor-expanding up to quadratic order in \(D/L_1\). The total potential can then be written as a sum of an achiral reference part \(U_N^{(0)}\) and a chiral term \(U_N^{(c)}\):

\[\beta U_N = \beta U_N^{(0)} + \beta U_N^{(c)} + O((D/L_1)^3)\]
(4)
The reference potential \(U_N^{(0)}\) in equation (4) is of \(O(\lambda_B/L_1)\) and represents the pair potential between two screened line charges of lengths \(L_1\) and \(L_2\) interacting through a Yukawa potential [61]. Taking the limit \(D/L_1\) to zero in equation (3) yields for equation (2)

\[\beta U_N^{(0)}(\Delta r, \hat{u}_1, \hat{u}_2) = \frac{1}{4} Z_1 Z_2 \frac{\lambda_B}{L_1} \int_{-1}^{1} dt_1 \int_{-1}^{1} dt_2 \frac{\exp[-\kappa L_1|\Delta \hat{r}|]}{|\Delta \hat{r}|} \]
(5)
where \(\Delta \hat{r}\) represents the distance between the positions \(t_1\) and \(t_2\) along the contour of the line charge (all distances are expressed in units \(L_1\)):

\[\Delta \hat{r}^2 = \Delta r^2 + [t_2(\hat{u}_1 \cdot \Delta \hat{r}) - t_1(\hat{u}_1 \cdot \Delta \hat{r})] + \frac{\ell}{4} [\hat{r}_1^2 + \hat{r}_2^2 - 2 \hat{r}_1 \hat{r}_2] \]
(6)
where \(\ell = L_2/L_1\) is the length ratio. The potential in equation (5) is strictly achiral and shall be disregarded in the remainder of this paper. The second term in equation (4) is the leading order chiral potential \(U_N^{(c)}\) imparted by the internal helical structure of the rods. This contribution requires a little effort to derive but can be obtained in a straightforward manner by linearizing the double contour integral in equation (2) with respect to \(D/L_1\). The resulting expression can be simplified considerably by applying the standard trigonometric addition...
formulae and exploiting the orthogonality of the unit vectors that make up the particle frame. The chiral potential is of quadratic order in $D/L_1$ and can be cast in the following form:

$$\beta U^{(c)}(\Delta r, \hat{u}_1, \hat{u}_2, \psi_1, \psi_2) = -\frac{1}{4} Z_1 Z_2 \left( \frac{\lambda B}{D} \right) \left( \frac{D}{L_1} \right)^2 \int_{-1}^{1} \int_{-1}^{1} d_1 d_2 U^c_1(\Delta r) \times \{ A \cos \psi_1 + B \cos \psi_2 + C \sin \psi_1 + D \sin \psi_2 \}.$$  

(7)

This expression will be the focus of our further analysis. The chiral potential depends on the derivative of the Yukawa potential $U^c_0(x) = -\delta(\exp[-\kappa L_1 x]/x)\partial x$ and thus decays much more steeply with the rod separation distance than the achiral Yukawa reference potential in equation (5). The chiral symmetry of equation (7) is reflected by the coefficients $A$ to $D$ which are all variant upon applying a parity transformation $\Delta r \rightarrow -\Delta r$:

$$A = -\cos(k_1 t_1)(\hat{v} \cdot \Delta r) - \sin(k_1 t_1)(\hat{w}_1 \cdot \Delta r)$$

$$B = \cos(k_2 t_2)(\hat{v} \cdot \Delta r) + \sin(k_2 t_2)(\hat{w}_2 \cdot \Delta r)$$

$$C = \sin(k_1 t_1)(\hat{v} \cdot \Delta r) - \cos(k_1 t_1)(\hat{w}_1 \cdot \Delta r)$$

$$D = -\sin(k_2 t_2)(\hat{v} \cdot \Delta r) + \cos(k_2 t_2)(\hat{w}_2 \cdot \Delta r)$$

(8)

The next step is to construct an angle-averaged potential $\beta U^{(c)}_1$ which eliminates the explicit dependence on the internal azimuthal angles. This procedure essentially quantifies the degree of azimuthal correlations between the helical particles. In the case of azimuthally uncorrelated rods all azimuthal angles $\psi_i$ are equally probable and the chiral potential reduces to zero, as can be inferred from integrating equation (7) over the range of $\psi_i$ [42]. In reality, the correlations between the azimuthal orientations are nonzero as they constitute a prerequisite for the stability of cholesteric order [37]. A physically intuitive way to incorporate these correlations is by requiring the Helmholtz free energy of the azimuthally averaged potential to be equal to that of the original $\psi$-dependent potential. The procedure leads to the following expression for the angle-averaged potential [62]:

$$\beta U^{(c)}_1(\Delta r) \equiv -\ln[\exp[-\beta U^{(c)}_1(\psi)]]_\psi = (\beta U^{(c)}_1(\psi)) - \frac{1}{2} ([\beta U^{(c)}_1(\psi)]^2) + O([\beta U^{(c)}_1(\psi)]^3)$$

(9)

where the brackets denote a double integral over the internal angles, i.e. $\langle \psi \rangle = (2\pi)^{-1} \int_0^{2\pi} d \psi$. A similar expression can be obtained starting from a self-consistent Boltzmann-weighted average of the chiral potential, i.e. $\bar{U} = \langle U \exp[-\beta U] \rangle / \langle \exp[-\beta U] \rangle$ and Taylor-expanding for small $U$. This will give the same result up to a constant prefactor in the fluctuation term [63, 64]. The leading-order contribution $(\beta U^{(c)}_1(\psi))_\psi$ vanishes upon integrating over $\psi$, (as it does in the case of a point dipole interaction) so that we need to consider the next-order fluctuation term in equation (9).

Using the isotropic averages $\langle \cos^2 \psi \rangle_\psi = (\sin^2 \psi) = 1/2$ the angle-averaged chiral potential becomes

$$\beta U^{(c)}_1(\Delta r, \hat{u}_1, \hat{u}_2) \simeq -\frac{1}{16} Z_1^2 Z_2^2 \left( \frac{\lambda B}{D} \right) \left( \frac{D}{L_1} \right)^4 \left( \hat{A}^2 + \hat{B}^2 + \hat{C}^2 + \hat{D}^2 \right)$$

(10)

where

$$\hat{A} = \int_{-1}^{1} \int_{-1}^{1} d_1 d_2 U^c_1(\Delta r) A \int_{-1}^{1} d_1 d_2 U^c_1(\Delta r) \int_{-1}^{1} d_1 d_2 U^c_1(\Delta r) \int_{-1}^{1} d_1 d_2 U^c_1(\Delta r)$$

and identical relations for the other coefficients $\hat{B}$, $\hat{C}$ and $\hat{D}$. A close inspection of the coefficients (cf equation (8)) reveals that only those terms proportional to the pseudo-scalar $\hat{v} \cdot \Delta r$ contribute to the chiral potential. These are given by products involving the first and third terms in equation (8). All other contributions are invariant under a parity transformation which renders them irrelevant for the present analysis. If we use the standard representation for the triple product $\hat{u}_1 \times (\hat{u}_1 \times \hat{u}_2) = \hat{u}_1 (\hat{u}_1 \cdot \hat{u}_2) - \hat{u}_2 (\hat{u}_1 \cdot \hat{u}_1)$ so that $-\hat{w}_1 \cdot \hat{u}_2 = \hat{w}_2 \cdot \hat{u}_1 = \sin \gamma$ (with $\gamma$ the angle between the main axes of the helices) the chiral potential simplifies to

$$\beta U^{(c)}_1(\Delta r, \hat{u}_1, \hat{u}_2) \simeq -\frac{1}{32} Z_1^2 Z_2^2 \left( \frac{\lambda B}{D} \right) \left( \frac{D}{L_1} \right)^2 \times F_{12}(\Delta r, \hat{u}_1, \hat{u}_2, k_1, k_2)_{T_{12}}$$

(12)

in terms of a pseudo-scalar $T_{12}$ which changes sign under a parity transformation [45]:

$$T_{12} = (\hat{u}_1 \times \hat{u}_2 \cdot \Delta \hat{r})$$

(13)

with $\Delta \hat{r} = \Delta r/|\Delta r|$ the centre-of-mass unit vector. The function $F_{12}$ depends on the interparticle distance and helix orientations and is invariant under parity change:

$$F_{12}(\Delta r, \hat{u}_1, \hat{u}_2, k_1, k_2) = -\langle \cos(k_1 t_1) \rangle_\psi \langle \ell t_2 \sin(k_1 t_1) \rangle_\psi \langle \cos(k_2 t_2) \rangle_{\psi} \langle \ell t_2 \sin(k_2 t_2) \rangle_\psi$$

(14)

where the brackets are shorthand notation for the double contour integration over $U^c_1$:

$$\langle \psi \rangle = \Delta r^{1/2} \int_{-1}^{1} d_1 d_2 U^c_1(\Delta r).$$

(15)

Since the prefactor $F_{12}$ depends rather intrinsically on the centre-of-mass distance and orientations it is desirable to seek a simplified form. This can be achieved by ignoring the interactions involving the ends of the helix. In the limit of $L_1/D \rightarrow \infty$ the second contribution in equation (6), which embodies the interaction between the end of one rod with the main section of the other, becomes vanishingly small. An equivalent approach would be to fix the centre-of-mass distance vector along the unit vector $\Delta \hat{r} = \Delta \hat{r}$. In either case, the segment–segment distance equation (6) simplifies to

$$\Delta r^2 \simeq \Delta r^2 + \frac{1}{2}(\hat{u}_1^2 + \hat{u}_2^2 - 2\ell t_1 t_2 \cos \gamma)$$

(16)
where the orientation dependence is contained in the angle \( \gamma \) (with \( \cos \gamma = \hat{u}_1 \cdot \hat{u}_2 \)) between the main axes of the helices. The dependence of the chiral potential on \( \gamma \) at a fixed centre-of-mass distance is depicted in figure 2 and reveals a marked non-monotonic relation. In a concentrated cholesteric nematic phase the rods are usually strongly aligned along the local director so that \( \gamma \) will, on average, be very small. In the asymptotic limit of strong local orientational order it is justified to set \( \gamma = 0 \) which gives the following scaling expression for the chiral potential:

\[
\beta U_Y^{(c)} \sim \gamma F_{12}(\Delta r, k_1, k_2)(\hat{v} \cdot \Delta \hat{r})
\]  

where \( \Delta r = [\Delta r^2 + \frac{1}{2}(t_1 - t_2)^2]^{1/2} \). It is clear from the local minima appearing in figure 2 that the asymptotic approximation has to be taken with some care in the dilute regime where the average value of \( \gamma \) is no longer very small. A striking anomaly occurs for \( k = 4 \) where the direction of the chiral torque \( (\partial U_Y^{(c)}/\partial \gamma)_{\gamma=0} \) is opposite to that of the other cases shown. Moreover, the local and global minimum appearing for \( k = 4 \) correspond to opposite twist directions. This hints to a subtle relationship between the magnitude of the internal pitch and the sense of the cholesteric director field which is explored in detail in subsequent sections. In the asymptotic approximation, the distance dependence of the chiral potential is incorporated in the chiral amplitude \( F_{12}(\Delta r, k_1, k_2) \) which will be analysed in the following paragraphs where we focus on identical and enantiomeric helices, respectively.

2.1. Identical helices

If the helices are identical, then \( L_1 = L_2 = L \) (\( \ell = 1 \), \( k_1 = k_2 = k \) and \( Z_1 = Z_2 = Z \). The double contour integration in equation (15) is invariant under interchanging \( t_1 \leftrightarrow t_2 \) and we can exploit this symmetry to simplify equation (14) as follows:

\[
F(\Delta r, k) = -2(\cos(kt_1) - t_2 \sin(kt_1)) \ell + 2(\sin(kt_1) - t_2 \cos(kt_1))\ell.
\]  

The second contribution involves odd terms in \( t_1 \) and \( t_2 \) which vanish on performing the double contour integration (cf equation (15)). This leaves us with the following set of double contour integrals:

\[
F(\Delta r, k) = -2\Delta r \int_{-1}^{1} dt_1 \int_{-1}^{1} dt_2 U_Y^{(c)}(\Delta \hat{r}) \cos(kt_1) \\
\times \left( \int_{-1}^{1} dt_1 \int_{-1}^{1} dt_2 U_Y^{(c)}(\Delta \hat{r}) t_2 \sin(kt_1) \right)
\]  

which implicitly depends on the reciprocal pitch \( k \) and Debye screening length \( \kappa L \). The chiral potential between two identical helical Yukawa rods can now be expressed as

\[
\beta U_Y^{(c)}(\Delta r, \hat{u}_1, \hat{u}_2) \simeq -\frac{1}{32}Z^2 \left( \frac{\lambda_0}{D} \right)^2 \left( \frac{D}{L} \right)^4 \frac{\Delta r}{L} F(\Delta r, k)T_{212}.
\]  

The explicit form of the chiral potential is depicted in figure 3, and it is found to decay steeply with increasing rod centre-of-mass inter-separation. Owing to the intractable nature of the double contour integrations, the distance dependence of the potential is essentially non-algebraic and does not obey a simple power-law scaling with respect to the interparticle separation \( \Delta r \). At short distances the amplitudes appear to depend principally on the internal pitch rather than the screening constant.

It is worthwhile to compare the form of the chiral potential in equation (20) to the one proposed by Goossens [44, 54]. This potential emerges as the leading order contribution from a multipole expansion of the interaction potential between two molecules, each composed of an array of dipoles (then described in terms of Maier–Saupe-type quadrupole interactions). This potential takes the following generic form:

\[
U_{GS}(\Delta r, \hat{u}_1, \hat{u}_2) = -U_0 \left( \frac{\Delta r}{L} \right)^{\gamma} (\cos \gamma) T_{212}
\]  

where the sign of the amplitude \( U_0 \) determines the handedness of the chiral interaction. Both chiral potentials are invariant with respect to an inversion of the rod orientation \( \hat{u}_i \rightarrow -\hat{u}_i \).
or equivalently γ → γ ± πl. As can be gleaned from Figure 3, the distance dependence of the chiral Yukawa potential for short helix inter-separations is much weaker than that of the Goosens potential, indicating that the chiral forces are much longer ranged in the present case.

2.2. Enantiomers: helices with opposed handedness

Let us now consider two helices of identical length L1 = L2 = L and charge Z1 = Z2 = Z but with opposite internal pitch sense k1 = −k2. The corresponding cross-interaction between the right-handed and left-handed helices then follows from equation (14):

\[ \mathcal{F}_{12}(\Delta \ell, k_1, -k_1) = -\langle \cos(k_1 \ell_1) \rangle_t \langle t_2 \sin(k_1 \ell_2) \rangle_t 
- \langle \cos(-k_1 \ell_2) \rangle_t \langle t_2 \sin(-k_1 \ell_1) \rangle_t 
+ \langle \sin(k_1 \ell_1) \rangle_t \langle t_2 \cos(k_1 \ell_2) \rangle_t 
+ \langle \sin(-k_1 \ell_2) \rangle_t \langle t_2 \cos(-k_1 \ell_1) \rangle_t, \]

irrespective of the magnitude of the internal pitch. That the unlike interaction vanishes in this case is not surprising: this implies that an equimolar binary mixture of helices of opposite handedness (a so-called ‘racemic’ mixture) does not exhibit cholesteric order. If the rods are of different lengths (l ≠ 1) the particles no longer form an enantiomeric pair and the chiral interaction will generally be nonzero.

3. Prediction of the cholesteric pitch

A study of the relationship between the internal helical structure of the particles and the (macroscopic) cholesteric order requires a statistical theory which is able to make a connection between the pair interaction of the particles and the local equilibrium orientational distribution, characterized by the single-particle function f(\*u - \*n), and cholesteric pitch. Such a theory can be devised starting from the statistical theory of Onsager [52] for infinitely thin hard rods which exhibit common uniaxial nematic order. The theory was generalized by Straley [65, 66] for aligned fluids with weakly non-uniform director fields, such as a cholesteric liquid crystal, in which case elastic contributions must be incorporated into the free energy. The Helmholtz free energy density \( F/V \) of a binary mixture of chiral rods in a cholesteric phase of volume V takes the following form:

\[
\beta F/V = \rho (\ln \rho \overline{\nu} - 1) + \rho \sum_i \int d\*u f_i(\overline{\nu}) \ln[x_i 4 \pi f_i(\overline{\nu})]
+ \beta \sum_i \sum_j x_i x_j \left( K^{ij}_0 - K^{ij}_1 q + \frac{K^{ij}_2}{2} q^2 \right) \]

where \( \overline{\nu} = \prod_i V_i \) is a weighted product of the thermal volume \( V_i \) of each particle i which includes contributions arising from the translational and rotational momenta. The first two terms in the free energy describe the ideal translational, mixing and orientational entropy of the system while the last represents the residual free energy which accounts for the interactions between the rods at the approximate second-virial level. The latter consists of three contributions. The first, \( K_0 \), refers to the (achiral) nematic reference state and involves a double weighted average in terms of the orientational distribution functions (ODFs) \( f_i(\hat{u}) \) of the respective species [52]:

\[
\beta K^{ij}_0 = \frac{\beta}{2} \int d\*u_1 f_i(\overline{\nu}) \int d\*u_2 f_j(\overline{\nu}) M^{ij}_0(\overline{\nu}^-) \]

where the generalized kernel is defined as

\[ M^{ij}_0(\hat{u}_1, \hat{u}_2) = -\int d\Delta \*r(\Delta \*z)^n [\exp(-\beta U_{ij}) - 1]. \]

For hard anisometric bodies, the pair potential \( U_{ij} \) is infinitely large if the rods overlap and zero otherwise. The spatial integral \( M^{ij}_0 \) then yields the excluded volume \( v_{ij}^{excl}(\hat{u}_1, \hat{u}_2) \) between particles of species i and j (which is equal to twice the second-virial coefficient [52]). The second and third contributions in the residual free energy represent the change of free energy due to the twist deformation of the director field. The strength of this deformation is characterized by a helical wavenumber \( q = 2\pi/p, \) with \( p \gg p_{\text{int}} \) the macroscopic pitch length associated with the helical director field. Since the present theory is only valid for long-wavelength distortions of the director field it is required that \( p \gg L (qL \ll 1) \). The torque-field contribution, proportional to \( K^{ij}_1 q \), arises from the chiral torque imparted by the chirality of the particles and leads to a reduction of the free energy on the formation of a macroscopic cholesteric structure. Opposing this, there is an elastic response counteracting the helical deformation of the director field. The corresponding free energy penalty \( K^{ij}_2 q^2 \) is proportional to the twist-elastic constant \( K^{ij}_2 \). As with the excluded-volume contribution \( K_0 \), the torque-field and twist-elastic constants are given by double orientational averages of \( M^{ij}_0 \), albeit in a more complicated way [66]:

\[
\beta K^{ij}_1 = \frac{\beta}{2} \int d\*u_1 f_i(\overline{\nu}) \int d\*u_2 f_j(\overline{\nu}) (\overline{\hat{u}}_1 \cdot \overline{\hat{y}}) M^{ij}_1(\overline{\nu}^-) 
\times \int d\*u_2 f_j(\overline{\nu}) (\overline{\hat{u}}_2 \cdot \overline{\hat{y}}) M^{ij}_1(\overline{\nu}^-) \]

where \( \hat{f} \) represents the derivative of the ODF with respect to its argument. In arriving at equation (26) we have implicitly fixed the pitch direction along the z direction of the laboratory frame with the local nematic director \( \overline{\hat{n}}(z) \) pointing along the \( x \) direction of the Cartesian laboratory frame \( \{\overline{x}, \overline{y}, \overline{z}\} \).

Let us now consider a model binary mixture of hard rods of different lengths (l ≠ 1) decorated with a weak chiral potential of the form proposed in the previous section (cf equation (12)). The twist-elastic constant is not affected by the weak chiral potential but only by the non-chiral excluded-volume and electrostatic contributions arising from the Yukawa potential. If we neglect the electrostatic contributions, the kernels \( M^{ij}_n \) reduce to integrals over the excluded-volume manifold of two thin hard cylinders weighted over powers of the pitch distance variable \( \Delta z \):

\[ M^{ij}_n(\hat{u}_1, \hat{u}_2) = \int_{[\Delta \*r(\Delta \*z) = n]} d\Delta \*r(\Delta \*z)^n, \quad n = 0, 2, \]

(27)
These quantities have been calculated for hard spherocylinders of arbitrary shape in [54]. Here, we only need the leading order contributions for large \( L_1 / D \):

\[
M_{ij}^{\ell}(\hat{u}_1, \hat{u}_2) = v_{\text{excl}}^{ij}(\hat{u}_1, \hat{u}_2) = 2L_1L_D |\sin \gamma|
\]

\[
M_{ij}^{\ell}(\hat{u}_1, \hat{u}_2) = \frac{L_1^2}{4}L_D |\sin \gamma| I^{ij}(\hat{u}_1, \hat{u}_2, \hat{z}^2)
\]

The effect of the Yukawa reference potential could, in principle, be taken into account by introducing an effective hard-core diameter \( D_{\text{eff}} > D \) which depends on the range of the electrostatic potential. Due to symmetry reasons the torque-field constant \( K_1 \) depends primarily on the chiral part of the potential. For weak chiral potentials considered here it is justified to approximate the Mayer function in equation (25) as \[ \exp\left(-\beta U_i\right) \cong -\beta U_i \text{ (if no particles overlap; otherwise it is -1)} \] analogous to a van der Waals perturbation approximation generalized to liquid crystals [54, 58, 67, 68]. The spatial integration pertaining to \( M_{ij}^{\ell} \) then becomes

\[
M_{ij}^{\ell}(\hat{u}_1, \hat{u}_2) = \int_{\Delta r, \Delta z} d\Delta r d\Delta z \beta U_j^{\ast}(\Delta r, \hat{u}_1, \hat{u}_2).
\]

Note that the integral runs over the ‘free’ volume, i.e. the space complementary to the excluded volume of the particles. By exploiting the cylindrical symmetry of the cholesteric system one can parametrize the distance vector in terms of cylindrical coordinates so that \( \Delta r = r \sin \zeta \hat{x} + r \cos \zeta \hat{y} + \Delta z \hat{z} \) (\( 0 \leq \zeta \leq 2\pi \)). With this, one can then write

\[
M_{ij}^{\ell}(\hat{u}_1, \hat{u}_2) = \frac{1}{4} \rho Z_1^2 Z_2^2 \lambda_0^2 D^2 \mathcal{W}(k_i, k_j) (\hat{u}_1 \times \hat{u}_2) \cdot \hat{z}
\]

where \( \mathcal{W} \) represents a spatial integral over the amplitude of the chiral potential for a given helicoidal wavenumber \( k_i \) of species \( i \): 

\[
\mathcal{W}(k_i, k_j) = -4\pi \int_0^\infty dr \int_0^{L_1} d\Delta z \left( \Delta z \right)^2 F_{ij}(\Delta r, k_i, k_j)
\]

with \( \Delta r = (r^2 + \Delta z^2)^{1/2} \) the centre-of-mass interparticle distance parametrized in terms of cylindrical coordinates \( \Delta r \) and \( r \) (both in units of \( L_1 \)). We remark that equation (30) is valid only if both rods are oriented perpendicular to the pitch axis \( \hat{z} \). The approximation can be justified in the present situation in which the local nematic order is assumed to be asymptotically large.

The next step is to perform double orientational averages of the moment contributions \( M_{ij}^{\ell} \) according to equation (26). It is expedient to adopt the Gaussian approximation, in which the ODF is represented by \( f_j(\hat{u}) \propto \exp\left(-\alpha_i(\hat{u} \cdot \hat{u})^2/2\right) \) in terms of a single variational parameter \( \alpha_i \) with an equilibrium value which corresponds to a minimum in the total free energy. If the local nematic order is strong enough (\( \alpha_i \gg 1 \)) the orientational averages can be estimated analytically by means of an asymptotic expansion for small inter-rod angles \( \gamma \). This procedure has been outlined in detail in [69, 54]. The result for the nematic reference contribution \( K_{ij}^{0} \) can be expressed (up to leading order in \( \alpha_i \)) as

\[
\beta K_{ij}^{0} \sim \rho^2 L_1 L_D \langle \gamma \rangle_0
\]

\[
\sim \rho^2 L_1 L_D \left( \frac{\pi}{2} \right)^{1/2} \left( \frac{\alpha_i + \alpha_j}{\alpha_i \alpha_j} \right)^{1/2}
\]

where the double brackets \( \langle \gamma \rangle_0 \) denote Gaussian orientational averages, specified in the appendix. Similarly, one can express the twist-elastic constant as

\[
\beta K_{ij}^{1} \sim \frac{\rho^2}{192} L_1 L_D \alpha_i \alpha_j \left( \frac{L_1^2 \langle \gamma \rangle_0^2}{\langle \gamma \rangle_0} \right)_0 - \langle \gamma \rangle_0 \left( \frac{\gamma \gamma^2}{\gamma_0^2} \right)_0
\]

\[
= \frac{\rho^2}{192} \left( 2\pi \right)^{1/2} L_1 L_D \left( \frac{L_1^2 \langle \gamma \rangle_0^2}{\langle \gamma \rangle_0} \right)_0
\]

\[
= \frac{L_1^2}{192} \left( 3\alpha_i^2 + 4\alpha_i \alpha_j \right) + L_1^2 \left( 3\alpha_j^2 + 4\alpha_i \alpha_j \right) \frac{\alpha_i^{1/2} \alpha_j^{1/2}}{\alpha_i + \alpha_j}^{3/2}
\]

Finally, the torque-field contribution can be written as

\[
\beta K_{ij}^{1} \sim \frac{\rho^2}{32} Z_1^2 Z_2^2 \lambda_0^2 D^2 \mathcal{W}(k_i, k_j)
\]

With this, the free energy is fully specified. Minimization with respect to \( q \) yields the equilibrium pitch as

\[
q = \frac{\sum_i \sum_j q_i q_j K_{ij}^{ij}}{\sum_i \sum_j q_i q_j K_{ij}^{ij}}
\]

For weakly cholesteric states (\( q L_1 \ll 1 \)), the local nematic order is only slightly affected by the twist director field and the equilibrium values for \( \alpha_i \) depend only on the free energy of the nematic reference state. Minimizing the free energy of the achiral system with respect to \( \alpha_i \) and rearranging terms leads to the following set of coupled equations:

\[
\alpha_1 = \frac{4\pi}{\pi} (x_1 + 2L_1^2 x_2 (1 + Q^{-1})^{-1/2})
\]

\[
Q = \left( \frac{2^{1/2} x_1 (1 + Q^{-1})^{-1/2} + x_2 \ell^2}{x_1 + 2^{1/2} x_2 (1 + Q^{-1})^{-1/2}} \right)^2
\]

expressed here in terms of the ratio \( Q = \alpha_2 / \alpha_1 \) and the overall dimensionless concentration \( c = NL_1^2 D/V \). These equations cannot be solved analytically but the solutions are easily obtained by iteration. It is important to note that both \( \alpha_1 \) and \( \alpha_2 \) increase quadratically with the concentration \( c \) since their ratio \( Q \) only depends on the mole fractions \( x_i \).

3.1. Monodisperse systems

For pure systems of infinitely thin helical particles, the twist-elastic constant in the asymptotic limit of strong orientational order (\( \alpha_i \gg 1 \)) simplifies to

\[
\beta K_D \sim \frac{14c}{192}
\]

as found by Odijk [33]. The macroscopic pitch can then be characterized in terms of the helical wavenumber as

\[
q L = \frac{2\pi L}{p} = \frac{K_1 Q}{K_2} \sim \frac{12}{7} c E_c
\]
where $E_c$ is a dimensionless parameter pertaining to the chiral potential which combines all of the microscopic characteristics of the helical particle such as the aspect ratio, surface charge and internal pitch (namely from equation (30)):

$$E_c \sim \frac{1}{4} Z^4 \left( \frac{\lambda_B}{D} \right)^2 \left( \frac{D}{L} \right)^3 W(k). \quad (39)$$

Since the electrostatic screening $k D$ depends on the rod concentration the variation of the pitch with concentration is strictly nonlinear, as shown in figure 4. To simplify matters we may state that typically $\lambda_B/D \sim O(10^{-1})$ for rod-like colloids in water. The rod charge $Z$ is expected to be directly proportional to the rod length $L$. Let us further introduce a charge density $\sigma_Z$, defined as the number of unit charges per unit length, so that $Z \sim \sigma_Z L$ and $Z^4 (D/L)^3 \sim O(L/D)$ (assuming the charge density $\sigma_Z D$ to be of order unity). The pitch length $p$ shown in figure 4 corresponds to 100–1000 particle lengths, a range which is commonly found in experiment [17, 18].

From figure 4 one can see that the pitch is a monotonically decreasing function of the rod concentration with the magnitude depending strongly on the salt concentration. At high $c_s$ the electrostatic repulsion between the Yukawa sites on the rods is strongly screened and the resulting chiral interaction will be attenuated significantly, corresponding to progressively longer pitches. The screening effect is common in dispersions of fd and DNA and supports the idea that chiral interactions are primarily mediated via long-range electrostatic interactions [19, 60]. We remark that for short-fragment (146 base pair) DNA the opposite trend is observed [17]; in this case the pitch is found to decrease with respect to salt concentration, i.e. charge screening leads to stronger chiral interactions between the DNA chains. This trend is most likely explained by the steric effect associated with the double helical backbone which becomes more pronounced as the charged phosphate groups residing on the backbone become increasingly screened. Clearly, the excluded volume of the helical grooves (neglected in this study) must be included explicitly to give a proper account of both steric and electrostatic contributions to microscopic chirality in DNA [42]. It is also possible that the salt may cause a structural change in the DNA (which is very sensitive to pH) which would change the disposition of the electrostatic groups.

Since our analysis is based on results from the (linearized) Poisson–Boltzmann equation all correlations between the co- and counterions that may be present at high salinities are neglected. These correlation effects may lead to qualitatively changes in the pitch behaviour as a function of salt concentration and temperature. We remark that the effect of the temperature on the chiral strength is rather trivial in the present picture: at high temperatures the chiral dispersion potential will become increasingly less important than the achiral hard-core potential associated with the cylindrical backbone which results in an increase of the pitch. This effect has been observed in systems of fd virus rods [18, 60].

The symmetry of the chiral interaction is governed entirely by the spatial integral over the chiral potential which depends rather intricately on the internal pitch of the Yukawa helix and the Debye screening length. The typical behaviour of the intrinsic chiral strength for two helical rods with $L/D = 50$ as a function of the internal pitch is shown in figure 5. For small helical wavenumbers, i.e. weakly coiled helical rods with a large internal pitch, the handedness of the helical director field is always commensurate with that of the internal helix, so that a right-handed cholesteric phase is formed from right-handed helices and a left-handed one from left-handed helices. A further increase of $\kappa$ leads to a reduction of the chiral strength and eventually a change of sign of the intrinsic chiral...
strength at $k = 3.26$ which corresponds to a sense inversion of the cholesteric helix. If $|k|$ exceeds this value the handedness of the cholesteric structure is no longer commensurate with that of the microscopic helical particles and a left-handed cholesteric state is obtained from right-handed particles and vice versa. Increasing $k$ even further reveals a strongly oscillatory relation between the microscopic and macroscopic pitch sense. The inversion nodes depend primarily on the shape of the internal Yukawa helix and are not affected by the electrostatic screening $\kappa D$. At high $k$, the twisting potential strongly decays and vanishes asymptotically for tightly coiled Yukawa rods ($k \to \infty$, $p_{\text{int}} \downarrow 0$) where the effective ‘width’ of the helical grooves becomes negligibly small.

3.2. Binary mixtures of helical rods of equal lengths ($\ell = 1$)

For a mixture of rods of equal length but different internal pitches ($k_1 \neq k_2$) and/or surface charges ($Z_1 \neq Z_2$), the situation is comparable to the monodisperse case since the twist-elastic constant is independent of these properties. Furthermore, we have $\alpha_1 = \alpha_2 = \alpha$ and the inverse cholesteric pitch is expressed by a form analogous to equation (38) as

$$q L = \frac{2\pi L}{p} \sim \frac{12c}{7} \xi_c.$$  

in terms of an effective chiral strength given by a simple (van der Waals one-fluid-like) mole fraction average of the different pair contributions

$$\xi_c = \sum_i \sum_j x_i x_j \xi_{ci} \xi_{cj}$$  

with $\xi_{ij}$ being a generalized version of equation (39):

$$\xi_{ij} = \frac{1}{4} \left( \frac{L_i}{D} \right)^2 \left( \frac{D}{D} \right)^3 \mathcal{W}(k_i, k_j).$$

3.3. Binary mixtures of helical rods of unequal lengths ($\ell \neq 1$)

In the case of a binary mixture of rods of different lengths the description is more complicated and most of the thermodynamic properties such as the cholesteric pitch can only be assessed numerically. Let us first investigate the effect of a weak chiral potential on the phase behaviour of mixtures of chiral rods with different length ratios. We must first consider the free energy of a binary mixture of infinitely thin hard rods of length ratio $\ell$ in the nematic phase. Within the Gaussian approximation it is given by [69, 70]

$$\frac{\beta F_{\text{nem}}}{N} \sim \ln c + \sum_i x_i (\ln x_i \alpha_i - 1) + c \sum_i \sum_j x_i x_j \frac{L_i L_j}{L} \langle \gamma \rangle$$

$$\sim \ln c + \sum_i x_i (\ln x_i \alpha_i - 1) + c \left( \frac{\pi}{\alpha_1} \right)^{1/2}$$

$$\times \left( x_1^2 + 2^1/2 x_1 x_2 \ell (1 + Q^{-1})^{1/2} + x_2^2 Q^{-1/2} \right).$$

For an isotropic phase the free energy simplifies to

$$\frac{\beta F_{\text{iso}}}{N} \sim \ln c + \sum_i x_i \ln x_i + c \frac{2\pi}{4} (x_1^2 + 2x_1 x_2 \ell + x_2^2 \ell^2).$$  

In the cholesteric phase we must take into account the change of free energy associated with the weak helical distortion of the director field as discussed in the preceding section:

$$\frac{\beta F_{\text{chol}}}{N} \sim \frac{\beta F_{\text{nem}}}{N} + \frac{1}{c} \sum_i \sum_j x_i x_j (\tilde{K}_{ij} (Q) \tilde{q} + \frac{1}{2} \tilde{K}_{ij} (Q) \tilde{q}^2)$$  

which upon minimization with respect to the inverse cholesteric pitch $\tilde{q} = 2\pi L_1/p$ yields

$$\frac{\beta F_{\text{chol}}}{N} \sim \frac{\beta F_{\text{nem}}}{N} - \frac{1}{2c} \sum_i \sum_j x_i x_j \tilde{K}_{ij} (Q).$$

We reiterate that this expression is only applicable in the regime $\tilde{q} \ll 1$ where the weak helical distortion of the director field does not interfere with the local orientational order. Since the twist-elastic constants are strictly positive, the second term in the free energy must be negative which implies that a small degree of chirality always leads to a reduction of the free energy of the system. Explicitly, the twist-elastic contributions are given by

$$\tilde{K}_{11} = \beta K_{11} D \sim \frac{7c^2}{192} \left( \frac{\pi}{\alpha_1} \right)^{1/2}$$

$$\tilde{K}_{22} = \beta K_{22} D \sim \frac{7c^2}{192} \left( \frac{\pi}{\alpha_1} \right)^{1/2} \ell^3 Q^{-1/2}$$

$$\tilde{K}_{12} = \beta K_{12} D \sim \frac{7c^2}{192} \left( \frac{\pi}{\alpha_1} \right)^{1/2} g(Q)$$

with

$$g(Q) = \frac{2^{1/2} (3Q^2 + 4Q) \ell + (3 + 4Q) \ell^3}{7Q^{1/2}(1 + Q)^{3/2}}.$$  

Similarly, one can express the torque-field contributions as

$$\tilde{K}_{ij} = \beta K_{ij} D L_1 \sim \frac{c^2}{8} \xi_{ij}.$$  

The free energy of the cholesteric phase for a binary mixture with $\ell \neq 1$ can now be rewritten as

$$\frac{\beta F_{\text{chol}}}{N} \sim \frac{\beta F_{\text{nem}}}{N} - \frac{3c^2}{28} G(x_i, Q) \xi_c^2$$

with

$$G(x_i, Q) = \left( \frac{x_1 + 2^{1/2} x_1 x_2 Q (1 + Q^{-1})^{-1/2}}{x_1^2 + 2x_1 x_2 Q (1 + Q^{-1})^{-1/2}} \right).$$

The corresponding cholesteric pitch wavenumber takes the following form:

$$\tilde{q} = \frac{2\pi L_1}{p} \sim \frac{12c}{7} \xi_c G(x_i, Q).$$
As required, this expression reduces to the form proposed in the previous subsections (cf equations (38) and (40)) upon substituting $\ell = 1$ and $Q = 1$. Recalling that $Q = Q(x)$, one can infer that the concentration dependence of the pitch is identical for mixtures and pure systems. The behaviour of the pitch with respect to the mole fraction $x_2 = 1 - x_1$, however, is non-trivial as we will see later on.

Let us now consider a binary mixture of helical rods with equal charge density $\sigma_c$ so that the mole-fraction-averaged chiral parameter $\vec{\xi}$ can be written in compact form as

$$\vec{\xi} = \xi_0(x_1^2\xi_{11} + 2x_1x_2\xi_{12} + x_2^2\xi_{22})$$  \hspace{1cm} (53)$$

in terms of an amplitude $\xi_0$ and phase factors $\xi_{ij}$:

$$\xi_0 = \frac{1}{4}(\sigma_c D)^2 \left( \frac{\lambda_B}{D} \right)^2 \left( \frac{L_1}{D} \right)$$  \hspace{1cm} (54)$$

$$\xi_{ij} = \mathcal{W}(k_i, k_j)$$

which need to be specified for the mixture of interest.

We first examine the case $\ell = 3$ with $k_1 = -k_2 = 1.4$, i.e. a mixture of short right-handed helices mixed with long left-handed ones of equal pitch magnitude. To simplify matters only dispersions with excess monovalent salt are considered such that the screening constant is fixed to $k L_1 = 50$, independent of the rod concentration. The phase diagrams of the chiral systems and the corresponding achiral hard-rod reference system are shown in figure 6. At low pressure the isotropic–nematic transition is only marginally affected by the chirality. At large pressure, however, the cholesteric phase shows a demixing into two coexisting cholesteric phases with opposite handedness. The demixing region is bounded by a lower critical point located at $qL = 0$, indicating that the cholesteric pitch diverges at the critical point. Note that a corresponding nematic–nematic demixing is not encountered for a hard-rod system at this particular length ratio. Within the Gaussian approximation this type of demixing only occurs above a critical length ratio $\ell > 3.167$ [70]. For mixtures of hard rods of different length but the same diameter the nematic–nematic binodals do not meet at a lower critical point but merge with the isotropic–nematic ones to produce an isotropic-nematic–nematic triphasic equilibrium, irrespective of the length ratio $\ell$; in the case of mixtures of rods of different diameters and lengths; however, a nematic–nematic critical point is possible [71–73]. The cholesteric–cholesteric demixing is driven primarily by the small chiral dispersion contribution to the rod interaction potential and does not arise from an interplay of the various entropic contributions (associated with mixing, free volume and orientational order), as is the case for the hard-rod mixtures. A similar demixing is observed for a mixture of right-handed helices with $k_1 = k_2 = 1.4$ at $\ell = 3$ and an amplitude of $\xi_0 = 0.4$, albeit at a much higher osmotic pressure. It is worth noting that in this case the cholesteric pitch does not diverge at the critical point but attains a finite value. For the case $\ell = 1$, i.e. helices of equal lengths, no demixing of the cholesteric state was found. This suggests that opposite handedness alone is insufficient to destabilize the uniform cholesteric phase and that a considerable asymmetry in length is required.

The behaviour of the cholesteric pitch across the range of mole fractions is shown in figure 7. For the first mixture of particles with opposite handedness, a quasi-linear reduction of the pitch wavenumber is observed, accompanied by a change of handedness upon increasing the mole fraction of the left-handed species.

![Figure 6](image_url)
Figure 7. The variation of the cholesteric pitch wavenumber $qL_1$ versus mole fraction at constant osmotic pressure and chiral amplitude $\varepsilon_0 = 0.4$: (a) helices of opposite handedness ($k_1 = -k_2 = 1.4, \ell = 3$) and (b) helices of equal handedness ($k_1 = k_2 = 1.4, \ell = 3$). (c) The behaviour of the pitch wavenumber as a function of the isotropic–cholesteric coexistence pressure for $k_1 = -k_2 = 1.4$ and $\ell = 3$. (d) As for (c) but with $k_1 = k_2 = 1.4, \ell = 3$.

handed 'dopant' particles. The zero-point corresponding to a diverging pitch is virtually (but not strictly) independent of the osmotic pressure of the suspension. For the second mixture of species with the same handedness the trend is completely different and features a non-monotonic change of the pitch wavenumber with mole fraction. In both mixtures, the pitch shows a strong non-monotonic behaviour as a function of the pressure of the cholesteric phase in coexistence with the achiral isotropic phase.

4. Conclusions

It is instructive to compare the present Yukawa-type chiral potential with a much simpler model potential employed in a previous study [54]. There, a square well (SW) chiral potential was used based on the Goossens form (cf equation (21))

$$U_{SW}(\Delta r, \hat{u}_1, \hat{u}_2) = -\varepsilon_{SW}H(\Delta r - \lambda)(\cos \gamma)T_{212}$$

with $H(\Delta r - \lambda)$ a Heaviside step function. The main parameters characterizing the chiral interaction are the SW range $\lambda > (1 + D/L)$ and depth $\varepsilon_{SW}$. The key advantage of using the SW form is that it renders the spatial integrations over the potential analytically tractable. The result for the torque-field constant is very simple: $\beta K_1 D^2 \sim (\pi \epsilon^2 / 6) \beta \varepsilon_{SW} \lambda^4$. Comparing this with equation (34) and setting the reduced SW range $\lambda$ to unity allows us to make an explicit link between the SW depth and the microscopic parameters pertaining to the electrostatic interactions between the helical particles:

$$\beta \varepsilon_{SW} \sim \frac{3Z^4}{16\pi} \left( \frac{\lambda_B}{D} \right)^2 \left( \frac{D}{L} \right)^4 W(k).$$

The justification for this relation lies in the notion that most thermodynamic properties are governed by the spatially integrated pair potential rather than the bare interaction. A prominent example is the classical van der Waals model for fluids, the universal nature of which stems from the fact that any arbitrary (but weakly) attractive potential can be mapped onto a single integrated van der Waals energy which, along with the excluded-volume contribution, fully determines the equation of state and hence the thermodynamics of the fluid state.

In summary, we have proposed a simple helical Yukawa segment model to describe the chiral interaction between charged rod-like helices. An analysis is given of the chiral potential associated with the Yukawa segment interactions for the general case of rods with different lengths and pitch of the internal helical structure. The resulting chiral potential is similar to the Goossens potential [44], albeit with a different scaling with respect to the interparticle centre-of-mass distance. Contrary to the Goossens form, our potential provides an explicit reference to the microscopic properties of the rods.

The potential is subsequently employed in a second-virial theory to study the structure and thermodynamic stability of the cholesteric state as a function of the rod density, the internal
microscopic pitch and the electrostatic screening parameter. While the magnitude of the cholesteric pitch is very sensitive to the concentration of rods and added salt, the handedness of the phase is governed mainly by the shape of the internal Yukawa helix. The handedness of the cholesteric phase need not be equivalent to that of the individual helices but may differ, depending on the precise value of the internal pitch. Within certain intervals of the internal pitch, right-handed Yukawa helices may generate left-handed cholesteric order and vice versa. The opposing helical handedness on the microscopic and macroscopic scale induced by the charge-mediated chiral interactions is consistent with experimental observations in M13 virus systems [60] and various types of fragmented DNA [7, 42, 74] where left-handed cholesteric phases are formed from right-handed helical poly-electrolyte conformations. Small variations in the shape of the internal helix, induced by, for example, a change of temperature, may lead to a sense inversion of the cholesteric helix. Such an inversion has been found in thermotropic (solvent-free) polypeptides [75] and cellulose derivatives [76], and in mixtures of right-handed cholesterol chloride and left-handed cholesterol myristate [77].

Our model also predicts that a very small degree of microscopic helicity is necessary in order to maximize the twisting potential of the helical particles. The optimum is reached when the pitch of the helix is about 2.5 times the rod length. Mixing helical rods of sufficiently different lengths may lead to a demixing of the cholesteric phase at high osmotic pressures (corresponding to high concentrations), whereby two cholesteric fractions with different macroscopic pitches coexist. The demixing region is bounded by a critical point upon lowering the osmotic pressure.

The present model could be interpreted as a simple prototype for complex biomacromolecules such as DNA and fd which are characterized by a helical distribution of charged surface groups. Other lyotropic cholesteric systems, such as cellulose and chitin microfibers in solution, could also be conceived as charged rods with a twisted charge distribution [14]. Small changes in the internal twist of the fibrils could be induced (e.g. by applying an external field or varying the temperature) in order to tune the handedness of the cholesteric phase. This could be of importance for the use of chiral nanocrystals in optical switching devices and nanocomposites. We remark that a more accurate description of the pitch, particularly for DNA systems, could be formulated by accounting for the steric contributions associated with the helical backbone of the chains as well as the influence of chain flexibility. The effect of flexibility could be included in an effective way, e.g. following the ideas of Khokhlov and Semenov [78], Odijk [79, 80] or Evans [81], or by examining segment models of mesogens such as hard-sphere chains [82].

This could open up a route towards understanding the unusual behaviour of the pitch on varying the particle and salt concentration as encountered in DNA [7, 17] using simple coarse-grained models. Furthermore, a quantitative comparison of the predicted pitch distances with experimental data should be possible for rigid, slender poly-electrolytes with a well-defined surface charge and internal pitch. Most chiral systems studied to date, however, do not fulfil these criteria, which makes it difficult to put our predictions to a quantitative test. An exception could be the viral systems which tend to have a very regular protein coat [8, 60].

Future work will be aimed at studying the sensitivity of the pitch beyond the purely Gaussian approximation. This can be done by adopting a numerical approach to determine the local orientational distribution function in a self-consistent way. This approach could unveil the much more complex relation between the pitch handedness and system density (or temperature) as suggested by the intricate angle dependence of the chiral potential shown in figure 2. Such a sense inversion upon changing temperature has been described theoretically by Kimura et al [83, 34] within a simple mean-field (Maier–Saupe) treatment of the hard-rod model combined with a Goossens-type chiral potential. It would be intriguing to see whether a similar effect could be generated from the present Yukawa model. Investigations along these lines are currently being undertaken. Another avenue of future study could involve an examination of the effect of adding achiral species, of the medium (solvent mixtures), or of the addition of a depleting agent such as a polymer (e.g. the studies of the effect of a polymer on the nematic phases exhibited by colloid systems [84, 85]) on the stability of the cholesteric phase and the consequences for the pitch.

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Appendix

The Gaussian averages required for the calculation of the twist-elastic constant are taken from [86]. We quote them here for completeness:

\[
\langle\langle y \rangle\rangle_0 \sim \left(\frac{\pi}{2}\right)^{1/2} \left(\frac{\alpha_i + \alpha_j}{\alpha_i \alpha_j}\right)^{1/2} \quad (A.1)
\]

\[
\langle\langle y^3 \theta^2 \rangle\rangle_0 \sim 3 \left(\frac{\pi}{2}\right)^{1/2} \left(\frac{\alpha_i + \alpha_j}{\alpha_i \alpha_j}\right)^{1/2} \left(\frac{2\alpha_i + 5\alpha_j}{\alpha_i^2 \alpha_j}\right) \quad (A.2)
\]

\[
\langle\langle y^2 \theta (\theta^2 + \beta^2) \rangle\rangle_0 \sim \left(\frac{\pi}{2}\right)^{1/2} \times \left[6\alpha_i^3 + 19\alpha_i^2 \alpha_j + 30\alpha_i \alpha_j^2 + 15\alpha_j^3\right] \quad (A.3)
\]

\[
\times \left(\frac{\alpha_i^{5/2} \alpha_j^{3/2}}{\alpha_i^2 \alpha_j^3}\right) \left(\alpha_i + \alpha_j\right)^{3/2}.
\]
