Self-Consistent Field Theory for Smectic Ordering of Semiflexible Homo-polymers

by

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Abstract

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A model of liquid crystalline homopolymers using self-consistent field theory (SCFT) for semiflexible spherocylinder-shaped particles is developed that can form the isotropic (I) phase, nematic (N) phase and smectic-A phase (SmA). As in previous works by Chen and Düchs et al. the excluded volume interaction based on a second virial approximation (SVA) due to Onsager is employed, which is able to stabilize the N phase for wormlike chains. To stabilize the SmA phase, the excluded volume interaction between cylindrical segments and the terminal end segments is included, as in Hidalgo et al. However Hidalgo et al. contains two limitations, which are addressed in this study: Their numerical algorithm cannot obtain solutions for strongly ordered states, which occur for molecular length to diameter ratio $L/D > 10$. Also, the phase boundaries occur for packing fractions that are too high, due to their use of SVA. A Crank-Nicolson type method applied to the orientations is developed, having better convergence for strongly ordered states, and obtains solutions for $L/D$ as high as $\sim 55$ for the N-SmA transition. A technique based on the method of Parsons and Lee is also implemented which goes beyond the SVA, successfully predicting the N-SmA boundary very close to that predicted by the computer simulations by Bohuis and Frenkel. N ordering and SmA ordering are looked at in some detail and comparison to Monte Carlo simulations and measurements on virus particles are made. The stability of rigid chains in the SmA phase is predicted to increase with increasing $L/D$. However, the SmA phase loses its stability for only a small amount of flexibility due to the relative contributions of the segment-segment and end-segment intermolecular interactions.
I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.
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Chapter 1

Introduction: A Brief History of Lyotropic Liquid Crystals

Liquid crystals generally refer to states of matter that exhibit behaviour that is neither in a pure liquid phase or crystalline phase, but contains some aspects of both. Liquid-type behaviour is understood to occur when the particle-particle (molecules, atoms, etc.) correlations are completely lost after some finite length scale. These correlations can be in terms of the positions of the particles or the particle orientation if the particles happen to be anisotropically shaped. Crystalline, behaviour denotes the existence of correlations over an infinite length scale in at least one direction, giving rise to a macroscopic anisotropy. Technically, a liquid crystal can then be defined as a system in which liquid-like behaviour exists in at least one direction of space while there is also some degree of anisotropy [5].

Anisotropically-shaped particles often give rise to liquid-crystalline behaviour. These
Figure 1.1: Representative liquid-crystalline phases induced by a change particle concentration, such as in a lyotropic system. A thermotropic system can possess the same phases; however, they are induced by temperature changes. The director is in the direction of preferred molecular orientation. The SmC phase, however, has a tilted director. Pictures are taken from [6].

are typically shaped like flat disks or elongated rods; in this Thesis focus is given to structures resembling the latter. Some possible phases formed are shown in Fig. 1.1. The lower symmetry phase typically occurs with either decreasing temperature, or with increasing molecular packing fraction, $\eta$ (or solute concentration). Temperature sensitive systems are identified as thermotropic liquid crystals, while concentration dependent systems are identified as lyotropic liquid crystals. The phase with the greatest amount of symmetry is called the isotropic (I) phase and behaves like a positionally-disordered liquid in all three dimensions, in addition to having no orientational order. The simplest type of nematic (N) phase exhibits symmetry breaking in one dimension where there is a preferred molecular
orientation direction, called the director, shown in Fig. 1.1 (b). A typical feature for liquid crystalline phases is that for molecules in which one end is distinguishable from the other the orientation, \( u \), is indistinguishable from the reverse direction, \(-u\). In a given phase there are as many molecules pointing in the \( u \) direction as the \(-u\) direction. There are other types of more complicated N phases in which the director orientation varies in space. However we will only be concerned with the simplest type, the uniaxial nematic (Fig. 1.1 (b)), which occurs for molecules having an interaction potential with cylindrical symmetry. The smectic phases are generally characterized by an additional symmetry breaking for which the molecular density has a periodic modulation in space analogous to a lamellar phase of amphiphilic molecules, shown in Fig. 1.1 (c) and (d). The smectic-A (SmA) phase is the simplest smectic having uniaxial orientational order in which the director is perpendicular to the layer spacing. The smectic-C (SmC) phase is given by biaxial orientational ordering giving rise to a tilted director with respect to the direction perpendicular to the layer spacing. This can be achieved when the molecular shape, or the intermolecular potential, does not possess cylindrical symmetry.

Liquid-crystalline ordering gives rise to all sorts of exotic behaviours such as that seen in many biological contexts as well as in technological applications, [7]. The first observations occurred in the late 1880’s by Friedrich Reinitzer and Otto Lehmann when the small elongated organic molecule, cholesteryl benzoate, was observed to melt from a solid phase to a cloudy liquid (nematic) phase at 145.5 °C, then melt again to a clear liquid (isotropic) phase at 178.5 °C.

Thermotropic molecules are generally of lower molecular weight than lyotropic molecules.
A common molecular structure of thermotropic liquid crystals is that of two parasubstituted aromatic rings linked by different types of functions preserving the long axis of the molecules, or one parasubstituted aromatic ring and one parasubstituted cyclohexane linked by the same type of functions. Another favourable class is obtained with cholesterol esters \([5]\). Some examples are \(p\)-azoxyanisole (PAA) having an effective length \(\sim 20\ \text{Å}\) and width \(\sim 5\ \text{Å}\). Another example is 5CB and other cyanobiphenyls which made the twisted nematic LCD popular in the 1970’s.

In this Thesis focus is given only to lyotropic liquid crystals, which typically consist of colloids, long polymers and other large structures. The rod structure itself tends to be rather unstable with respect to temperature changes thus eliminating the possibility of thermally inducing phase transitions. Therefore, the solute concentration is a more natural parameter that can be varied \([8]\). High molecular weight long helical rods such as synthetic polypeptides and other rigid polymers in suitable solvents also have rod-like conformations with typical lengths of order \(L \sim 300\ \text{Å}\) and effective diameter \(D \sim 20\ \text{Å}\), \([9]\). Hydrated DNA molecules can also exhibit liquid-crystallinity in that the packing of the strands themselves are disordered but the base-pair columns within the molecule have nematic ordering. This played a part in the discovery of its internal structure by Francis Crick and James Watson via X-ray diffraction \([10]\). The packing of DNA strands can also be understood by physical models of liquid crystal ordering \([11, 12]\). The type of systems that are most relevant to this Thesis are certain viruses such as the tobacco mosaic virus (TMV), with length 2820 \(\text{Å}\) and width 180 \(\text{Å}\) \([13]\), and fd virus particles, with length 8800 \(\text{Å}\) and width 66 \(\text{Å}\) \([14]\), shown in Fig. 1.2, which can exhibit liquid crystal phases.
Figure 1.2: Top: Differential interference contrast optical micrograph of semiflexible fd viruses in a SmA state. Taken from [14]. Bottom: a calculated density distribution $\rho(z)$ as a function of distance $z$ perpendicular to the smectic layers. The gap half-width $\sigma$ between layers is 90 nm and the smectic layer spacing $\lambda$ is 920 nm.

The protein M13 is closely related to fd, differing only by one amino acid per major coat protein. The advantage of studying virus particles is that they can be prepared to be highly monodisperse in size and in the case of M13, it has been possible to create mutants which differ only in contour length [15]. A disadvantage of these virus particles is that their study is complicated by having a surface charge. While the influence of surface charge on lyotropic colloids has been investigated theoretically [7, 16], we do not study these effects in this Thesis.

It is well known that anisotropic repulsive interactions are sufficient for stabilizing liquid-crystalline phases. The first investigation of this dates back to Onsager’s work on infinitely thin rigid hard rods - or equivalently, rods with infinite length-diameter ratio ($L/D$). The molecules interact via the two-body excluded volume [17] (see Section 2.6).
but this interaction is valid only in the limit of vanishing particle concentration. This model predicts an I-N transition with a finite phase coexistence region (i.e., a first order transition), consistent with the computer simulations of Bolhuis and Frenkel [12] (see Fig. 1.5). A later work by Zwanzig dealt with an idealized model where the orientation is restricted to be along either of the three coordinate axes, and a first order transition was also predicted [18]. These predictions are consistent with experiments on thermotropic [19, 20] and lyotropic [21] systems. Since many of the lyotropic colloidal molecules cannot be considered infinitely thin, the Onsager theory is of somewhat limited use. In Fig. 1.3 for TMV \((L/D = 16.7)\) [21] it is seen that the experimental transition is much lower than the Onsager theory predicts. The fd virus, however, is very slender \((L/D \sim 133)\) [14]. The predicted transition for the fd virus by the Onsager theory for ionic strength 0.01M (including electrostatic effects of charged virus particles [22]) at 12 mg ml\(^{-1}\) is very close to the experimental value of 11 mg ml\(^{-1}\) showing that the theory is very good in this case [23].

The effects of flexibility on the I-N transition of semiflexible “wormlike” chain molecules in the limit of large \(L/D\) are fairly well understood. The extension of Onsager’s theory to semiflexible molecules predicts that the transition moves to higher concentration (or packing fraction) while decreasing the coexistence width with increasing degree of flexibility [1, 24, 25]. These theories typically only consider the interaction due to the relative orientation between overlapping chain segments, but not the interaction due to the molecule ends. These predictions agree qualitatively with work on suspensions of virus particles by Tang and Fraden [26] as well as computer simulations [27].
Extension of the theory to the N-SmA transition did not begin until much later. The density-functional approach using the second virial approximation by Mulder [29] for perfectly aligned hard cylinders predicts a second order transition (L/D isn’t specified). However Poniewierski [30] predicts a first order transition in the limit of large L/D. NPT Monte Carlo simulations by McGrother et al. [31] and the simulations by Bolhuis and Frenkel [12], Fig. 1.4, indicate that for low L/D the rigid-rod transition is clearly first order, while remaining unclear for high L/D. For the limit of high L/D the Monte Carlo simulations by Polson and Frenkel [32] indicate the transition is first order.

The phenomenological theory of Tkachenko [35] for very flexible chains indicates that flexibility drives the N-SmA transition to be first order while it decreases the smectic period compared to rigid rods. The theory of van der Schoot [4], employing an extension of the Khokhlov-Semenov theory for wormlike chains [24, 36], in the complementary limit of weak flexibilities gives a similar result. These findings qualitatively agree with computer simulations by Bladon and Frenkel [3] and with the study on virus suspensions by Dacic.
Figure 1.4: Phase diagram of rigid, hard spherocylinders of aspect ratio $L/D < 5$, obtained by computer simulation, [12] in terms of the reduced packing fraction $\eta^* = \eta / \eta_{cp}$. $\eta_{cp}$ is the close-packed packing fraction. Two-phase regions are shaded. The high $\eta^*$ plastic (P) and solid (S) phases are not studied in this Thesis.
Figure 1.5: Phase diagram of rigid, hard spherocylinders with $L/D$ between 0 and 100, obtained by computer simulation, [12] and in terms of the reduced packing fraction $\eta^* = \eta/\eta_{cp}$, (see Fig. 1.4). The high $\eta^*$ ABC and AAA phases are solid crystalline phases, not considered in this Thesis.
Figure 1.6: Phase diagrams for rod-coil copolymers in the $C$ vs. $f$ plane with rigid portion, $\xi_{\text{rigid}} = 10$ and flexible portion, $\xi_{\text{flexible}} = 0.1$. $\xi$ is the reduced bending rigidity. (a) The results of Düchs and Sullivan [33]. (b) The result of Song et al. [34].

and Fraden [14]. However these theories do not make quantitative predictions on the effects of flexibility.

More recent work is based on the self consistent field theory (SCFT) for wormlike chains using the Onsager second-virial approximation as developed by Chen [1]. SCFT is well grounded in the theory of block copolymers in the Gaussian (highly flexible) limit where the mean-field approximation is easily seen to be valid [37]. For semiflexible chains the applicability of the mean-field approximation is more difficult to assess, as discussed at the beginning of Chapter 2.

The work of Düchs and Sullivan, using a spherical harmonic representation to describe the segment orientations, [33] applied the framework by Chen [1] to rod-coil diblock copolymer systems in the limit of $L/D \to \infty$. Aside from having different flexibility, each rod and coil portion of the molecule is otherwise chemically similar. The fraction $f$ is defined
as the length of the rigid portion divided by the total polymer length. It was shown (Fig. 1.6 (a)) by [33] that molecules of uniform flexibility do not form a smectic phase using the Onsager segment-segment excluded volume interaction, i.e. ignoring the excluded volume due to the ends. But for a certain fraction $f$, with an intermediate amount of rigid and flexible region, a SmA phase can form. This is shown in the $C$ vs. $f$ phase diagram, Fig 1.6 (a), where $C$ is a reduced number density, discussed more in Table 2.1 and Eq. (2.170). The more recent SCFT study on the same system by Song et al. [34], has also obtained this result in addition to predicting a SmC phase. The numerical approach uses a novel real-space approach to describe the orientations which utilizes a unit sphere with an icosahedron triangular mesh to describe the orientations and has very good agreement with that of Düchs and Sullivan, see Fig. 1.6 (b). The main conclusion from these rod-coil systems is that to generate smectic phases it is sufficient to distinguish rigid and flexible parts of the polymer by means of just their rigidities, and thus smectic ordering is a purely entropic phenomenon [33].

Another recent study by Hidalgo, Sullivan and Chen [2] considers the semiflexible homopolymer, i.e. uniform rigidity, and looks at the effect of the excluded volume due to the molecule ends in addition to the Onsager segment-segment excluded volume interaction. This model also accounts for a range of $L/D$ values in addition to a variable rigidity, $\xi$. The location of the phase boundaries and the width of the phase gap is in general agreement with the aforementioned studies. The prediction of a first order I-N transition is also in agreement with experiments [21] and previous theories [1, 22, 24, 27]. The N-SmA transition is generally found to be first order for lower $L/D$ with a tendency toward
second order as \(L/D\) increases. These results are summarized in the phase diagram shown in Fig. 1.7 and are in qualitative agreement with simulations, Figs. 1.4, 1.5 of Bolhuis and Frenkel [12] for the I, N, SmA phase boundaries of rigid molecules, in addition to making predictions for semiflexible molecules.

However, there are some limitations. We see that the predictions of the phase boundary are generally too high, as a result of the Onsager approximation. In fact, in some regimes the N-SmA boundary is unphysically predicted to occur at concentrations higher than the close packed limit \(\eta_{cp} \approx 0.91\). Another limitation is that the phase boundary extends only up to value of \(L/D < 10\). This is a result of the spherical harmonic representation of the molecular orientations, which is known to have difficulty converging for strong nematic ordering that occur for higher \(L/D\).

The purpose of this Thesis is to address the limitations encountered in [2] which certainly would occur in other systems where there is strong nematic ordering and where phase behaviour is of interest for concentrations higher than that of the vanishing limit. A real-space numerical implementation based on the Crank-Nicolson finite difference scheme, which is able to obtain solution convergence for \(L/D > 10\), is developed. Also, an extension to the second virial approximation is applied to the problem by using a rescaling technique due to Parsons and Lee [28, 38]. This technique, discussed in Section 2.11, has often been used to rescale the Onsager type interaction in the free energy, with improved results [21, 39-41]. An example of this method on a different system is shown in Fig. 1.3.

This Thesis is organized as follows. In Chapter 2 the theory for the required polymer statistics, order parameters, SCFT, and numerical algorithms are developed. Chapter 3
Figure 1.7: Phase diagrams from [2] for different rigidities: (a) infinitely rigid molecules, $\xi = \infty$, (b) $\xi = 10$, and (c) $\xi = 1$. The solid and dashed lines define the coexistence regions of first-order phase transitions and the critical packing fraction $\eta_{\text{crit}}$ for second-order phase transition, respectively.
begins by briefly examining the accuracy of the numerical calculations and comparing to previous results where possible. The main results of this Thesis are presented in the rest of Chapter 3 where the N-SmA phase transitions are examined along with an analysis of the N and SmA ordering. Comparison to Monte Carlo simulations and experiments on virus particles are also made. The Thesis work is summarized in Chapter 4.
Chapter 2

Self-Consistent Field theory (SCFT) for Semiflexible Polymers

In this Chapter the theoretical methods for solving the wormlike chain model for semiflexible polymers are introduced. An important simplification in the theory is that solvent effects are ignored by considering the polymer chains to be embedded in a structureless solvent, which behaves just like a vacuum. The total volume of the chains, which move through the solvent due to their thermal motion, plus the volume of the solvent, is then equal to the system volume, $V$.

A single polymer chain is comprised of many monomer units and thus possesses a huge number of degrees of freedom. It is therefore valid to use the methods of statistical mechanics on an individual polymer chain. However, real systems of polymer chains can be enormously complex in that they comprise many chains that are possibly interacting
with each other. Therefore, in this Thesis the mean-field approximation (MFA) [42, 43] is used, in which consideration is placed upon a single chain in an external field due to the presence of all the other chains. For atomic or small molecular fluids that have a low coordination number, $C_{nn} \sim 10$, this external field would have large fluctuations and the mean-field approach would not be a great approximation. For polymer solutions and melts at the atomic scale this approach would not help much either. However at the mesoscopic scale, greater than $\sim 1$ nm [37], polymer coils can interpenetrate each other and the external field fluctuations are now averaged out. All configurations of the external field can then be neglected except for the most probable one, located at the saddle point of the free energy, which in turn causes mean-field theory techniques to become highly effective [43]. The validity of the MFA is generally tested by the Ginzburg criterion. This describes the extent to which the saddle point field dominates the configuration space through a *Ginzburg parameter* which, in this case, is $C_{nn}$.

Consider a melt (negligible free volume between adjacent molecules) of polymer coils of high flexibility, each one consisting of $N$ effective segments. In the ideal limit ($N \to \infty$) the well known Gaussian model is obtained [42–44], where the coordination number is given by

$$C_{nn} = \rho R_g^3,$$  \hfill (2.1)

where $\rho = n/V$ is the average number density of chains and $R_g$ is the radius of gyration. $C_{nn}$ is the number of other polymer chains within the volume (estimated as $R_g^3$) of the occupied region of the one chain of interest. In the ideal limit $R_g^3 = b (N/6)^{3/2}$ and $\rho = 1/(v_0 N)$, where $v_0$ is the volume of each effective segment and $b$ is the length of each effective segment.
It follows that $C_{nn} \sim (b^2/v_0) N^{1/2}$. Therefore the coordination number grows as the square root of the molecular weight which can be very large, the saddle point field does indeed dominate the configuration space [45] and therefore the MFA is valid for the Gaussian model. However the MFA is not as accurate for the semiflexible polymer where there is less interdigitation between chains, especially for the limit of rigid rods. In addition, an analysis of the validity of the MFA with respect to finite chain flexibility is more difficult to perform. Nonetheless, the MFA is employed as in previous works on semiflexible chains [1, 2, 46].

A well studied polymer chain model is the random flight chain model which describes a chain in the absence of an external field and whose chain statistics depend only on the positional degrees of freedom ($r_0, r_1, \ldots, r_n$) of all the monomers (or equivalently the bond vectors, $R_j = r_j - r_{j-1}$). Examples of the random flight chain model include the freely jointed chain model, bead-spring models and the continuous Gaussian chain model. The wormlike chain model is a relatively complicated model in that not only are the positional degrees of freedom of importance but the same holds for the rate at which the bond vectors change direction. This second consideration will be shown to be necessary to model the resistance to bending.

With this in mind, this Chapter is organized in the following way. The random flight chain model (Section 2.1) for a single polymer chain is first described to give an introduction to the type of mathematics that are generally used in chain statistics. This will also lead into the concept of the equivalent chain and the Kuhn segment (Section 2.2). The Wiener measure is then derived in Section 2.3. With the chain statistics of positionally
dependent systems laid out, the wormlike chain model is introduced in Section 2.4 which takes into account the resistance to bending. In Section 2.5 the atomistic view of \( n \) discrete particles (or chains) is considered by using density operators. Then the complimentary idea of the statistical field is discussed by using the corresponding distribution functions. Section 2.6 discusses the excluded volume interaction that gives rise to liquid-crystalline ordering. Section 2.7 introduces the nematic and smectic order parameters. Sections 2.8 and 2.9 develop the mean-field theory and self-consistent equations. Section 2.11 then introduces a modification to the second virial approximation, known as the decoupling approximation, which approximates the higher virial coefficients. 2.12 looks at the theory of phase equilibrium and phase coexistence.

### 2.1 Random flight chain model

In this Section the number \( M \) denotes the number of actual bonds, or segments, in a polymer chain. In Section 2.2 the effective segment is introduced which approximates a collection of actual segments. The number \( N \) denotes the number of these effective segments. From Section 2.3 onward the theory will exclusively deal with effective segments, i.e., the number \( N \), unless otherwise noted.

The simple case of a single polymer chain in the absence of an external force is first considered. The chain is composed of \( M + 1 \) monomers, numbered 0, 1, 2, ..., \( M \) from one end to the other. The set of coordinates \( \{r_k\} = (r_0, r_1, ..., r_M) \) describes the position of each monomer with respect to an arbitrary origin in space. The potential energy of the
system is then:

\[ U \left( \{r_k\} \right) = \sum_{j=1}^{M} u_j (r_{j-1}, r_j) + W \left( \{r_k\} \right) \] (2.2)

where \( u_j \) accounts for the chain connectivity, while \( W \) accounts for external interactions. All the statistical properties of the chain are then contained in the following un-normalized distribution

\[ G \left( \{r_k\} \right) = \exp \left[ -\beta U \left( \{r_k\} \right) \right] \] (2.3)

where \( \beta = 1/kT, T = \text{temperature and } k = \text{Boltzmann's constant}. \) From this, the configurational partition function, which omits the kinetic factor, can be calculated:

\[ Z = \int d \{r_k\} G \left( \{r_k\} \right), \] (2.4)

where

\[ d \{r_k\} = \prod_{j=0}^{M} d\mathbf{r}_j. \] (2.5)

The normalized distribution function can now be written as

\[ P \left( \{r_k\} \right) = Z^{-1} G \left( \{r_k\} \right). \] (2.6)

It is convenient to consider the bond vectors \( \mathbf{R}_j = \mathbf{r}_j - \mathbf{r}_{j-1} \) instead of the monomer positions \( \mathbf{r}_j \), since the chain is sequentially bonded. This is illustrated in Fig. 2.1. The
Figure 2.1: Schematic representation of the bond vector $\mathbf{R}_j = \mathbf{r}_j - \mathbf{r}_{j-1}$ and the end-to-end vector $\mathbf{R}$. This particular illustration shows a special case of the random flight chain, the freely jointed chain, in which all bonds are of equal length.

Chain connectivity is then expressed, generally, in terms of the bond “probabilities”

$$\tau (\mathbf{R}_j) \equiv \exp \left[ -\beta u_j (\mathbf{R}_j) \right]$$

(2.7)

where $u_j (\mathbf{R}_j) \equiv u_j (\mathbf{r}_j, \mathbf{r}_{j-1})$ and $\tau (\mathbf{R}_j)$ is typically chosen to be normalized. $\tau (\mathbf{R}_j)$, which can be specialized to a model of interest, is the probability that the $j$th bond has length $R_j$ and points in the direction $\mathbf{R}_j$. $G (\{\mathbf{r}_k\})$ as defined by Eq. (2.3) is now

$$G (\{\mathbf{r}_k\}) = \prod_{j=1}^{M} \tau (\mathbf{R}_j) \exp \left[ -\beta W (\{\mathbf{R}_k\}) \right].$$

(2.8)

Eq. (2.8) is a very general equation that contains more information than is typically needed so at this point it is desirable to specialize (2.8) to obtain the normalized end-to-end distribution function $P (\mathbf{R}; M)$ for the random flight chain. The random flight chain is
analogous to a random walk of $M$ steps (bonds) where the length of each step is governed by the probability distribution $\tau(R_j)$. The unbiased random walk nature is obtained by setting $W(\{R_k\}) = 0$. $P(R; M)$ is the probability that the position of monomer $M$, $r_M$, is located at position $R$, given that monomer $M = 0$ is at the origin. $R$ is given by (see Fig. 2.1) the end-to-end vector

$$R = r_M = \sum_{j=1}^{M} R_j.$$  \hfill (2.9)

$P(R; M)$ is a reduced distribution with respect to Eq. (2.8) obtained by integrating over each bond vector according to the constraint given by (2.9), given as follows

$$P(R; M) = \int d\{R_k\} \left[ \prod_{j=1}^{M} \tau(R_j) \right] \delta \left( \sum_{j=1}^{M} R_j - R \right).$$  \hfill (2.10)

Eq. (2.10) connects the study of chain statistics and random walks, and hence also connects to Brownian motion and diffusion [46].

The simplest model of a real polymer chain is one in which each bond has the same length $l$, known as the freely jointed chain model. Specializing Eq. (2.7) to this case gives [37]:

$$\tau(R_j) = \frac{1}{4\pi l^2} \delta (|R_j| - l).$$  \hfill (2.11)

Thus in terms of Eq. (2.11), $P(R; M)$ corresponds to a random walk of $M$ steps of equal length $l$. 

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In order to evaluate Eq. (2.10) the delta function is represented as a Fourier integral:

$$\delta \left( \sum_{j=1}^{M} \mathbf{R}_j - \mathbf{R} \right) = \int \frac{d^3 k}{(2\pi)^3} \exp \left[ i \mathbf{k} \cdot \left( \sum_{j=1}^{M} \mathbf{R}_j - \mathbf{R} \right) \right]$$

(2.12)

which gives a product of $M$ identical factors:

$$P(\mathbf{R}; M) = \int \frac{d^3 k}{(2\pi)^3} \exp \left( -i \mathbf{k} \cdot \mathbf{R} \right) \prod_{j=1}^{M} \left[ \int d\mathbf{R}_j \tau(\mathbf{R}_j) \exp \left( -i \mathbf{k} \cdot \mathbf{R}_j \right) \right]$$

(2.13)

resulting in

$$P(\mathbf{R}; M) = \int \frac{d^3 k}{(2\pi)^3} \exp \left( -i \mathbf{k} \cdot \mathbf{R} \right) \left[ K(\mathbf{k}; M) \right]^M$$

(2.14)

where

$$K(\mathbf{k}; M) = \int d\mathbf{R} \tau(\mathbf{R}) \exp \left( -i \mathbf{k} \cdot \mathbf{R} \right).$$

(2.15)

Using Eq. (2.11) for constant bond lengths the probability distribution function becomes

$$P(\mathbf{R}; M) = \int \frac{d^3 k}{(2\pi)^3} \exp \left( -i \mathbf{k} \cdot \mathbf{R} \right) \left[ \frac{\sin(kl)}{kl} \right]^M$$

(2.16)

where $k = |\mathbf{k}|$. In the limit of large $M$, $K(\mathbf{k}; M)$ will approach zero unless $kl \ll 1$ so $K(\mathbf{k}; M)$ will contribute to the integral in Eq. (2.14) only for $kl \ll 1$. In this region, $K(\mathbf{k}; M)^M$ can be approximated by

$$\left[ \frac{\sin(kl)}{kl} \right]^M \approx \left[ 1 - \frac{k^2 l^2}{6} \right]^M \approx \exp \left( -Mk^2 l^2 / 6 \right)$$

(2.17)
and substituting the above approximation into Eq. (2.16) gives

\[
P (R; M) = \int \frac{d^3k}{(2\pi)^3} \exp (-i\mathbf{k} \cdot \mathbf{R}) \exp (-Mk^2l^2/6)
\]

\[= \left( \frac{3}{2\pi l^2 M} \right)^{3/2} \exp \left( -\frac{3R^2}{2Ml^2} \right)\]  

(2.18)

A convenient property is that all random flight polymers give the Gaussian distribution (2.18) for long enough chains and for distances much less than full extension. Since the constant bond length “probability”, Eq. (2.11), leads for general \(M\) and \(R\) to a rather complicated distribution \(P (R; M)\), it is desirable to obtain a different \(\tau (R_j)\) than (2.11) which reproduces (2.18) yet is mathematically less cumbersome. It turns out ([47]) that this can be done using a chain with Gaussian links, given by

\[
\tau (R_j) = \left( \frac{3}{2\pi l^2} \right)^{3/2} \exp \left( -\frac{3R_j^2}{2l^2} \right).
\]

(2.19)

From the Gaussian distribution, (2.18), one can obtain the \(p^{th}\) moment of \(R\). A standard result is the second moment:

\[
\langle R^2 \rangle = ML^2 = lL
\]

(2.20)

where \(L = Ml\), geometrically, is the contour length of the chain. This result defines \(l\) for the flexible chain, given the mean square-end-to-end distance \(\langle R^2 \rangle \) of the chain.
2.2 The equivalent chain, a coarse-grained approach

An expression as simple as (2.19) for a chain with Gaussian links is applicable for systems exhibiting ideal behaviour. At small enough length scales however, the behaviour of real chain systems can be quite complex. When dealing with such a non-ideal situation it is common to apply a *coarse-grained* approach and replace the real polymer chain by the so-called *Kuhn* effective random flight chain. An effective chain is one with $N$ segments, less than $M$, of effective length $\Delta s$ such that $N \Delta s = L$ and $\langle R^2 \rangle$ is given by (2.20). The quantity $\Delta s$ is commonly known as the *Kuhn segment* length.

To obtain the expression for the bond probability $\tau(R_j)$ in terms of $\Delta s$, consider writing the $l^2$ term in the exponential of (2.19) according to (2.20)

$$\frac{R^2_{\text{actual},j}}{l^2} = \frac{M R^2_{\text{actual},j}}{\langle R^2 \rangle}.$$  \hfill (2.21)

The subscript *actual* refers to the bond vector of the actual segment of length $l$, which is first introduced in Eq. (2.11) for the freely jointed chain model. The desired analogous expression to Eq. (2.21) for a chain of $N$ equivalent segments of effective length $\Delta s$ is

$$\frac{N R^2_{\text{equiv},j}}{\langle R^2 \rangle},$$  \hfill (2.22)

where the subscript *equiv* now refers to the bond vector of the equivalent segment. Eq. (2.20) written in terms of equivalent segments can be written as $\langle R^2 \rangle = lN \Delta s$ since the
length of the polymer chain, \( L = N\Delta s \). This now gives

\[
\frac{NR^2_{\text{equiv},j}}{\langle R^2 \rangle} = \frac{R^2_{\text{equiv},j}}{l\Delta s}.
\] (2.23)

Replacing (2.21) for a real chain with the above gives the desired normalized bond probability for the equivalent chain

\[
\tau (R_j) = \left( \frac{3}{2\pi l\Delta s} \right)^{3/2} \exp \left( -\frac{3R^2_j}{2l\Delta s} \right),
\] (2.24)

with \( R_j \) now representing \( R_{\text{equiv},j} \) for the effective segment. From now on, polymer chains will be described as \( N \) effective segments instead of the \( M \) actual segments.

### 2.3 The Weiner measure

The Weiner measure for the random flight chain will now be constructed in terms of effective segments. Using Eq. (2.8) with respect to the equivalent chain bond probability, Eq. (2.24), for \( W = 0 \) and no constraints leads to the probability distribution function for the entire chain configuration. Eq. (2.6) becomes:

\[
P (\{r_k\}) = \mathcal{N} \exp \left[ -\sum_{i=1}^{N} \frac{3(r_j - r_{j-1})^2}{2l\Delta s} \right],
\] (2.25)

where

\[
\mathcal{N} = \left( \frac{3}{2\pi l\Delta s} \right)^{3N/2}
\] (2.26)
is a normalization factor fixed by the condition that the sum of all possible chain conformation probabilities is unity.

It should be clear that the chain configuration \( \{ \mathbf{r}_k \} = (\mathbf{r}_0 \equiv \mathbf{0}, \mathbf{r}_1, \ldots, \mathbf{r}_N) \) is the discrete version of the continuous curve \( \mathbf{r} (s) \). The correspondence between the discrete monomer position and the location of the point on a continuous curve is then

\[
\mathbf{r}_j = \mathbf{r} (j \Delta s) \equiv \mathbf{r} (s_j). \quad (2.27)
\]

The sum in the exponential of (2.25) over relative positions between adjacent monomers can be represented as follows in the “continuous chain” limit (denoted by \( \lim_{\text{CC}} \)) in which \( \Delta s \to 0, N \to \infty, \) and \( N \Delta s \to L \):

\[
\lim_{\text{CC}} \sum_{i=1}^{N} \left[ \frac{\mathbf{r} (s_i) - \mathbf{r} (s_{i-1})}{\Delta s} \right]^2 \Delta s \equiv \int_0^L ds \left[ \frac{\partial \mathbf{r} (s)}{\partial s} \right]^2 \\
= \int_0^L ds \left[ \dot{\mathbf{r}} (s) \right]^2 \\
= \frac{1}{L} \int_0^1 dt \left[ \dot{\mathbf{r}} (t) \right]^2,
\]

where the contour length \( 0 < s < L \) has been replaced by the dimensionless parameter \( 0 < t < 1 \). The dot denotes differentiation with respect to \( s \) or \( t \). The discrete sum was approximated by an integral and the ratio of relative position over bond length was approximated by the partial derivative. The probability that the chain configuration lies between the two curves \( \mathbf{r} (t) \) and \( \mathbf{r} (t) + \delta \mathbf{r} (t) \) is given by the following continuum limit of
the discrete chain probability

$$\lim_{CC} P (\{r_k\}) \prod_{j=1}^N dr_j = \lim_{CC} P (\{r_k\}) \int D r \to P [r (t)] \delta r (t),$$

where the standard notation

$$\prod_{j=1}^N dr_j = D r$$

is used throughout this work. The new notation $[r (t)]$ now refers to a continuous set of points in space indexed by the parameter $t$, i.e. a curve. By rescaling the curve differential by $N$ with $N \delta r (t) \equiv D_N [r (t)]$ the chain configuration probability becomes

$$P [r (t)] \delta r (t) = D_N [r (t)] \exp \left[ -\frac{3}{2lL} \int_0^1 [\dot{r} (t)]^2 dt \right].$$

This is the well-known Weiner measure.

The continuous chain limit of Eq. (2.25) becomes

$$P [r (t)] = \mathcal{N} \exp \left[ -\frac{3}{2lL} \int_0^1 [\dot{r} (t)]^2 dt \right]$$

where $P [r (t)]$ is now a functional of the chain configuration.

### 2.4 The wormlike chain model

The various types of random flight chains discussed in the previous sections are useful for describing flexible polymer chains in which there is zero correlation between segments
along the chain. However, for a chain that has some finite resistance to bending, or rigidity, it is necessary to take into account correlations along the chain. Polymers of this type are termed semiflexible. They often exhibit behaviour that is associated with rigid rod shaped molecules such as the formation of liquid crystalline type phases. The model used to describe such systems is the Kratky-Porod model [48]. This model is also commonly referred to as the wormlike chain. The ingredients for this model are as follows.

### 2.4.1 The persistence length

To quantify how polymer rigidity affects chain conformation consider the persistence length, which is the length scale at which bending correlations along the chain exponentially die out [49]. The mechanism used in this work for bending correlations is the freely rotating chain model in the limit of vanishing segment length ($l \to 0$) and parallel adjacent bonds ($\theta \to \pi$), shown in Fig. 2.2. The flexibility is at the junction points, but there other possible views of the bending mechanism [50].

In this chain the bond angles $\theta$ are fixed, and it is assumed that the chemical nature of the bonds are such that the bonds are free to rotate around the junction points. From Fig. 2.2, assume that bonds $\mathbf{R}_{j-1}$ and $\mathbf{R}_j$ lie in the plane of the paper while the rotation of $\mathbf{R}_{j+1}$ lies on a cone specified by $|\mathbf{R}_{j+1}| = l$ and the angles $\theta$ and $\varphi$. $\theta$ is the bending angle between adjacent bonds and $\varphi$ is the bond rotation angle. The average with respect to $\phi$ of the projection of bond $\mathbf{R}_{j+1}$ on bond $\mathbf{R}_j$ is

$$ \langle \mathbf{R}_j \cdot \mathbf{R}_{j+1} \rangle = l^2 \cos (\pi - \theta) = -l^2 \cos \theta. \quad (2.33) $$

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Using the end-to-end distance of the chain $\mathbf{R} = \sum_{j=1}^{N} \mathbf{R}_j$, the mean-squared end-to-end distance is

$$\langle \mathbf{R}^2 \rangle = \sum_{j=1}^{N} \langle \mathbf{R}_j^2 \rangle + 2 \sum_{j=1}^{N} \sum_{s=1}^{N-j} \langle \mathbf{R}_j \cdot \mathbf{R}_{j+s} \rangle. \quad (2.34)$$

The second term in (2.34) is evaluated simply by making projections of bond $\mathbf{R}_j$ onto bond $\mathbf{R}_{j+1}$ successively up to $\mathbf{R}_{j+s}$

$$\langle \mathbf{R}_j \cdot \mathbf{R}_{j+s} \rangle = l^2 \left[ -\cos \theta \right]^s \quad (2.35)$$

By combining Eqs. (2.34) and (2.35) a geometric series is obtained which is summed up to give

$$\langle \mathbf{R}^2 \rangle = Nl^2 \left[ \frac{1 - \cos \theta}{1 + \cos \theta} + \frac{2 \cos \theta}{N} \frac{1 - (-\cos \theta)^N}{(1 + \cos \theta)^2} \right]. \quad (2.36)$$

The above expression is a general result for the mean square end-to-end distance for a polymer chain. Now Eq. (2.36) is applied to the semiflexible polymer chain. To start off I will define the persistence length:

$$l_p \triangleq \frac{l}{1 + \cos \theta}, \text{ for } N \rightarrow \infty, |\cos \theta| < 1. \quad (2.37)$$

The meaning of this will become clear shortly. The wormlike chain model is obtained by taking the limit $l \rightarrow 0$, $N \rightarrow \infty$, $Nl \rightarrow L$, $\theta \rightarrow \pi$. The term $(-\cos \theta)^N$ in Eq. (2.36)
Figure 2.2: The freely rotating chain. Bond lengths and bond angles, $\theta$, are fixed. There is free rotation about the bond direction.
simplifies as

\[
(- \cos \theta)^N = \exp \left[ \log (- \cos \theta)^N \right] = \exp \left[ N \log (1 - 1 - \cos \theta) \right] \\
= \exp \left[ N \log (1 - l/l_p) \right] \\
\cong \exp (-N l/l_p) \\
= \exp (-L/l_p)
\]

(2.38)

where the logarithm term has been expanded to first order since in this limit \(l/l_p \cong \theta^2/2 \rightarrow 0\). In the above as well as the following expression for \(\langle R^2 \rangle\), use of the substitutions \(1 + \cos \theta = l/l_p, 1 - \cos \theta = 2 - l/l_p\) and \(\cos \theta = -1 + l/l_p\) has been made:

\[
\langle R^2 \rangle \cong Nl^2 \left[ \frac{2 - l/l_p}{l/l_p} + \frac{-2 + 2l/l_p - 1 - \exp (-L/l_p)}{N \frac{l^2/l_p^2}} \right] \\
= Nl l_p \left[ 2 - l/l_p + \left[ -\frac{2l/l_p}{L} + \frac{2}{N} \right] \left[ 1 - \exp (-L/l_p) \right] \right].
\]

(2.39)

Looking at the pre-factor of the decay term in the second line of Eq. (2.39), \(2/N\) is negligible compared to \(2l/l_p/L\) which varies from zero to very large. The decay term is \(O(1)\) or less and can be comparable to the 2. The \(l/l_p\) term is also negligible. Rearranging (2.39):

\[
\langle R^2 \rangle \cong 2L l_p - 2l_p^2 \left[ 1 - \exp (-L/l_p) \right].
\]

(2.40)

The persistence length \(l_p\), which was defined earlier in Eq. (2.37) is now seen to be a natural scale for which correlations along the chain decay.

There are two simple limits for Eq. (2.40). The ideal chain limit occurs for chains much
longer than their persistence length:

\[ \langle R^2 \rangle \cong 2l_p = \Delta sL, \quad \text{for } L \gg l_p. \quad (2.41) \]

The result that the Kuhn length \( s \) is twice the persistence length for a \emph{flexible} wormlike chain has been used. See Eq. (2.44) in Section 2.4.2. The rigid rod-like limit is for chains much shorter than their persistence length \( (L \ll l_p) \). Expanding the exponential to second order in Eq. (2.40) gives

\[ \langle R^2 \rangle \cong L^2. \quad (2.42) \]

The mean squared end-to-end distance of the wormlike chain in Eq. (2.39) is a smooth crossover between these two simple limits [51]. In this work where liquid crystalline phases of semiflexible polymer chains are examined, the effects of changing the persistence length are of importance. The dimensionless persistence length \( \xi \), in units of \( L \), called the \emph{bending rigidity} is defined here[2]:

\[ \xi = l_p/L. \quad (2.43) \]

2.4.2 Relation between Kuhn length and persistence length

For a wormlike chain in the flexible limit it is now shown that the Kuhn length, \( \Delta s = 2l_p \). For a flexible chain \(|\cos \theta| < 1\), and the second term in Eq. (2.36) can be neglected for large enough \( N \). From Section 2.2 the equivalent segment length was given by \( \Delta s = \langle R^2 \rangle / L \). Using Eq. (2.36) with the second term omitted gives the following:
\[
\Delta s \approx \frac{Nl^2}{L} \frac{1 - \cos \theta}{1 + \cos \theta} = l_p (2 - l/l_p) \approx 2l_p.
\]

In the second line the relation between \( \cos \theta \) and \( l/l_p \), Eq. (2.37) has been used and in the third line \( l/l_p \to 0 \) has been used. This is the desired result.

### 2.4.3 The partition function for the semiflexible chain

This Section further develops the continuous space curve description of the polymer started in Section 2.3 to take into account the stiffness of the wormlike chain. In the random flight chain the local chain stretching was taken into account by the \( \dot{r} (t) \) term while the chain bending was ignored. In contrast, each differential segment of the wormlike chain is constrained to be inextensible, but there is a harmonic energy penalty for the local bending.

The local bending conformation depends on the tangent vector given by \( \mathbf{u} (t) = d\mathbf{r} (t)/dt \) at location \( t \) and is constrained to be a unit vector \(|\mathbf{u} (t)| = 1\), (see Fig. 2.3). The local bending energy at location \( t \) depends on the curvature (equal to \(|d\mathbf{u} (t)/dt| = |d^2 \mathbf{r} (t)/dt^2|\)) at that point. Summing up harmonic curvature contributions along the chain contour gives the bending energy of the wormlike chain:

\[
\beta U_0 (\{\mathbf{r}, \mathbf{u}\}) = \frac{\xi}{2} \int_0^1 dt \left| \frac{d\mathbf{u}(t)}{dt} \right|^2
\]  

(2.45)
Making explicit use of the two constraints $u(t) = d\mathbf{r}(t)/dt$ and $|u(t)| = 1$, the partition function, Eq. (2.4), for the wormlike chain with no external field is:

$$Z_0 = \int D\mathbf{r} \int D\mathbf{u} \exp\left(-\beta U_0(\{\mathbf{r}, \mathbf{u}\})\right) \prod_t \left[ \delta \left( u(t) - \frac{d\mathbf{r}(t)}{dt} \right) \delta \left( |u(t)| - 1 \right) \right]$$

where the product over $t$ is a discrete approximation over an infinite number of infinitesimal segments of length $dt$. Thus in computing $Z_0$, the integral is over all chain contours $\mathbf{r}(t)$ consistent with $u(t)$ being a unit tangent vector at all contour locations $t$.

The constraints in Eq. (2.46) make it hard to evaluate directly as a path integral so instead a stochastic process approach is used. Consider a reduced distribution function $p_0(\mathbf{r}, \mathbf{u}, t)$. This quantity is defined as the normalized probability density that the end of a wormlike chain of length $t$ is located at position $\mathbf{r}$ with orientation $\mathbf{u}$. Much of what follows in this section is taken from [37]. The Chapman-Kolmogorov equation for the probability
density $p_0 (r, u, t)$ is

$$p_0 (r, u, t + \Delta t) = \int d(\Delta r) \int d(\Delta u) \Psi (\Delta r, \Delta u; r - \Delta r, u - \Delta u) p_0 (r - \Delta r, u - \Delta u, t)$$

(2.47)

where $\Delta u$ denotes a differential displacement in the tangent vector and $\Delta r$ is a differential displacement of the end position associated with adding a chain segment of length $\Delta t$. The function $\Psi (\Delta r, \Delta u; r, u)$ is the normalized conditional transition probability that the added chain segment has positional and orientational displacements $\Delta r$ and $\Delta u$ given that the original chain end had position $r$ and orientation $u$. The distribution for the first chain segment is uniform, giving $p_0 (r, u, 0) = 1$. The relation between $p_0 (r, u, t)$ and $Z_0$ is then

$$Z_0 = \int dr \int du p_0 (r, u, 1).$$

(2.48)

The expression for $\Psi (\Delta r, \Delta u; r, u)$ is simplified by using the following relation between $\Delta r$ and $\Delta u$:

$$\Delta r = \int_t^{t + \Delta t} dt \ u (t) = u \Delta t + O (\Delta t^2).$$

(2.49)

This shows that $\Delta r$ depends, to first order, on $\Delta t$ and therefore the stochastic nature of process (2.47) can be restricted to either $\Delta r$ or $\Delta u$. This is physically analogous to the Brownian motion of a free particle. Choosing to work with the variable $\Delta u$, the transition probability then becomes

$$\Psi (\Delta r, \Delta u; r, u) = \Phi (\Delta u; r, u) \delta (\Delta r - u \Delta t)$$

(2.50)
where \( \Phi(\Delta \mathbf{u}; \mathbf{r}, \mathbf{u}) \) is a normalized transition probability for orientational displacements \( \Delta \mathbf{u} \) on the unit sphere associated with a contour step of size \( \Delta t \). Substituting Eq. (2.50) into (2.47) gives the simplified Chapman-Kolmogorov equation

\[
p_0(\mathbf{r} + \mathbf{u} \Delta t, \mathbf{u}, t + \Delta t) = \int d(\Delta \mathbf{u}) \Phi(\Delta \mathbf{u}; \mathbf{r}, \mathbf{u} - \Delta \mathbf{u}) p_0(\mathbf{r}, \mathbf{u} - \Delta \mathbf{u}, t) .
\] (2.51)

As shown in Appendix A.1, it follows from the above equation that \( p_0(\mathbf{r}, \mathbf{u}, t) \) satisfies the following Fokker-Planck equation:

\[
\frac{\partial}{\partial t} p_0(\mathbf{r}, \mathbf{u}, t) = -\mathbf{u} \cdot \nabla_r p_0(\mathbf{r}, \mathbf{u}, t) + \frac{1}{2\xi} \nabla^2_{\mathbf{u}} p_0(\mathbf{r}, \mathbf{u}, t) ,
\] (2.52)

initial condition: \( p_0(\mathbf{r}, \mathbf{u}, 0) = 1 \)

The operator, \( \nabla^2_{\mathbf{u}} \), is often called the rotational diffusion operator because it generates rotational motion on the surface of the unit sphere [52]. The factor \( 1/(2\xi) \) can be thought of as a rotational diffusion coefficient.

In summary, the statistics of the wormlike chain in the absence of an external field can be found by solving the differential equation, (2.52), for \( p_0(\mathbf{r}, \mathbf{u}, t) \). This equation does not have a simple closed-form analytic solution; however its spatial Fourier transform can be developed in a continued fraction expansion [53]. The presence of an external field adds an extra term to Eq. (2.52) and one must use numerical methods to solve the corresponding Fokker-Planck equation. This case will be looked at in Section 2.8 when the excluded volume interaction is taken into account.
2.5 From an atomistic view to a statistical field theory of an $n$-particle system

This Section briefly introduces some distribution functions and operators that are useful for calculating the excluded volume and dealing with the mean-field approximation. With the statistics of a single polymer chain having been developed earlier, this can now be extended to a system of $n$ chains occupying a volume $V$ whose total average number density is

$$\rho = n/V. \quad (2.53)$$

The “atomistic” view of the system considers the individual positions and orientations of each segment of each polymer chain in the system, as one would do for a molecular dynamics calculation. This approach deals with the maximum amount of information. The Hamiltonian is written in terms of the individual configuration, $\{r, u\}$, over every chain. However, one could alternatively employ the microscopic $t$-segment density operator, $\hat{\psi}$, instead of $\{r, u\}$. It is given by

$$\hat{\psi} (r, u, t) = \frac{1}{\rho} \sum_{i=1}^{n} \delta (r - r_i (t_i)) \delta (u - u_i (t_i)) \quad (2.54)$$

which is non-zero only if a segment indexed by $t$ belonging to any of the $n$ molecules is located at position $r$ and orientation $u$. $t_i$ refers to the segment indexed by $t$ of molecule
The microscopic contour-averaged density operator is given by:

\[
\hat{\phi}(\mathbf{r}, \mathbf{u}) = \frac{1}{\rho} \sum_{i=1}^{n} \int_0^1 dt_i \delta(\mathbf{r} - \mathbf{r}_i(t_i)) \delta(\mathbf{u} - \mathbf{u}_i(t_i))
\]

which is non-zero only if any segments belonging to any of the \( n \) molecules are located at position \( \mathbf{r} \) and orientation \( \mathbf{u} \). Eq. (2.55) satisfies the normalization condition \( \int d\mathbf{r} \int d\mathbf{u} \hat{\phi}(\mathbf{r}, \mathbf{u}) = V \), where \( V \) is the volume of the system.

The single-molecule distribution function, \( \rho_m[\mathbf{r}(t), \mathbf{u}(t)] \) for a wormlike chain is now introduced, which is analogous to Eq. (2.32) for a random flight chain. An explicit form for this will not be shown at this point since it depends on the external field \( W \) acting on the polymer chain, which has not been discussed yet. \( \rho_m[\mathbf{r}(t), \mathbf{u}(t)] \) is the statistical distribution in which a polymer chain has a configuration \([\mathbf{r}(t), \mathbf{u}(t)]\) satisfying the normalization condition

\[
\int D\mathbf{r} \int D\mathbf{u} \rho_m[\mathbf{r}(t), \mathbf{u}(t)] = n.
\]

The alternative view to the atomistic description is the statistical field theory approach, used in this work. The Hamiltonian is now written not in terms of \( \{\mathbf{r}, \mathbf{u}\} \) (or equivalently \( \hat{\psi} \) and \( \hat{\phi} \)) but in terms of the statistical average of the densities \( \hat{\psi} \) and \( \hat{\phi} \), given by \( \psi \) and \( \phi \), and their thermodynamically conjugate chemical potential fields given by \( w_q \) and \( w \). \( w_q \) and \( w \) are discussed more in Section 2.8. The functions \( \psi \) and \( \phi \) are also called statistical density fields. The benefit of this approach is that since it employs system averages, there is less information to deal with and calculations that may have been too large to be practical using the atomistic approach are now feasible. The dimensionless \( t \)-segment density field is
a statistical average of Eq. (2.54) with respect to the single-molecule distribution function:

$$
\psi (\mathbf{r}, \mathbf{u}, t) = \frac{1}{\rho} \int D\mathbf{r} \int D\mathbf{u}_m \left[ \mathbf{r} (t), \mathbf{u} (t) \right] \sum_{i=1}^{n} \delta (\mathbf{r} - \mathbf{r}_i (t_i)) \delta (\mathbf{u} - \mathbf{u}_i (t_i)).
$$

(2.57)

And similarly, the dimensionless contour-averaged segment density field is the statistical average of Eq. (2.55)

$$
\phi (\mathbf{r}, \mathbf{u}) = \frac{1}{\rho} \int D\mathbf{r} \int D\mathbf{u}_m \left[ \mathbf{r} (t), \mathbf{u} (t) \right] \sum_{i=1}^{n} \int_{0}^{1} dt_i \delta (\mathbf{r} - \mathbf{r}_i (t_i)) \delta (\mathbf{u} - \mathbf{u}_i (t_i)).
$$

(2.58)

From Eqs. (2.56) and (2.58), it satisfies the normalization condition

$$
\int d\mathbf{r} d\mathbf{u} \phi (\mathbf{r}, \mathbf{u}) = V.
$$

(2.59)

It should be easy to see that $\phi (\mathbf{r}, \mathbf{u})$ can be concisely written in terms of $\psi (\mathbf{r}, \mathbf{u}, t)$:

$$
\phi (\mathbf{r}, \mathbf{u}) = \int_{0}^{1} dt \psi (\mathbf{r}, \mathbf{u}, t).
$$

(2.60)

### 2.6 The excluded volume interaction

Up until now the statistical mechanics of a single polymer chain in the absence of an external field ($W = 0$ in Eq. (2.2)) were considered. For these systems, the interactions due to the chain connectivity occur between a few neighbouring segments or, in the case of the wormlike chain, on a length scale of a few persistence lengths along the chain. These are
called \textit{bonded} interactions. \textit{Non-bonded} interactions occur between separate molecules or, if they are flexible enough, between separate parts within the same molecule. These consist of the short range hard-core repulsion and long range attractions between segments. In an exact theoretical treatment, non-bonded interactions in a many-particle system would be treated at the level of the equation of state by including every term in the full virial expansion.

The model interaction of choice used in this study is based on the second virial approximation, derived in Appendix B, which includes only the first two terms in the full virial expansion. This effectively takes into account the excluded volume between two segments, while ignoring interactions between three or more segments. Other detailed interactions such as hydrogen bond forces and long range Van der Waals interactions are ignored. In this Section, the excluded volume interaction \cite{5}, \cite{17} between wormlike chains is discussed which accounts for the simple fact that two chain segments cannot occupy the same position in space. It is repulsive in nature and tends to decrease the entropy, therefore increasing the energy of the system.
An example of perhaps the simplest type of excluded volume interaction is that between two spheres of radius \( r_1 \) and \( r_2 \), illustrated in Fig. 2.4. The excluded volume for this is the volume that is inaccessible to the centre of sphere 2 due to the presence of sphere 1, given by the dashed line. For spheres of equal volume this is 8 times the volume of an individual sphere.

2.6.1 The Maier-Saupe interaction

One of the earliest and simplest theories of nematic ordering is the interaction due to Maier and Saupe [54, 55] for uniaxial systems, discussed here. While a general orientation-dependent intermolecular interaction potential \( V(u) \) includes all the terms in a spherical harmonic expansion of the orientational variables, \( \theta \) and \( \varphi \), the Maier-Saupe interaction, \( V_{M-S} \), is proportional only to the second order, \( \theta \)-dependent term, which is equivalent to the second-order Legendre polynomial, \( P_2 (\cos \theta) = (3 \cos^2 \theta - 1) / 2 \). The absence of any odd terms as well as the absence of the azimuthal dependence \( \varphi \) is consistent with the cylindrical symmetry of the molecules. This is also consistent with the energetic preference of the molecules to be aligned parallel to each other and not perpendicular. The average orientation is an arbitrary direction, which picks out the director, and the angles, \( \theta \) and \( \varphi \), are with respect to the director. Furthermore, the potential \( V_{M-S} \) representing the field of intermolecular interaction forces should be a minimum when the phase is highly ordered and should vanish when the phase becomes disordered [8]. Thus, \( V_{M-S} \) should be proportional to the degree of order, \( \langle P_2 (\cos \theta) \rangle = \int d\mathbf{u} \phi (\theta) \frac{1}{2} (3 \cos^2 \theta - 1) \), equal to the nematic order parameter, \( O_{nem} \) from Eq. (2.76). The discussion of the nematic order
parameter is given in Section 2.7. Also, $V_{M-S}$ should contain a factor $v$ that accounts for the interaction strength. Combining the above gives a mean-field approximation to the orientational potential energy function of a single molecule:

$$V_{M-S} (\cos \theta) = -v P_2 (\cos \theta) \langle P_2 (\cos \theta) \rangle. \quad (2.61)$$

Using the rules of classical statistical mechanics for rigid molecules to write out Eq. (2.76) for the nematic order parameter gives

$$\langle P_2 \rangle = \frac{\int_0^1 P_2 (\cos \theta) \exp \left[ \beta v P_2 (\cos \theta) \langle P_2 \rangle \right] d (\cos \theta)}{\int_0^1 \exp \left[ \beta v P_2 (\cos \theta) \langle P_2 \rangle \right] d (\cos \theta)} \quad (2.62)$$

which is a self-consistent equation for $\langle P_2 \rangle$ in terms of the temperature. This equation predicts a jump in $O_{nem}$ from 0 to 0.43 at the transition temperature. Both smaller and larger values have been observed experimentally. When steric effects are included in the theory, one tends to get a more strongly first-order transition. On the other hand, when one takes into account the fact that actual molecules do not have cylindrical symmetry the discontinuity in the order parameter tends to be smaller [56].

The Maier-Saupe interaction has found application to semiflexible polymers in the work of Duchs and Sullivan [33] for the nematic to smectic-A transition in rod-coil diblock copolymers. In this case the spherical harmonic expansion of the excluded volume interaction has been truncated to the second order Legendre polynomial. The work of Netz and Schick [57] on symmetric $AB$ diblock copolymers also uses a Maier-Saupe type interaction in addition to the Flory-Huggins [44, 58] interaction to look at the interplay between alternating $A-B$
lamellar ordering and nematic ordering of semiflexible polymers.

2.6.2 The Onsager excluded volume interaction

The Onsager excluded volume interaction is applied to a monodisperse solution of rigid-rod molecules modelled as spherocylinders, that is, a cylinder of length $L$ and diameter $D$ capped on each end with a hemisphere of diameter $D$. The total length of the spherocylinder is thus $L + D$, not to be confused with $L$, and one could take the limit $L \to 0$ to obtain a sphere of diameter, $D$. The excluded volume of a given spherocylinder of orientation $\mathbf{u}$
due to the presence of another spherocylinder of orientation $u'$ is [7]

$$V_{rod-rod} (u, u') = 2L^2 D |u \times u'| + 2\pi D^2 L + \frac{4}{3} \pi D^3. \quad (2.63)$$

This expression would be more complicated if each rod was a different size. The first term is due to the cylinder side of each rod sliding against each other, traversing a parallelogram shape (see Fig. 2.5). The second term is due to both of the hemisphere ends of one rod against the cylinder part of the other rod, and vice versa. The last term is due to both hemisphere ends against each other. A common approximation [1, 2, 33, 36, 59], valid in the limit $L \gg D$, is to ignore the last two terms which are at least of order $D/L$ smaller than the leading term. Eq. (2.63) becomes

$$V_{rod-rod} (u, u') \simeq 2L^2 D |u \times u'|$$

$$\simeq 2L^2 D |\sin \gamma|, \quad (2.64)$$

where $\gamma$ is the relative orientation between the two rods.

Ignoring terms that are $O(\rho^3)$ and higher, the free energy for a spatially uniform system as derived by Onsager then has the form [5]:

$$\beta F = \beta F_0 + n \int du \phi (u) \log [4\pi \phi (u) \rho] + \frac{\rho^2 V}{2} \int du \int du' V_{rod-rod} (u, u') \phi (u) \phi (u') \quad (2.65)$$

where $\phi (u)$ is the distribution function for rigid rod molecules, normalized according to $\int du \phi (u) = 1$, $n$ is the number of particles, $V$ is the system volume and $\rho$ is the particle
number density, see Table 2.1. The above is the second virial approximation to the free energy, having the form of Eq. (B.3) as discussed in Appendix B. The ideal contribution $F_{\text{ideal}}$, to the free energy is given by the first two terms and the two-body interaction free energy $F_{\text{int}}$, by the last term. For rod-shaped particles the second term in the above accounts for the orientational entropy. Since the interaction potential between hard contacts is essentially infinite, all the behaviour of this system is independent of temperature [5].

The free energy, Eq. (2.65), successfully predicts an isotropic-nematic phase transition for rigid rods in the limit $L \gg D$. However, as mentioned in Appendix B, this is exact only in the limit of vanishing concentration, $\rho$.

### 2.6.3 Modification of Onsager’s model for semiflexible chains:

**The segment-segment interaction**

To apply the excluded volume approach to semiflexible polymer chains the chain is modelled as a spherocylinder of length $L$ and diameter $D$, as in the previous Section, but now incorporates a finite flexibility, as in Fig. 2.7. Using the notation of Section 2.4, the flexibility is modelled by considering the spherocylinder to be constructed of $N$ cylindrical segments each parameterized by the index $t$ which varies between 0 and 1. The length of each segment is therefore $L/N = L dt$ with diameter $D$, as shown in Fig. 2.6.

The excluded volume between two segments, located at the same position $\mathbf{r}$, in the limit of $L dt \gg D$, and of relative angle $\gamma$ has the exact same form as in Eq. (2.64) and is illustrated in Fig. 2.8 (a). This is also a parallelogram of side lengths $L dt$ and $L dt'$.
and thickness $2D$ given by $V_{excl} = 2L^2Ddtdt'|\sin \gamma|$. Using a delta function to account for whether the segment locations $\mathbf{r}$ and $\mathbf{r}'$ are the same, this is relabelled in terms of the segment orientations $\mathbf{u}$ and $\mathbf{u}'$ as

$$v_{seg-seg}(\mathbf{r}, \mathbf{u}, dt; \mathbf{r}'\mathbf{u}', dt') \simeq \delta (\mathbf{r} - \mathbf{r}') 2L^2Ddtdt'|\mathbf{u} \times \mathbf{u}'|.$$ (2.66)

The above excluded volume between two segments is known to induce nematic ordering in semiflexible polymer chains [1, 17].
Figure 2.8: (a) Excluded volume between two rigid rods of lengths $L dt$, $L dt'$ and widths $D$, $D$. This is taken in the limit where $L dt \gg D$ and $L dt' \gg D$. The angle $\gamma$ is fixed when finding this excluded volume. (b) Excluded volume between a cylindrical segment and a hemispherical end segment.

The external interaction, Eq. (2.2), due to the excluded volume, Eq. (2.66), between all segments in the system of $n$ polymer chains, $W_{\text{seg-seg}} ([r(t), u(t)], n)$ can now be computed. The notation $([r(t), u(t)], n)$ denotes the configuration $[r(t), u(t)]$ for $n$ different continuous polymer chains. Summing over all segment pairs $(t, t')$ between two molecules, then summing over all molecule pairs $(j, j')$ and using Eq. (2.66) for $v_{\text{seg-seg}}$ gives

\[
\beta W_{\text{seg-seg}} ([r(t), u(t)], n) = \frac{1}{2} \sum_{j=1}^{n} \sum_{j'=1}^{n} \int_{t=0}^{1} dt \int_{t'=0}^{1} dt' \int d\mathbf{r} d\mathbf{r}' d\mathbf{u} d\mathbf{u}' \\
\times \delta (\mathbf{r} - \mathbf{r}') 2L^2 D dt dt' |\mathbf{u} \times \mathbf{u}'| \\
\times \delta (\mathbf{r} - \mathbf{r}_j (t)) \delta (\mathbf{u} - \mathbf{u}_j (t)) \delta (\mathbf{r}' - \mathbf{r}_{j'} (t')) \delta (\mathbf{u}' - \mathbf{u}_{j'} (t'))
\]

(2.67)

where the integrals $\int d\mathbf{r} d\mathbf{r}' d\mathbf{u} d\mathbf{u}'$ and the delta functions account for the relative positions.
\((r_j(t_j), r_{j'}(t_{j'}))\) and relative orientations \((u_j(t_j), u_{j'}(t_{j'}))\) between all \(N \times n\) segments in the system. Using the relation for \(\rho \hat{\phi}(r, u)\) from Eq. (2.55) and collapsing the double integral \(\int dr \int dr'\) with the delta function in (2.67), the latter becomes

\[
\beta W_{\text{seg-seg}}([r(t), u(t)], n) = \frac{\rho^2}{2} \int dr du d u' 2L^2 D |u \times u'| \hat{\phi}(r, u) \hat{\phi}(r, u')
= \frac{\rho^2}{2} \int dr du d u' V_{\text{seg-seg}}(u, u') \hat{\phi}(r, u) \hat{\phi}(r, u')
\]

where \(V_{\text{seg-seg}}(u, u')\) is now independent of \(r\) and \(dt\) and, in fact, is now equal to the Onsager approximation, \(V_{\text{rod-rod}}(u, u')\) from Eq. (2.64). However, throughout this work the notation

\[
V_{\text{seg-seg}}(u, u') = 2L^2 D |u \times u'|
\]

will be used to describe the interaction between the segments, even though it contains the polymer chain length \(L\) instead of the segment length, \(Ldt\). This is not as misleading as it may seem; physically it contains information about the system average of the segment-segment excluded volume interactions, as shown above, rather than the details of every segment-segment interaction.

For the second virial approximation to be truly valid here \(Ldt \gg D\) must hold. Or in other words, \(D \to 0\) for finite length, \(L\). However, in the limit of the semiflexible polymer, \(dt \to 0\). For the second virial approximation to be compatible with the semiflexible limit, one would need to have \(dt \gg D\), and \(D\) should approach zero faster than \(dt\). This could be strictly enforced in the theory here; however, in the calculations of this Thesis and other works \([2, 33]\), this is not satisfied. For example in Chapter 3 it is seen that while \(dt\) can be
made to be $> 10^{-2}$, the examined $L/D$ in the SmA phase is always less than $\sim 10^2$ and therefore $dt \gg D$ is not satisfied. This inconsistency may be viewed as a limitation of the theory even though sensible results can still be obtained.

### 2.6.4 Including the end-segment interaction

The excluded volume interaction between a cylindrical segment located along the backbone of a polymer chain and a hemispherical end segment for the semiflexible polymer chain (see Fig. 2.8 (b)) is given by,

$$v_{end-seg}(r, u; r', u', dt') = \delta(r - r') V_{end-seg}(u, u') dt'. \tag{2.70}$$

A similar form as $v_{seg-seg}$ in Eq. (2.66) is used. The above interaction was originally introduced by Hidalgo et al. [2]. The term $V_{end-seg}$ is

$$V_{end-seg}(u, u') = \pi D^2 L/2 \tag{2.71}$$

and $V_{end-seg}(u, u') dt'$ is equal to half the volume of a cylinder of length $Ldt'$ and diameter $D$. A subtle point is that this expression is smaller than that for the rigid-rod in the Onsager excluded volume, Eq. (2.63), by a factor of $\frac{1}{4}$. This difference is because the corresponding term in the Onsager expression, $2\pi LD^2$, considers the side/end excluded volume due to rod 2 of rod 1 as a whole. In what follows, $V_{end-seg} dt' (u, u')$ corresponds to for the four different possible types of contact pairs $(t = 0, t'), (t = 1, t'), (t, t' = 0)$ and
\((t, t' = 1)\) between two molecules, where \(t = 0\) or \(1\) indexes the position of the hemispherical end, and \(0 < t < 1\) indexes the position of a cylindrical segment anywhere between the ends. This interaction conveniently does not depend on the relative segment orientations, thereby making calculations simpler, whereas if the molecules had flat ends this would not be the case.

As was done for the segment-segment interaction the contribution to the external interaction due to the total end-segment interaction, \(W_{\text{end-seg}}([r(t), u(t)] , n)\), in a system of \(n\) polymer chains can be calculated. In the following, \(\delta (r - r_j (0))\) means that the delta function is accounting for the segment indexed by \(t = 0\) of molecule \(j\) etc. Analogous to Eq. (2.67), this gives

\[
\beta W_{\text{end-seg}} ([r(t), u(t)], n) = \frac{1}{2} \sum_{j=1}^{n} \sum_{j'=1}^{n} \int drdr'dudu' \left[ \right.
\left. \int_{t=0}^{1} \delta (r - r') V_{\text{end-seg}} (u, u') dt \delta (r - r_j (t)) \delta (u - u_j (t)) \right.
\left. + \int_{t'=0}^{1} \delta (r - r') V_{\text{end-seg}} (u, u') dt' \delta (r - r_{j'} (t')) \delta (u' - u_{j'} (t')) \right]
\right] .
\]

Note how there are four terms for each pair of molecules. Two terms are for each end indexed by \(t = 0\) and \(t = 1\) while the role of the segment-end pair interaction is reversed as all possible interactions are summed. Now using the relation \(\rho \hat{\phi} (r, u, t)\) and \(\rho \hat{\phi} (r, u)\) from Eqs. (2.54) and (2.55), and using the delta function to collapse the double integral
\[ \int drdr', \text{ Eq. (2.72)} \text{ becomes} \]

\[
\beta W_{\text{end-seg}} ([r(t), u(t)], n) = \frac{\rho^2}{2} \int drdu\hat{u}' V_{\text{end-seg}} (u, u') \times
\left\{ \hat{\phi} (r, u) \left[ \hat{\psi} (r, u', 0) + \hat{\psi} (r, u', 1) \right] + \hat{\phi} (r, u) \left[ \hat{\psi} (r, u', 0) + \hat{\psi} (r, u', 1) \right] \right\}
\]

\[ = \rho^2 \int drdu\hat{u}' V_{\text{end-seg}} (u, u') \hat{\phi} (r, u) \left[ \hat{\psi} (r, u', t = 0) + \hat{\psi} (r, u', t = 1) \right] \]

### 2.6.5 \text{ The total excluded volume interaction} \\

The last possible excluded volume is between the two hemispherical ends and tends to repel the ends of adjacent molecules. This corresponds to the last term of Eq. (2.63). This interaction is neglected in this Thesis as it is lower than the other two by at least a factor of \( D/L \). The total interaction energy of this system is obtained by combining Eq. (2.68) and (2.73)

\[
\beta W ([r(t), u(t)], n) = \beta W_{\text{seg-seg}} ([r(t), u(t)], n) + \beta W_{\text{end-seg}} ([r(t), u(t)], n).
\]

### 2.7 \text{ The order parameters} \\

It is important to quantify the amount of either orientational or positional ordering. Knowledge of the distribution function \( \phi (r, u) \) or \( \psi (r, u, t) \) can indeed tell what phase the system is in. However, from a theoretical viewpoint, this is typically too much information. Therefore, a much more concise viewpoint is to consider the relevant order parameters, which
Figure 2.9: Cartesian co-ordinate system and the director. The angle $\theta$ is with respect to the $z$ axis, defined to be perpendicular to the lamellar plane. The average orientation of the segments is given by the director. For the N and SmA phase the director is in the $z$ direction. For the SmC phase, the director is tilted with respect to the $z$ direction; this is not shown. The tilt direction within the $x,y$ plane is given by $\varphi$.

are single valued quantities that attempt to capture the ordered structure of the phase of interest.

To examine nematic ordering the order parameter $O_{nem}$, is defined. This is zero in the isotropic phase and non-zero in the nematic phase. For conventional nematics, (ignoring position dependence here), $\phi (u) = \phi (\theta)$ since there is complete cylindrical symmetry and $\phi (\theta) = \phi (\pi - \theta)$ since one end of the rigid rod is indistinguishable from the other. The angle $\theta$ is with respect to the director, which is defined to be the direction of average orientation, shown in Fig. 2.9. A naive assignment to $O_{nem}$ would be the average of the first Legendre polynomial, $P_1 (\cos \theta) = \cos \theta$:

$$\langle \cos \theta \rangle = \int d\mathbf{u} \phi (\theta) \cos \theta,$$

(2.75)
where \( \int du = \int_0^{2\pi} d\varphi \int_0^\pi \sin \theta d\theta \). But this gives a value of zero, as would any odd \( P_1 \) due to the indistinguishability of rod ends. A common definition of a nematic order parameter, and the one that is adopted in this Thesis, is given by the lowest non-trivial Legendre polynomial with non-vanishing average

\[
O_{\text{nem}} = \langle P_2 (\cos \theta) \rangle = \int d\mathbf{u} \phi (\theta) \frac{1}{2} (3 \cos^2 \theta - 1).
\]  

(2.76)

This is proportional to the second coefficient in the Legendre polynomial expansion for \( \phi (\theta) \), see Appendix C.1.

As noted in Appendix C.1, it is not out of the question to investigate different nematic order parameters. Some work has been done to investigate the “higher degree order parameter”, \( \langle P_4 (\cos \theta) \rangle \). Earlier studies on nematic ordering involved comparing measurements on thermotropic systems using Raman scattering [19], electron paramagnetic resonance [60], and coherent neutron scattering [61] of \( \langle P_4 (\cos \theta) \rangle \) to the mean-field theory prediction by Humphries, James, and Luckhurst [62]. However, \( \langle P_4 (\cos \theta) \rangle \) is not studied in this work.

The smectic-A order parameter, \( O_{\text{smA}} \), should be zero in the isotropic and nematic phase and non-zero in the smectic-A phase. This is satisfied by all but the lowest purely translational coefficients in the spectral decomposition of \( \phi (z, \theta) \) (see Appendix C.2), where for this phase only the position, \( z \), perpendicular to the smectic layers is needed. A common definition for \( O_{\text{smA}} \) is the lowest non-vanishing of these coefficients given by the average \( \langle \cos (2\pi z/\lambda) \rangle \), where \( \lambda \) is the width of the smectic layers [63, 64]. However, in this
Thesis a different definition \cite{2,33} for \( O_{sm,A} \) is used:

\[
O_{sm,A} = \left( \frac{1}{\lambda} \int_{0}^{\lambda} dz \left[ \int du \phi(z,u) - 1 \right]^2 \right)^{1/2}, \tag{2.77}
\]

where \( \int du \phi(z,u) \) is equal to \( \sqrt{4\pi} \phi_0(z) \) and \( \phi_0(z) \) is the lowest term of the spherical harmonic expansion (see Eq. \cite{C.12}) of \( \phi(z,u) \). \( O_{sm,A} \) in previous work \cite{2,33} is written in terms of \( \sqrt{4\pi} \phi_0(z) \), since a spherical harmonic expansion is used. But in this work Eq. \eqref{2.77} is in terms of \( \int du \phi(z,u) \), since a real space approach for the orientations is used. Eq. \eqref{2.77} is in fact related to the infinite sum of the squared Fourier coefficients (see Appendix C.2).

The above discussion can apply to simple rigid rod type molecules or it can apply to flexible polymers consisting of a chain of rigid segments attached end to end. For the latter case, the quantity \( \phi(z,u) \) would then correspond to an average over all the individual distribution functions, \( \psi(z,u,t) \), for each rigid rod segment, indexed by \( t \), within the chain. This is illustrated by Eq. \eqref{2.60} and the related discussion.

### 2.8 Mean-field theory and free energy

The mean-field approach consists of imagining just one molecule in the presence of an external field which is generated by all the other molecules. Each molecule is then viewed like this, which enables the mean-field approach to describe the whole system. For a system of \( n \) chains and using the potential energy Eq. \eqref{2.2} with external field, \( W \), given by the
excluded volume expressions Eqs. (2.68, 2.73) and (2.74), the partition function Eq. (2.4) in the canonical ensemble can be written as

\[ Z = \int D_n \{ \cdot \} \exp \left( -\beta W (\{ r(t) , u(t) \} , n) \right) \]  

(2.78)

where

\[ \int D_n \{ \cdot \} = \frac{1}{n!} \prod_{i=1}^{n} \int D r_i \int D u_i P \{ r_i , u_i ; [0, 1] \} \]  

(2.79)

and

\[ P \{ r_i , u_i ; [t_1 , t_2] \} \propto \exp \left( -\frac{\xi}{2} \int_{t_1}^{t_2} dt \left| \frac{du(t)}{dt} \right|^2 \right) \prod_{t=t_1}^{t_2} \left[ \delta \left( u_i (t) - \frac{dr_i (t)}{dt} \right) \delta (| u_i (t) | - 1) \right] \]  

(2.80)

where \( \beta U_0 (\{ r , u \}) = \frac{\xi}{2} \int_{0}^{1} dt \left| \frac{du(t)}{dt} \right|^2 \) corresponding to \( t_1 = 0 \) and \( t_2 = 1 \) is the bending energy from Eq. (2.45). The external field \( W \) was written in Eq. (2.74) in terms of the microscopic densities, Eqs. (2.54) and (2.55), which are too complicated to deal with. Therefore the statistical field theory approach is employed by converting the microscopic densities into the corresponding density fields given by Eqs. (2.58) and (2.57). First the partition function Eq. (2.78) is multiplied by \( 1 = \int D [\phi (r,u)] \delta \left[ \phi (r,u) - \hat{\phi} (r,u) \right] \) and \( 1 = \int D [\psi (r,u,t)] \delta \left[ \psi (r,u,t) - \hat{\psi} (r,u,t) \right] \). There are two such factors for \( \hat{\psi} \): one for \( t = 0 \) and one for \( t = 1 \). This allows the replacement of \( \hat{\psi} \) and \( \hat{\phi} \) within \( W \) by the fields \( \psi \)
and $\phi$. Next, the exponential representation of the delta function is used:

$$
\delta \left[ \phi(r, u) - \hat{\phi}(r, u) \right] \equiv \int D[w(r, u)] \\
\times \exp \left\{ i \int dr du \left[ \phi(r, u) - \hat{\phi}(r, u) \right] \right\},
$$

with the same thing done for $\psi$ at $t = 0$ and $t = 1$. Eq. (2.78) then becomes

$$
Z = \int D[-iw] \int D[\phi] \int D[-iw_q(t = 0)] \int D[\psi(t = 0)] \\
\times \int D[-iw_q(t = 1)] \int D[\psi(t = 1)] \\
\times \exp \left( -F[w, \phi, w_q(t = 0), \psi(t = 0), w_q(t = 1), \psi(t = 1)] \right)
$$

with $F$ identified as the free energy of the system. $F$ is given by:

$$
\beta F = \frac{\rho^2}{2} \int dr du u' V_{seg-seg}(u, u') \phi(r, u) \phi(r, u') \\
+ \rho^2 \int dr du u' V_{end-seg}(u, u') \phi(r, u) [\psi(r, u', t = 0) + \psi(r, u', t = 1)] \\
- \rho \int dr du \left\{ w(r, u) \phi(r, u) - w_q(r(0), u(0)) \psi(r, u, 0) - w_q(r(1), u(1)) \psi(r, u, 1) \right\} \\
- \ln \left( \frac{Q^n}{n!} \right)
$$

where

$$
Q[-iw_q(r(0), u(0)), -iw, -iw_q(r(1), u(1))] = \int D_1 \{ \cdot \}
$$

$$
\exp \left\{ -w_q(r(0), u(0)) - \int_0^1 dt w(r(t), u(t)) - w_q(r(1), u(1)) \right\}
$$
is the partition function of a semiflexible chain in the external fields $w$ and $w_q (r (0), u (0))$ and $w_q (r (1), u (1))$. From now on the functional dependence of $Q$ on the fields will be not be shown, for brevity.

The mean-field equations are found by taking the saddle point of the free energy (2.83) with respect to $\phi (r, u), \ w (r, u), \ \psi (r (0), u (0)), \ w_q (r (0), u (0)), \ \psi (r (1), u (1))$ and $w_q (r (1), u (1))$, to give

$$w (r, u) = \rho \int du' \phi (r, u') V_{seg-seg} (u, u')$$
$$+ \rho \int du' V_{end-seg} (u, u') [\psi (r, u', t = 0) + \psi (r, u', t = 1)]$$

$$\phi (r, u) = -\frac{V}{Q} \frac{\delta Q}{\delta w (r, u)}, \ (2.86)$$

$$w_q (r(t), u(t)) = \rho \int du' V_{end-seg} (u, u') \phi (r, u'), \ t = 0 \text{ or } 1, \ (2.87)$$

$$\psi (r, u, t = 0) = -\frac{V}{Q} \frac{\delta Q}{\delta w_q (r (0), u (0))}, \ (2.88)$$

$$\psi (r, u, t = 1) = -\frac{V}{Q} \frac{\delta Q}{\delta w_q (r (1), u (1))}.$$

Using the above equations the equilibrium value of the free energy (2.83) is first solved. Substituting in $w (r, u)$ and $w_q (r, u)$ gives

$$\beta F = -\frac{\rho^2}{2} \int dr du du' V_{seg-seg} (u, u') \phi (r, u) \phi (r, u')$$
$$- \rho^2 \int dr du du' V_{end-seg} (u, u') \phi (r, u) [\psi (r, u', t = 0) + \psi (r, u', t = 1)]$$

$$- \ln \left( \frac{Q^n}{n!} \right). \ (2.89)$$

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and can be written as the free energy of an ideal fluid plus an excluded volume interaction term as follows:

$$\beta F = \beta F_{\text{ideal}} + \beta F_{\text{int}}. \quad (2.90)$$

$$\beta F_{\text{int}}$$ is given by

$$\beta F_{\text{int}} = -\frac{\beta^2}{2} \int dr du u' V_{\text{seg-seg}}(u, u') \phi(r, u) \phi(r, u')$$

$$- \rho^2 \int dr du u' V_{\text{end-seg}}(u, u') \phi(r, u) [\psi(r, u', t = 0) + \psi(r, u', t = 1)]. \quad (2.91)$$

In order to solve Eqs. (2.86) and (2.88) for the densities $$\psi$$ and $$\phi$$ it is customary to factorize $$Q[W]$$ in terms of the end-segment distribution functions defined, as in Hidalgo et al. [2], by

$$q(r, u, t) = \int D\{r_i, u_i\} P\{r_i, u_i; [0, t]\} \delta(r - r_i(t)) \delta(u - u_i(t))$$

$$\times \exp\left\{-w_q(r(0), u(0)) - \int_0^t dt' w[r(t'), u(t')]\right\}, \quad (2.92)$$

$$q^\dagger(r, u, t) = \int D\{r_i, u_i\} P\{r_i, u_i; [t, 1]\} \delta(r - r_i(t)) \delta(u - u_i(t))$$

$$\times \exp\left\{-\int_t^1 dt' w[r(t'), u(t')] - w_q(r(1), u(1))\right\}. \quad (2.93)$$

In the above expression, $$q$$ is also known as the chain propagator, or propagator for short. The above formulas for $$q$$ and $$q^\dagger$$ are explained in more detail in Appendix A.3. The interpretation of the propagator is that for a given segment indexed by $$t$$ located at position
Figure 2.10: The propagator, $q$. (a) For a conformation with segments indexed by $t'$ where $0 < t' < 1$, consideration is given to segment $t$ located at $r$ with orientation $u$. (b) $q(r, u, t)$ is the distribution of all possible conformations of segments indexed by $t' < t$, of which only a very small number are sketched. (c) Similarly, $q^\dagger(r, u, t) = q(r, -u, 1 - t)$ is the distribution of all possible conformations of segments indexed by $t' > t$.

$r$ and orientation $u$, it gives the probability distribution for the conformation of chain segments between $t' = 0$ and $t' = t$. An illustration of this is given in Fig. 2.10, where the interpretation of $q^\dagger(r, u, t)$ is that for a given segment indexed by $t$ located at position $r$ and orientation $u$ it gives the probability distribution for the conformation of chain segments between $t' = t$ and $t' = 1$. For the simplified case of homopolymers, the following equation holds for the propagators (see Appendix A.3):

$$ q(r, u, t) = q^\dagger(r, -u, 1 - t). \quad (2.94) $$

while $Q$ is given by

$$ Q = \int dr du q(r, u, t) q^\dagger(r, u, t). \quad (2.95) $$

It is then necessary to solve for the propagators. Similar to Eq. (2.47) in the absence of
an external field, a Chapman-Kolmogorov equation can be constructed and using a similar method in obtaining Eq. (2.52) (see Appendix A.3), it is seen that $q(r, u, t)$ and $q^\dagger(r, u, t)$ obey the following Fokker-Planck equation

$$
\frac{\partial}{\partial t} q(r, u, t) = \left[ -L u \cdot \nabla_r + \frac{1}{2\xi} \nabla_u^2 - w(r, u) \right] q(r, u, t),
$$
$$
\frac{\partial}{\partial t} q^\dagger(r, u, t) = \left[ -L u \cdot \nabla_r - \frac{1}{2\xi} \nabla_u^2 + w(r, u) \right] q^\dagger(r, u, t). \tag{2.96}
$$

The above equation satisfies the following initial condition

$$
q(r, u, t \to 0) = \exp \left(-w_q(r(0), u(0))\right) \tag{2.97}
$$

which can be seen by examining Eq. (2.92) for the limit $t \to 0$. Similarly, the initial condition on $q^\dagger$ is

$$
q^\dagger(r, u, t \to 1) = \exp \left(-w_q(r(1), u(1))\right). \tag{2.98}
$$

Note that the term $-L u \cdot \nabla_r$ does not change sign in the Fokker-Planck equation for both $q$ and $q^\dagger$. With the above definitions of $Q, q$ and $q^\dagger$, the mean-field equations (2.85-2.88) give for the density fields, Eqs. (2.57) and (2.58)

$$
\psi(r, u, t) = \frac{V}{Q} q(r, u, t) q^\dagger(r, u, t) \tag{2.99}
$$
$$
\phi(r, u) = \frac{V}{Q} \int_0^1 dt q(r, u, t) q^\dagger(r, u, t). \tag{2.100}
$$

The main result of this section is that to solve for the phase behaviour of this system,
the Fokker-Planck equation (2.96) must be solved for the propagators $q$ and $q^\dagger$. Once these are found, the statistical fields $\psi$ and $\phi$, and the free energy energy (2.89) are easily obtained. The solutions of the non-trivial nematic, smectic-A, smectic-C phases of (2.96) are not exact and require numerical methods of solving differential equations. These details are covered in Sections 2.9, 2.10 and 2.12.

### 2.9 Self-consistent calculations

The wormlike chain model has $5N$ degrees of freedom in total per particle: for each segment the $x$, $y$, $z$ coordinate in space plus the orientation $\theta$ (polar angle) and $\varphi$ (azimuth angle) with respect to the director (see Fig. 1.1 a) and b)). Note that $\varphi$ is not to be confused with $\phi$ for the contour averaged density field. In this Section the theory is specialized to describe the I, N and SmA phases. Since the N phase is homogenous in space but uniaxially anisotropic, the only coordinate needed in the densities is $\theta$. The SmA phase exhibits periodic lamellar-like variation in the $z$ direction in addition to uniaxial ordering, so therefore for this phase there are two relevant coordinates, $z$ plus $\theta$. The SmC phase is similar to the SmA phase yet in addition, exhibits biaxial ordering. This phase requires the extra coordinate $\varphi$ to describe the direction in the $x,y$ plane of the molecular tilt, shown in Fig. 2.9. Since this adds one extra dimension to the problem, a basic finite grid type numerical approach to this problem takes much longer. In the case of this Thesis this approach was not considered since it is extremely prohibitive using current computer processor technology. However, it is definitely not out of the question to consider
a perturbative approach [65] to search for a possible bifurcation of the SmC free energy from the SmA state.

First the symmetry relations for the propagators \( q \), and the densities \( \phi \) and \( \psi \) are given. These are useful for optimizing the numerical solution algorithm, discussed in Section 2.10. The propagators satisfy

\[
q (r, u, t) = q (\lambda - r, -u, t),
\]

(2.101)

where \( \lambda \) denotes the three-dimensional crystal lattice translation vector of the unit cell of the phase [66]. This relation comes from examining the Fokker-Planck equation, (2.96), term by term. The first term involves the product \( Lu \cdot \nabla r \), in which the negative signs cancel. The Laplacian term, \( \frac{1}{2\xi} \nabla^2 u \) is similar. The field term, \( w \), is more subtle. From (2.85), \( w \) depends on \( V_{\text{seg-seg}} \) which satisfies \( V_{\text{seg-seg}}(u, u') = V_{\text{seg-seg}}(-u, u') \), explained in Section 2.9.1, Eq. (2.112) below. \( w \) also depends on \( \psi \) and \( \phi \), which in turn both depend on \( q \) from (2.99) and (2.100). This shows that Eq. (2.96) is a self-consistent equation for \( q \), since \( w \) can be written in the form, \( w = w(q(r, u, t)) \) (see Section 2.9.1 as well). Eq. (2.96) can be then written as:

\[
\frac{\partial}{\partial t} q (r, u, t) = \left[ -Lu \cdot \nabla r + \frac{1}{2\xi} \nabla^2 u - w(q(r, u, t)) \right] q (r, u, t).
\]

(2.102)

Substituting \( q (\lambda - r, -u, t) \) in the above gives

\[
\frac{\partial}{\partial t} q (\lambda - r, -u, t) = \left[ -Lu \cdot \nabla r + \frac{1}{2\xi} \nabla^2 u - w(q(\lambda - r, -u, t)) \right] q (\lambda - r, -u, t).
\]

(2.103)
Since $q(r, u, t)$ and $q(\lambda - r, -u, t)$ satisfy the same equation, the symmetry $q(r, u, t) = q(\lambda - r, -u, t)$ holds.

The $t$-segment density field satisfies

$$\psi(r, u, t) = \psi(r, -u, 1 - t)$$  \hspace{1cm} (2.104)$$

which follows easily from Eq. (2.94). From (2.94) and (2.101) the following also holds

$$\psi(r, u, t) = \psi(\lambda - r, u, 1 - t).$$  \hspace{1cm} (2.105)$$

The contour average segment density field satisfies

$$\phi(r, u) = \phi(r, -u) = \phi(\lambda - r, u)$$  \hspace{1cm} (2.106)$$

which follows by looking at (2.100) written as

$$\phi(r, u) = \frac{V}{Q} \int_0^1 dt q(r, u, t) q(r, -u, 1 - t)$$  \hspace{1cm} (2.107)$$

and from the other relations (2.104) and (2.105).

The calculations in this Section use a real space approach in which the equations are presented in the most obvious form, in terms of $z$ and $\theta$ (actually $\cos \theta$). Previous works on lamellar ordering [57, 67] and smectic ordering [2, 33, 68] of semiflexible polymers have employed a spherical harmonic expansion to express the orientational dependence of the
mean-field quantities:

\[ \phi (z, u) = \sum_{l,m} \phi_{l,m}(z) Y_{l,m}(u) \]  

(2.108)

with similar expansions for \( w(z, u), q(z, u, t), q^\dagger(z, u, t) \). Since in these works the systems have cylindrical symmetry, only the \( m = 0 \) terms are used, which are proportional to Legendre polynomials. Other work on interfacial behaviour of semiflexible homogenous polymers also has made use of the spherical harmonic expansion [59, 69]. While the spherical harmonic expansion approach may have sufficed for interfacial and confinement ordering, in the study by Hidalgo it presented the problem that the solutions were difficult to converge for states of high nematic ordering, which typically occur for length to diameter ratio, \( L/D > 10 \). Another study [34] on the ordering of semiflexible A-B block copolymers describes the orientations using a polyhedral mesh of around 380 points which approximates the unit sphere. Since these points are distributed in the \( \theta \) and \( \varphi \) direction, it is able to locate a SmA-SmC transition (see Fig. 1.6).

### 2.9.1 1-dimensional theory

The coordinate system is shown in Fig. 2.9 with the origin coinciding with \( z = 0 \). It will now be shown that the theory for one-dimensional uniaxial ordering can be written in terms of just the polar angle. First, it is more concise to work in terms of the cosine of the polar angle which happens to be the \( z \) projection of the orientation vector \( u \),

\[ u_z = \cos(\theta). \]  

(2.109)
The orientation integrals then become
\[ \int d\mathbf{u} = \int_0^{2\pi} d\varphi \int_0^\pi \sin(\theta) \, d\theta = \int_0^{2\pi} d\varphi \int_{-1}^1 du_z. \tag{2.110} \]

The azimuthal angle \( \varphi \) cannot be ignored but is present only in the interaction potential, \( V_{seg-seg}(\mathbf{u}, \mathbf{u}') \). The only occurrence of \( V_{seg-seg} \) in the theory is inside the integral of Eq. (2.85), which has the following form:
\[ \int d\mathbf{u}' \phi(\mathbf{r}, \mathbf{u}') \, V_{seg-seg}(\mathbf{u}, \mathbf{u}') = 2 \int_0^1 du'_z \phi(z, u'_z) \int_0^{2\pi} d\varphi V_{seg-seg}(\mathbf{u}, \mathbf{u}'). \tag{2.111} \]

The simplification of the \( du_z \) integral to half of the domain is enabled by the symmetry relations \( \phi(z, u_z) = \phi(z, -u_z) \), see Eq. (2.106), and the symmetry of the excluded volume:
\[ V_{seg-seg}(\mathbf{u}, \mathbf{u}') = V_{seg-seg}(\mathbf{u}, -\mathbf{u}') = V_{seg-seg}(-\mathbf{u}, \mathbf{u}'). \tag{2.112} \]

This is seen by noting \( V_{seg-seg} \sim |\mathbf{u} \times \mathbf{u}'| \) is simply the area of a parallelogram which is independent of reversing the direction of \( \mathbf{u} \) or \( \mathbf{u}' \). While the operation \( \mathbf{u} \rightarrow -\mathbf{u} \) gives \( u_z \rightarrow -u_z \) and \( \varphi \rightarrow \pi + \varphi \), the effect on the integral (2.111) over \( \varphi \) remains unchanged, since it only applies to \( V_{seg-seg} \). This integral is denoted as
\[ \int_0^{2\pi} d\varphi V_{seg-seg}(\mathbf{u}, \mathbf{u}') = \bar{V}^{\varphi}_{seg-seg}(u_z, u'_z) \tag{2.113} \]
where the overbar and superscript \( \varphi \) in (2.113) denotes an average with respect to \( \varphi \). The
explicit formula for $\bar{V}_{\text{seg-seg}}'$ is

$$\bar{V}_{\text{seg-seg}}'(u_z, u_z') = \int_0^{2\pi} d\varphi \left[ 1 - \left( \cos \varphi \sqrt{1 - u_z^2} \sqrt{1 - u_z'^2} + u_z u_z' \right)^2 \right]^{1/2}, \quad (2.114)$$

and is derived by first writing out the orientations, $\mathbf{u}, \mathbf{u}'$, in terms of the $(x, y, z)$ components, then taking the absolute value of the cross-product, $|\mathbf{u} \times \mathbf{u}'|$. The next step is to integrate this with respect to $\varphi$. To simplify, $\varphi'$ is set to zero when integrating over $\varphi$. $\bar{V}_{\text{seg-seg}}'(u_z, u_z')$ is now defined as the segment-segment excluded volume with respect to just the polar angles, $u_z$ and $u_z'$ and, as desired, the theory no longer contains the coordinate $\varphi$. This is similar to a method used in [65].

The mean-field equations are now as follows for the density fields:

$$\psi (z, u_z, t) = \frac{V}{Q} q (z, u_z, t) q^\dagger (z, u_z, t) \quad (2.115)$$

$$\phi (z, u_z) = \frac{V}{Q} \int_0^1 dq \int_0^1 \psi (z, u_z, t) \psi^\dagger (z, u_z, t). \quad (2.116)$$

$$Q = 4\pi A \int_0^\Lambda dz \int_0^1 du_z q (z, u_z, t) q^\dagger (z, u_z, t) \quad (2.117)$$

where $A$ is the cross sectional area of the volume integration in the $x$ and $y$ directions. For the one-dimensional smectic-A phase, the mean-field equations (2.115-2.117) are independent of this area, and it is set to $A = 1$. The Fokker-Planck equation, Eq. (2.96) is
now

\[
\frac{\partial}{\partial t} q(z, u_z, t) = \left[ -L u_z \frac{\partial}{\partial z} + \frac{1}{2\xi} \nabla^2_u - w(z, u_z) \right] q(z, u_z, t),
\]

\[
\frac{\partial}{\partial t} q^+(z, u_z, t) = \left[ -L u_z \frac{\partial}{\partial z} - \frac{1}{2\xi} \nabla^2_u + w(z, u_z) \right] q^+(z, u_z, t).
\]

(2.118)

with the following initial condition

\[ q(z, u_z, t \to 0) = e^{-w_q(z, u_z)}. \]

(2.119)

The external fields are now

\[ w_q(z, u_z) = 4\pi C_2 \int_0^1 du_z \phi(z, u_z), \]

(2.120)

for Eq. (2.87). This is conveniently independent of \( u_z \), due to the integration over the orientation \( u_z \), and satisfies \( w_q(z, u_z) = w_q(\lambda - z, u_z) \). \( C_2 \) is given by

\[ C_2 = \frac{\pi}{2} \rho D^2 L. \]

(2.121)

\( w \), Eq. (2.85), is now

\[
w(z, u_z) = 2C' \int_0^1 du'_z \bar{V}_{\text{seg-seg}}(u_z, u'_z) \phi(z, u'_z) + 4\pi V_Q C_2 e^{w_q(z, u_z)} \int_0^1 du_z [q(z, u'_z, 1) + q(\lambda - z, u'_z, 1)]
\]

(2.122)

where in the last term, the expression \( \psi(z, u_z, t) = \frac{V}{Q} q(z, u_z, t) q(z, -u_z, 1 - t) \) for \( t = 0 \)
and \( t = 1 \) has been used, along with the initial condition and symmetry relations for \( q(z, u_z, t) \). \( C \) is given by

\[
C = \rho DL^2. \tag{2.123}
\]

The basic approach to solve the mean-field equations (2.115 - 2.122) is standard and is called \textit{self consistent field theory}. The numerical algorithm developed to solve the mean-field equations in this particular system is described in Section 2.10 and follows a different approach than previous works [2, 33, 34, 68]. Formally, the first step is to input a \textit{guess} for the external fields, Eqs. (2.120) and (2.122). Next, the Fokker-Planck equation (2.118) is solved for the propagators using the initial condition (2.119). Since the input external fields are incorrect, the propagators will also be incorrect, however they are used to calculate an updated value of the external fields, using Eqs. (2.120) and (2.122). These updated external fields are combined with the previous external fields to give a new input \textit{guess}. With this updated input guess, the previous steps are repeated until there is a possible convergence of the solution. This is illustrated in Fig. 2.11.

In practice the calculation for this Thesis differs slightly from the formal explanation above in that the density fields \( \phi, \psi(z, u_z, 0) \) and \( \psi(z, u_z, 1) \) are considered as inputs instead of the external fields \( w(z, u_z) \) and \( w_q(z, u_z) \). But the mean-field equations only contain \( \psi \) for \( t = 0 \) and \( t = 1 \) to account for the end-segment interaction. Since \( \psi(z, u_z, 0) = \frac{V}{Q} q(z, u_z, 0) q(z, -u_z, 1) \) and \( \psi(z, u_z, 1) = \frac{V}{Q} q(z, u_z, 1) q(z, -u_z, 0) \), it is more concise to use just the propagators, \( q \), at \( t = 0 \) and \( t = 1 \) as inputs instead of \( \psi \) at \( t = 0 \) and \( t = 1 \). \( q(z, u_z, 0) \) is easily given in terms of the guessed input density field \( \phi(z, u_z) \), see
The mixing method is discussed more in Appendix D. Equations (2.119, 2.120). However, $q(z, u_z, 1)$ is unknown, so it must be entered as an input guess just like the density fields.

The mixing of the external fields is done by the same algorithm as [2, 33] and is described in Appendix D.

This Section concludes with a table listing the relevant parameters in this study (Table 2.1).

### 2.10 Solution method for the Fokker-Planck equation

The main computational effort in this Thesis is dedicated to numerically solving the Fokker-Planck equation (2.118). In this Section the Crank-Nicolson (CN) finite difference numerical algorithm [70] is developed, which is the algorithm of choice in this Thesis. Previous
Table 2.1: List of parameters used in this study

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average number density</td>
<td>Discussed in Section 2.5. $n$ is the number of particles and $V$ is the volume of the system.</td>
<td>$\rho = n/V$</td>
</tr>
<tr>
<td>Length to diameter ratio</td>
<td>Ratio of the length, $L$, of the spherocylinder to the diameter, $D$. See Fig. 2.7.</td>
<td>$\frac{L}{D}$</td>
</tr>
<tr>
<td>Rescaled average number density</td>
<td>Dimensionless factor which simplifies the free energy, Eqs. (2.169,2.171). First given in Eq. (2.123). Also used in [1, 2, 33, 34].</td>
<td>$C = \rho DL^2.$</td>
</tr>
<tr>
<td>Modified rescaled averaged number density</td>
<td>Dimensionless factor which simplifies the free energy, Eqs. (2.169,2.171). First given in Eq. (2.121). Introduced by [2].</td>
<td>$C_2 = \frac{\pi}{2} \rho D^2 L$</td>
</tr>
<tr>
<td>Packing fraction</td>
<td>By definition this is $\eta = n \frac{V_{molecule}}{V}$ where $V_{molecule}$ is the volume of a single polymer chain.</td>
<td>$\eta = \frac{\pi \rho L D^2}{4} \left(1 + \frac{2 D}{3 L}\right)$</td>
</tr>
<tr>
<td>Dimensionless bending rigidity</td>
<td>Discussed in Section 2.4.1. $l_p$ is the persistence length.</td>
<td>$\xi = \frac{l_p}{L}$</td>
</tr>
<tr>
<td>Dimensionless smectic period</td>
<td>The wavelength of the periodic lamellar thickness in the SmA phase, given in units of the molecular length, $L$.</td>
<td>$\lambda$</td>
</tr>
</tbody>
</table>
calculations done by Düchs et al. [33] and Hidalgo et al. [2] to examine the SmA phase have used the explicit forward time centered space algorithm (FTCS), described in subsection 2.10.1. The FTCS approach is relatively simple and in practice takes only one line of computer code per time step for each point \((z, u_z)\) in coordinate space. In the case of the spherical harmonic expansion method discussed earlier (see Eq. 2.108), this is for each point in the corresponding coordinate space \((z, l, m)\) where \(l\) and \(m\) are the spherical harmonic coefficient indices. But as discussed in Chapters 1 and 3, there are some limitations to the FTCS.

For this Section the notation for the \(z\) component of orientation \(u, u_z\) from Section (2.9), is replaced with \(\mu\) since subscripts will be used and it is more concise to place subscripts on \(\mu\):

\[
\mu = u_z, \text{ for this Section.} \tag{2.124}
\]

The Fokker-Planck equation (2.118) is now written as

\[
\frac{\partial}{\partial t} q(z, \mu, t) = \left[ -L \mu \frac{d}{dz} z + \frac{1}{2} \frac{\partial}{\partial \mu} \left( (1 - \mu^2) \frac{\partial}{\partial \mu} \right) - w(z, \mu) \right] q(z, \mu, t), \tag{2.125}
\]

where the Laplacian term in this uniaxial, \(\varphi\) independent system is given by \(\nabla_u^2 = \frac{\partial}{\partial \mu} \left[ (1 - \mu^2) \frac{\partial}{\partial \mu} \right] \), and \(\mu = \cos \theta\).

It may not be obvious how to correctly express the finite difference of the Laplacian so that is discussed here. A finite grid method is used to represent a function \(f(\mu)\) to enable finite precision computation. The grid points for \(\mu\), defined on the continuous domain \([-1,1]\) (i.e. for \(0 \leq \theta \leq \pi\)) are indexed by the integer \(k\), defined on the symmetric discrete
domain, $-k_{max} \leq k \leq k_{max}$ corresponding to the symmetric domain of $\mu$. Introducing a new function $g$ gives

$$
\nabla^2_u f = \frac{\partial}{\partial \mu} g
= \frac{g_{k+\frac{1}{2}} - g_{k-\frac{1}{2}}}{\Delta \mu},
$$

(2.126)

where $\Delta \mu$ is the distance between adjacent grid points, $k$ and $k + 1$, and $g$ is given by:

$$
g = (1 - \mu^2) \frac{\partial}{\partial \mu} f,
$$

(2.127)

and it is important to note that derivatives here cover one grid spacing $\Delta \mu$, necessitating the use of half-integer $k$ indices. This is valid since $\mu$ is continuous between two adjacent grid points, $k$ and $k + 1$. The derivative terms corresponding to $k + \frac{1}{2}$ and $k - \frac{1}{2}$ in Eq. (2.127) are:

$$
\left. \frac{\partial f}{\partial \mu} \right|_{k+\frac{1}{2}} = \frac{f_{k+1} - f_k}{\Delta \mu},
\left. \frac{\partial f}{\partial \mu} \right|_{k-\frac{1}{2}} = \frac{f_k - f_{k-1}}{\Delta \mu},
$$

(2.128)

leading to the following finite-difference expression for the Laplacian:

$$
\nabla^2_u f_k = \frac{\partial}{\partial \mu} \left( (1 - \mu^2) \frac{\partial}{\partial \mu} \right) f
= \left( 1 - \mu^2_{k+\frac{1}{2}} \right) \frac{f_{k+1} - f_k}{(\Delta \mu)^2} - \left( 1 - \mu^2_{k-\frac{1}{2}} \right) \frac{f_k - f_{k-1}}{(\Delta \mu)^2}
$$

(2.129)

where $\mu_{k+\frac{1}{2}}$ and $\mu_{k-\frac{1}{2}}$ indicate that $\mu$ is evaluated halfway between the grid points $k, k + 1$ and $k - 1, k$ respectively. This use of points midway between integer grid-points was observed to give much more accurate values as opposed to only considering integer values.
of the grid points corresponding to a derivative over two grid spacings, \(2\Delta \mu\). The CN algorithm is developed after discussing the simpler forward time centred space method.

### 2.10.1 FTCS scheme

The simplest differencing scheme considered is the \textit{forward time centered space} method or FTCS, also used by [33] and [2]. For simplicity, in this subsection the polar direction \(\mu\) is held constant to simplify the discussion, but in Section 2.10.3 this will not be the case.

Consider the \(t, z\) plane in Fig. (2.12 (a)) indexed by \(n\) and \(j\) respectively. Discretizing equation (2.125), this becomes

\[
\frac{1}{\Delta t} [q_j^{n+1} - q_j^n] = -\frac{L\mu}{2\Delta z} [q_{j+1}^n - q_{j-1}^n] - w_j q_j^n
\]

(2.130)

and can be rewritten as:

\[
q_j^{n+1} = [1 - \Delta tw_j] q_j^n - \frac{\Delta t L\mu}{2\Delta z} [q_{j+1}^n - q_{j-1}^n].
\]

(2.131)

This form gives \(q_j^{n+1}\) explicitly as a function of the previous time step. Therefore if the initial condition, \(q_j^0\) (corresponding to \(q(z, \mu, t = 0)\)) is known, then the solution at every higher value of \(n\) is easily found. In practice execution of only one line of computer code is required for each \(q_j^n\), giving a computational time complexity of only \(O(j_{\text{max}})\) per time-step \(n\), where \(j_{\text{max}}\) is the number of the grid points in the \(z\)-direction. This is a very fast algorithm that uses very little memory.

This method is not used, however. It can be shown that it is unconditionally unstable for solving Eq. (2.125) and it is only first order accurate with respect to \(\Delta t\).
Figure 2.12: Finite grid illustrations in the position, \( z \) axis, and time, \( t \) axis. The orientation coordinate, \( \mu \) (or \( u_z \)) is neglected. (a) Forward-time-centered-space algorithm. (b) Fully implicit. (c) Crank-Nicolson. Image taken from [71].
2.10.2  Fully implicit scheme

Eq. (2.125) could also be written in finite difference form with the right hand side evaluated at time-step $n + 1$, instead of $n$. As in the previous Section, the orientation coordinate $\mu$ is held constant to simplify the discussion. This will give:

$$\frac{1}{\Delta t} [q_j^{n+1} - q_j^n] = - \frac{L \mu}{2 \Delta z} [q_{j+1}^{n+1} - q_{j-1}^{n+1}] - w_j q_j^{n+1}$$  \hspace{1cm} (2.132)

and rewriting to have $q_j^{n+1}$ in terms of the previous time step, $n$, gives:

$$[1 + \Delta tw_j] q_j^{n+1} + \frac{\Delta t L \mu}{2 \Delta z} [q_{j+1}^{n+1} - q_{j-1}^{n+1}] = q_j^n$$  \hspace{1cm} (2.133)

or in matrix form:

$$\hat{M} \cdot \vec{q}^{n+1} = \vec{q}^n,$$  \hspace{1cm} (2.134)

where the matrix, $\hat{M}$, is given by:

$$\hat{M} = \begin{bmatrix}
[1 + \Delta tw_j] & \frac{\Delta t L \mu}{2 \Delta z} & 0 & \cdots & 0 & 0 \\
-\frac{\Delta t L \mu}{2 \Delta z} & [1 + \Delta tw_j] & \frac{\Delta t L \mu}{2 \Delta z} & 0 & \cdots & 0 \\
0 & \ddots & \ddots & \ddots & \ddots & 0 \\
\vdots & \ddots & \ddots & \ddots & \ddots & \vdots \\
0 & -\frac{\Delta t L \mu}{2 \Delta z} & [1 + \Delta tw_j] & \frac{\Delta t L \mu}{2 \Delta z} \\
0 & 0 & \cdots & 0 & -\frac{\Delta t L \mu}{2 \Delta z} & [1 + \Delta tw_j]
\end{bmatrix}$$  \hspace{1cm} (2.135)
and the vector $\mathbf{q}^n$ is

$\mathbf{q}^n = \begin{bmatrix} q_1^n \\ q_2^n \\ \vdots \\ q_{j_{\text{max}}}^n \end{bmatrix}$.

(2.136)

To solve this equation the tridiagonal matrix, $\hat{M}$, must be inverted. For periodic boundary conditions, $\hat{M}$ has the same form as Eq. (2.135) plus the term $-\frac{\Delta t \mu}{2\Delta z}$ at the top right corner and $\frac{\Delta t \mu}{2\Delta z}$ at the opposite corner. Solving Eq. (2.134) for $q_{j}^{n+1}$ has computational time complexity of $O(j_{\text{max}})$ if one uses the Thomas algorithm [72, 73] for tridiagonal matrices, where $j_{\text{max}}$ is the number of grid points in the $z$ direction. In the case of periodic boundary conditions, it takes about twice as long using a modification of the Thomas algorithm, which takes into account the presence of non-zero terms at the top right and bottom left corners. But either way it is much faster than a general matrix inversion, which is $O(j_{\text{max}}^3)$.

The system in this work is represented by a tridiagonal matrix with periodic boundary conditions. However, the Thomas algorithm cannot be used here for two coordinates ($z$ and $\mu$) because the matrix is in fact block tridiagonal, belonging to the band diagonal class of matrices. For two coordinates, an operator splitting algorithm is often used; however, in this work the method of solution uses an application of the Thomas algorithm for block diagonal matrices, described in the next subsection.

This method can be shown to be unconditionally stable when applied to the diffusion
equation [71]:

\[
\frac{\partial f}{\partial t} = \lambda \frac{\partial^2 f}{\partial x^2},
\]

(2.137)

where \( \lambda \) here is the diffusion coefficient. However, like the FTCS scheme, it is only first order accurate in \( \Delta t \). Therefore it is not used to solve Eq. (2.125). A stability analysis on Eq. (2.125) would be rather complicated but it is assumed that it would give a similar result for (2.137).

2.10.3 Crank-Nicolson scheme

The Crank-Nicolson scheme (CN) is a combination of the right hand sides of Eqs. (2.130) and (2.132) for the FTCS and fully implicit schemes, using equal contributions of both. When applied to the diffusion equation, Eq. (2.137), it is also unconditionally stable but it has the advantage in that it is second order accurate in \( \Delta t \), [71], and therefore superior to the fully implicit method. The Laplacian term (2.129) is now included, and Eq. (2.125) becomes

\[
\frac{1}{\Delta t} \left[ q_{j,k}^{n+1} - q_{j,k}^n \right] = -\frac{L\mu}{4\Delta z} \left[ q_{j+1,k}^n - q_{j-1,k}^n + q_{j+1,k}^{n+1} - q_{j-1,k}^{n+1} \right]
+ \frac{1}{4\xi} \left[ \left( 1 - \mu_{k+\frac{1}{2}}^2 \right) \frac{q_{j,k+1}^n - q_{j,k}^n}{(\Delta \mu)^2} - \left( 1 - \mu_{k-\frac{1}{2}}^2 \right) \frac{q_{j,k}^n - q_{j,k-1}^n}{(\Delta \mu)^2} \right]
+ \left( 1 - \mu_{k+\frac{1}{2}}^2 \right) \frac{q_{j,k}^{n+1} - q_{j,k}^n}{(\Delta \mu)^2} - \left( 1 - \mu_{k-\frac{1}{2}}^2 \right) \frac{q_{j,k}^n - q_{j,k-1}^n}{(\Delta \mu)^2}
\]

(2.138)

where the index \( k \) is now used for the orientation grid. Rearranging the above in a more convenient form with the \( n+1 \) indexed terms on the left hand side and \( n \) indexed terms
on the left hand side gives

\[
\left[ 1 + \frac{\Delta t w_{j,k}}{2} + \frac{\Delta t}{4 (\Delta \mu)^2 \xi} \left( 2 - \mu_{k+\frac{1}{2}}^2 - \mu_{k-\frac{1}{2}}^2 \right) \right] q_{j,k}^{n+1} + \frac{L \Delta t \mu_k}{4 \Delta z} \left[ q_{j+1,k}^{n+1} - q_{j-1,k}^{n+1} \right] \\
- \frac{\Delta t}{4 (\Delta \mu)^2 \xi} \left[ \left( 1 - \mu_{j,k+\frac{1}{2}}^2 \right) q_{j,k+1}^{n+1} + \left( 1 - \mu_{j,k-\frac{1}{2}}^2 \right) q_{j,k-1}^{n+1} \right] \\
= \left[ 1 - \frac{\Delta t w_{j,k}}{2} - \frac{\Delta t}{4 (\Delta \mu)^2 \xi} \left( 2 - \mu_{k+\frac{1}{2}}^2 - \mu_{k-\frac{1}{2}}^2 \right) \right] q_{j,k}^n - \frac{L \Delta t \mu_k}{4 \Delta z} \left[ q_{j+1,k}^n - q_{j-1,k}^n \right] \\
+ \frac{\Delta t}{4 (\Delta \mu)^2 \xi} \left[ \left( 1 - \mu_{j,k+\frac{1}{2}}^2 \right) q_{j,k+1}^n + \left( 1 - \mu_{j,k-\frac{1}{2}}^2 \right) q_{j,k-1}^n \right] \\
= 2 - a_{j,k} q_{j,k}^{n+1} + d_k \left[ q_{j+1,k}^{n+1} - q_{j-1,k}^{n+1} \right] + U_k q_{j,k+1}^{n+1} + L_k q_{j,k-1}^{n+1} \\
= \left[ 2 - a_{j,k} q_{j,k}^n - d_k \left[ q_{j+1,k}^n - q_{j-1,k}^n \right] - U_k q_{j,k+1}^n - L_k q_{j,k-1}^n \right] \\
\text{or}
\]

\[
a_{j,k} q_{j,k}^{n+1} + d_k \left[ q_{j+1,k}^{n+1} - q_{j-1,k}^{n+1} \right] + U_k q_{j,k+1}^{n+1} + L_k q_{j,k-1}^{n+1} \\
= \left[ 2 - a_{j,k} q_{j,k}^n - d_k \left[ q_{j+1,k}^n - q_{j-1,k}^n \right] - U_k q_{j,k+1}^n - L_k q_{j,k-1}^n \right] \\
\text{where}
\]

\[
a_{j,k} = 1 + \frac{\Delta t w_{j,k}}{2} + \frac{\Delta t}{4 (\Delta \mu)^2 \xi} \left( 2 - \mu_{k+\frac{1}{2}}^2 - \mu_{k-\frac{1}{2}}^2 \right), \\
d_k = \frac{L \Delta t \mu_k}{4 \Delta z}, \\
U_k = -\frac{\Delta t}{4 (\Delta \mu)^2 \xi} \left( 1 - \mu_{k+\frac{1}{2}}^2 \right), \\
L_k = -\frac{\Delta t}{4 (\Delta \mu)^2 \xi} \left( 1 - \mu_{k-\frac{1}{2}}^2 \right). \\
\]

(2.141)
The following $j_{max} \times j_{max}$ matrices are defined, where $j_{max}$ is the number of grid-points in the $z$ direction:

$$
\hat{A}_k =
\begin{bmatrix}
  a_{1,k} & d_k & 0 & \cdots & 0 & -d_k \\
  -d_k & a_{2,k} & d_k & 0 & \cdots & 0 \\
  0 & \cdots & \cdots & \cdots & \cdots & 0 \\
  \vdots & \cdots & \cdots & \cdots & \cdots & \vdots \\
  0 & -d_k & a_{j_{max}-1,k} & d_k & & \\
  d_k & 0 & \cdots & 0 & -d_k & a_{j_{max},k}
\end{bmatrix}
$$

$$
\hat{U}_k = U_k \hat{I}
$$

$$
\hat{L}_k = L_k \hat{I}
$$

with $\hat{I}$ as the $j_{max} \times j_{max}$ identity matrix, and the following array for a particular orientation index, $k$:

$$
\vec{q}_k^n =
\begin{bmatrix}
  q_{1,k}^n \\
  q_{2,k}^n \\
  \vdots \\
  q_{j_{max},k}^n
\end{bmatrix}
$$

(2.143)
The index $j$ is chosen to take on values $1 \leq j \leq j_{\text{max}}$ to correspond to the position over one period in the $z$ direction. Eq. (2.138) then has the following form:

$$\hat{L}_k \vec{q}_{k-1}^{n+1} + \hat{A}_k \vec{q}_k^{n+1} + \hat{U}_k \vec{q}_{k+1}^{n+1} = -\hat{L}_k \vec{q}_k^n + \hat{A}_k + 2\hat{I} - \hat{A}_k \vec{q}_k^n - \hat{U}_k \vec{q}_{k+1}^n. \quad (2.144)$$

Note that the vector sign on $\vec{q}_n^k$ means that the $j$ index is being suppressed. Rearranging the above in block matrix form gives

$$
\begin{bmatrix}
\hat{A}_{-k_{\text{max}}} & \hat{U}^\prime_{-k_{\text{max}}} & 0 & \cdots & 0 \\
\hat{L}_{-k_{\text{max}}-1} & \hat{A}_{-k_{\text{max}}+1} & \hat{U}_{-k_{\text{max}}-1} & 0 & \cdots \\
\vdots & \ddots & \ddots & \ddots & \ddots \\
\hat{L}_{k_{\text{max}}-1} & \hat{A}_{k_{\text{max}}-1} & \hat{U}_{k_{\text{max}}-1} & 0 & \cdots \\
0 & 0 & \hat{L}^\prime_{k_{\text{max}}} & \hat{A}_{k_{\text{max}}} & \cdots \\
\end{bmatrix}
\begin{bmatrix}
\vec{q}_{-k_{\text{max}}}^{n+1} \\
\vec{q}_{-k_{\text{max}}+1}^{n+1} \\
\vdots \\
\vec{q}_{k_{\text{max}}-1}^{n+1} \\
\vec{q}_{k_{\text{max}}}^{n+1} \\
\end{bmatrix}
= 
\begin{bmatrix}
\vec{b}_{-k_{\text{max}}}^n \\
\vec{b}_{-k_{\text{max}}+1}^n \\
\vdots \\
\vec{b}_{k_{\text{max}}-1}^n \\
\vec{b}_{k_{\text{max}}}^n \\
\end{bmatrix},
$$

with

$$-k_{\text{max}} \leq k \leq k_{\text{max}}, \quad \text{the orientation index on a symmetric domain.} \quad 1 \leq j \leq j_{\text{max}}, \quad \text{the position index on a domain over one period.} \quad (2.145)$$

The above equation has thus been formulated as a matrix equation for $\vec{q}_n^{n+1}$ and can be written concisely as:

$$\hat{F} \cdot \vec{q}^{n+1} = \vec{b}^n \quad (2.146)$$
where the double hat and double vector signs denote that both the orientation and position dimensions have been condensed into a single row or column. The array $\vec{b}_n$ is shorthand for the right hand side portion of Eq. (2.144), given by:

\[
\begin{bmatrix}
\vec{b}_{-k_{max}}^n \\
\vec{b}_{-k_{max}+1}^n \\
\vdots \\
\vec{b}_{k_{max}-1}^n \\
\vec{b}_{k_{max}}^n
\end{bmatrix} =
\begin{bmatrix}
2\hat{I} - \hat{A}_{-k_{max}} & -\hat{U}_{-k_{max}} & 0 & \cdots & 0 \\
-\hat{L}_{-k_{max}-1} & 2\hat{I} - \hat{A}_{-k_{max}+1} & -\hat{U}_{-k_{max}-1} & 0 \\
\vdots & \vdots & \ddots & \vdots \\
-\hat{L}_{k_{max}-1} & 2\hat{I} - \hat{A}_{k_{max}-1} & -\hat{U}_{k_{max}-1} & 0 \\
0 & 0 & -\hat{L}_{k_{max}} & 2\hat{I} - \hat{A}_{k_{max}}
\end{bmatrix}
\begin{bmatrix}
\vec{q}_{-k_{max}}^n \\
\vec{q}_{-k_{max}+1}^n \\
\vdots \\
\vec{q}_{k_{max}-1}^n \\
\vec{q}_{k_{max}}^n
\end{bmatrix}
\]

(2.147)

and is calculated explicitly in the algorithm. For example, in the first iteration, i.e., $n = 2$, $\vec{b}_k^n$ is found by the initial condition for $q(z,u_z,t=0)$, Eq. (2.119). The primed matrices $\hat{U}'$ and $\hat{L}'$ at $k = -k_{max}$ and $k = k_{max}$ indicate that they have a slightly different form from that of Eq. (2.142) because they occur at the endpoints of the $\mu$ coordinate, and are subject to a reflection boundary condition at the north and south poles due to the symmetry in polar co-ordinates (see Fig. A.1) $q(z,\theta,\varphi,t) = q(z,\theta,\varphi+\pi,t)$ for a uniaxial system. These are given by:

\[
\begin{align*}
\hat{U}'_{-k_{max}} &= \hat{U}'_{-k_{max}} \hat{I}, \\
\hat{L}'_{k_{max}} &= \hat{L}'_{k_{max}} \hat{I},
\end{align*}
\]

(2.148)

where $\hat{U}'_{-k_{max}} = -\Delta t/2\Delta \mu s \left[ 1 - \frac{\Delta \mu}{4} \right] = \hat{L}'_{k_{max}}$ where, once again, $\hat{I}$ is the $j_{max} \times j_{max}$ identity matrix.

The Fokker-Planck equation in block tridiagonal form, Eq. (2.145) is the most demand-
ing step to solve for the free energy. This is solved using the Thomas algorithm for block tridiagonal matrices, described in subsection 2.10.4. The block tridiagonal algorithm is rather subtle to implement since the order of multiplication for block matrices matters, whereas this is not the case for a simple tridiagonal matrix, which would be encountered for an N phase. Another subtlety here is that the block matrices (indexed by \( k \)) are not constant, due to the variable “velocity” term \( u \) (from the \( L u \cdot \nabla r \) term) and the external field, \( w(z, \mu) \). \( u \) gives rise to the terms \( \mu_{k \pm \frac{1}{2}} \) in Eqs. (2.141), while \( w(z, \mu) \) shows up as \( w_{j,k} \) on the diagonal elements. Other systems, such as the simple diffusion equation, have constant block matrices and do not need to be recalculated with each solution iteration, which is the case in this work, due to the \( w_{j,k} \) terms in the diagonal \( k \) blocks.

A significant improvement can be made on the computation time by using the symmetry relation \( q(z, \mu, t) = q(\lambda - z, -\mu, t) \), Eq. (2.101) derived in Section 2.9, and setting \( z = 0 \) to be the positional symmetry plane. Here, \( \lambda \) is the one-dimensional smectic period. The full position domain, indexed by \( 1 \leq j \leq j_{\text{max}} \), can be chosen with half the orientation domain indexed by \( -k_{\text{max}} \leq k \leq 0 \). Or half the position domain \( 1 \leq j \leq (j_{\text{max}} + 1)/2 \) (for odd \( j_{\text{max}} \)) can be chosen while using the full orientation domain \( -k_{\text{max}} \leq k \leq k_{\text{max}} \). The first choice is used, omitting matrix blocks with \( k > 0 \). The only block modified in the matrix is \( \hat{L}_0 \) at the symmetry centre, \( k = 0 \). Examination of the left side of Eq. (2.144) for \( k = 0 \) while considering only the upper and lower off-diagonal blocks, \( \hat{L}_0 \) and \( \hat{U}_0 \), gives the following:

\[
\hat{L}_0 \hat{q}^{-1}_{-1} + \hat{U}_0 \hat{q}^{n+1}_{1} = \hat{L}_0 (\hat{q}^{-1}_{-1} + \hat{q}^{n+1}_{1})
\] (2.149)

where, from Eq. (2.141), \( \hat{U}_0 = \hat{L}_0 \) only for \( k = 0 \). This is from \( \mu_{+1/2}^2 = \mu_{-1/2}^2 \) in which
\( \mu_0 = 0 \). In matrix form this is:

\[
\hat{L}_0 (q_{-1}^{n+1} + q_1^{n+1}) = L_0 \begin{bmatrix}
1 & 0 & \cdots & 0 & 0 \\
0 & 1 \\
0 & 1 & 0 \\
0 & 0 & \cdots & 0 & 1
\end{bmatrix} \begin{bmatrix}
qu_{1,-1}^{n+1} \\
qu_{2,-1}^{n+1} \\
qu_{j_{\text{max}}-1,-1}^{n+1} \\
qu_{j_{\text{max}},-1}^{n+1}
\end{bmatrix} + \begin{bmatrix}
qu_{1,1}^{n+1} \\
qu_{2,1}^{n+1} \\
qu_{j_{\text{max}}-1,1}^{n+1} \\
qu_{j_{\text{max}},1}^{n+1}
\end{bmatrix}
\]

(2.150)

The symmetry relation \( q(z, \mu, t) = q(\lambda - z, -\mu, t) \) corresponds to

\[
q_{j,1}^{n+1} = q_{j_{\text{max}}+1-j,-1}^{n+1}
\]

(2.151)

and Eq. (2.150) becomes

\[
\hat{L}_0 (q_{-1}^{n+1} + q_1^{n+1}) = L_0 \begin{bmatrix}
1 & 0 & \cdots & 0 & 0 \\
0 & 1 \\
0 & 1 & 0 \\
0 & 0 & \cdots & 0 & 1
\end{bmatrix} \begin{bmatrix}
0 & 0 & \cdots & 0 & 1 \\
0 & 1 \\
0 & 1 & 0 \\
1 & 0 & \cdots & 0 & 0
\end{bmatrix} \begin{bmatrix}
qu_{1,-1}^{n+1} \\
qu_{2,-1}^{n+1} \\
qu_{j_{\text{max}}-1,-1}^{n+1} \\
qu_{j_{\text{max}},-1}^{n+1}
\end{bmatrix}
\]

(2.152)

In the above the identity matrix is followed by a reflection of the identity matrix, for the
$z$ direction. The diagonal block $\hat{L}_0$ is now replaced by the following “X matrix” structure:

$$
\hat{L}_0 \rightarrow \begin{bmatrix}
L_0 & 0 & \cdots & 0 & L_0 \\
0 & L_0 & & L_0 & 0 \\
\ddots & \ddots & \ddots & \ddots & \ddots \\
0 & L_0 & & L_0 & 0 \\
L_0 & 0 & \cdots & 0 & L_0
\end{bmatrix} \cdot (2.153)
$$

In my calculations I chose $j_{\text{max}}$ to be an odd integer, resulting in the centre element having twice the magnitude of any other non-zero element. Choice of an even $j_{\text{max}}$ results in all non-zero elements having the same magnitude, but with a somewhat higher density of non-zero elements at the centre.

The block tridiagonal form of the Fokker-Planck equation, (2.145), consists of $N_\mu$ diagonal blocks each containing $N_z \times N_z$ elements and has computational time complexity of $O(N_z^3) \times O(N_\mu)$. An interesting point is that the linear time complexity in $N_\mu$ allows for many points in the orientational coordinate, and is important for enabling high resolution for the highly oriented states. The use of the symmetry above lowers the number of blocks from $2N_\mu + 1$ to $N_\mu + 1$, reducing the computation time by a factor of two.
2.10.4 Thomas Algorithm for block tridiagonal matrices

The block tridiagonal algorithm used to solve Eq. (2.145) is presented here. This algorithm [72] can be easily applied to a simple tridiagonal matrix (i.e., using $1 \times 1$ blocks) but for the block case, one must be careful about the order of the matrix products, since matrix multiplication does not commute. In this discussion the index, $i$, which goes from 1 to $N$ is used to label the square and nonsingular blocks $\hat{A}_i$, $\hat{L}_i$ and $\hat{U}_i$. The Fokker-Planck matrix equation, (2.145), is concisely given by:

$$
\begin{bmatrix}
\hat{A}_1 & \hat{U}_1 & 0 & 0 \\
\hat{L}_2 & \hat{A}_2 & \hat{U}_2 & 0 \\
0 & \cdots & \cdots & \cdots \\
0 & 0 & \hat{L}_N & \hat{A}_N
\end{bmatrix}
\begin{bmatrix}
\vec{q}_1 \\
\vec{q}_2 \\
\vdots \\
\vec{q}_N
\end{bmatrix} =
\begin{bmatrix}
\vec{b}_1 \\
\vec{b}_2 \\
\vdots \\
\vec{b}_N
\end{bmatrix},
$$

(2.154)

where the superscripts $n$ and $n + 1$ have been dropped for brevity. The matrix on the left-hand side above is written in the following block LU factorization:

$$
\begin{bmatrix}
\hat{A}_1 & \hat{U}_1 & 0 & 0 \\
\hat{L}_2 & \hat{A}_2 & \hat{U}_2 & 0 \\
0 & \cdots & \cdots & \cdots \\
0 & 0 & \hat{L}_N & \hat{A}_N
\end{bmatrix} =
\begin{bmatrix}
\hat{\alpha}_1 & 0 & 0 & 0 \\
\hat{L}_2 & \hat{\alpha}_2 & 0 & 0 \\
0 & \cdots & \cdots & \cdots \\
0 & 0 & \hat{L}_N & \hat{\alpha}_N
\end{bmatrix}
\begin{bmatrix}
\hat{I} & \hat{\gamma}_1 & 0 & 0 \\
\hat{L}_2 & \hat{\alpha}_2 & 0 & 0 \\
0 & \cdots & \cdots & \cdots \\
0 & 0 & \hat{L}_N & \hat{\alpha}_N
\end{bmatrix}
\begin{bmatrix}
\hat{\alpha}_1 & 0 & 0 & 0 \\
\hat{\alpha}_2 & 0 & 0 & 0 \\
\cdots & \cdots & \cdots & \cdots \\
0 & 0 & \hat{\alpha}_N & 0
\end{bmatrix}
\begin{bmatrix}
\hat{I} & \hat{\gamma}_1 & 0 & 0 \\
\hat{I} & \hat{\gamma}_2 & 0 & 0 \\
\vdots & \vdots & \vdots & \vdots \\
\hat{I} & \hat{\gamma}_N & 0 & 0
\end{bmatrix}.
$$

(2.155)
The algorithm to solve for $\vec{q}_i$ is as follows:

$$\hat{\alpha}_1 = \hat{A}_1, \quad \text{solve} \quad \hat{\alpha}_1 \hat{\gamma}_1 = \hat{C}_1, \quad \text{solve} \quad \hat{\alpha}_1 \vec{y}_1 = \vec{b}_1,$$

where $\vec{y}_i$ is an auxiliary vector.

for $i = 2 : N$

$$\hat{\alpha}_i = \hat{A}_i - \hat{L}_i \hat{\gamma}_{i-1}$$

solve $\hat{\alpha}_i \hat{\gamma}_i = \hat{U}_i$

solve $\hat{\alpha}_i \vec{y}_i = \left( \vec{b}_i - \hat{L}_i \vec{y}_{i-1} \right)$

(2.156)

$$\vec{q}_N = \vec{y}_N$$

for $i = N - 1 : 1$, increment by $-1$

$$\vec{q}_i = \vec{y}_i - \hat{\gamma}_i \vec{q}_{i-1}$$

### 2.11 Mean-field theory under simple functional scaling

So far the model in the second-virial approximation has been discussed, which accounts only for two-body interactions in terms of the positional and orientational degrees of freedom. While this approach has been used extensively in previous theories, it is known to
overestimate the packing fraction at which the I-N and N-SmA transitions occur [2, 33, 68]. An exact treatment for this system would involve all terms in the virial expansion for the free energy and would account for both positional and orientational degrees of freedom. However, obtaining a solution for this complicated type of interaction would be intractable. Therefore the *decoupling approximation* is used, commonly attributed to Parsons and Lee, which has successfully been applied to spatially uniform systems (for which $\phi(\mathbf{r}, \mathbf{u}) = \phi(\mathbf{u})$) of rigid particles [28, 38–40]. The decoupling approximation involves obtaining a rescaled interaction free energy, $\beta F'_{int}$, by mapping the free energy of hard semiflexible spherocylinders, $\beta F_{int}$, in terms of an effective system of hard spheres of the same packing fraction, $\eta$. A rigorous development of this method is shown by Parsons [38]. The development here, however will be quite informal, similar to that by Lee [28].

The Carnahan-Starling equation of state, [74], for a system of hard spheres is:

$$\frac{\beta P^{HS}}{\rho} = 1 + \eta + \eta^2 - \eta^3 \frac{(1 - \eta)^3}{(1 - \eta)}.$$  \hspace{1cm} (2.157)

This relatively simple form for the equation of state gives the best results for the behaviour of hard spheres even though its original derivation lacked physical rigor. It is simply based on a geometric series of integers, which approximated the known empirical values of the virial coefficients. The right hand side of Eq. (2.157) can be written as an ideal gas term plus a non-ideal term as follows:

$$\frac{\beta P^{HS}}{\rho} = 1 + \frac{4\eta - 2\eta^2}{(1 - \eta)^3},$$  \hspace{1cm} (2.158)

where the non-ideal term can be thought of as an intermolecular interaction term. The
free energy $\beta F_{HS}$ is obtained by integrating the equation of state with respect to volume, $V$, to obtain the following expression:

$$\beta F_{HS} = \beta F_{\text{ideal}} + \beta F_{\text{int}}$$

$$= \beta F_{\text{ideal}} + n \frac{\eta (4 - 3\eta)}{(1 - \eta)^2}$$

$$= \beta F_{\text{ideal}} + n 4\eta J(\eta) \quad (2.159)$$

where $\beta F_{\text{ideal}}$ is the ideal gas contribution to the free energy and $\beta F_{\text{int}}$ is the interaction contribution. Looking at the term $\beta F_{\text{int}}$ and substituting in $\eta = \frac{nV_{HS}}{V}$, where $V_{HS}$ is the volume of a single hard sphere particle:

$$\beta F_{\text{int}} = J(\eta) n 4 \frac{nV_{HS}}{V}$$

$$= J(\eta) \frac{1}{2} \frac{V}{V} 8 V_{HS} n^2 \frac{V}{V}$$

$$\beta F_{\text{int}} = J(\eta) \frac{V V_{excluded}}{2} \beta^2 \quad (2.160)$$

where $V_{excluded} = 8V_{HS}$ is the excluded volume of hard spheres, discussed in Section 2.6.

Eq. (2.161) is identical to the interaction free energy from the second virial approximation, $\beta F_{\text{int}} = \frac{\beta^2}{2} V V_{excluded}$ (see Eq. (B.7)), except that it is rescaled by a factor of $J(\eta)$, given by:

$$J(\eta) = \frac{(1 - \frac{3\eta}{4})}{(1 - \eta)^2} \quad (2.162)$$

This is the desired result: for hard spheres one can replace all known virial terms for the free energy with just a single two-body interaction term given by (2.161). The two-body second virial coefficient has effectively been rescaled in terms of all higher virial coefficients.
Without any rigorous justification at present this idea is applied to the system of semiflexible polymer chains by taking Eq. (2.161) and replacing the excluded volume for hard spheres with the corresponding excluded volume term, \( V^{SF}(\mathbf{u}, \mathbf{u}') \), for semiflexible polymers:

\[
\beta F'_{\text{int}} = \frac{\langle V^{SF}(\mathbf{u}, \mathbf{u}') \rangle}{V^{\text{excluded}}} \beta F_{\text{HS}}^{\text{int}}
\]
\[
= J(\eta) \frac{V \langle V^{SF}(\mathbf{u}, \mathbf{u}') \rangle}{2} \beta^2
\]
\[
= J(\eta) \beta F_{\text{int}}
\]

where \( \beta F_{\text{int}} \) is the original excluded volume interaction free energy, Eq. (2.91), for semiflexible polymers and \( \beta F'_{\text{int}} \) denotes the rescaled interaction energy. The angle brackets denote the average excluded volume with respect to the distribution functions \( \phi(\mathbf{r}, \mathbf{u}) \), \( \psi(\mathbf{r}, \mathbf{u}, t = 0) \), and \( \hat{\psi}(\mathbf{r}, \mathbf{u}, t = 1) \) since, in this more complicated case, the excluded volume between polymer chains depends on the relative orientation between segment pairs in addition to segment and end pairs. This average is given by

\[
\langle V^{SF}(\mathbf{u}, \mathbf{u}') \rangle = \frac{1}{V} \int d\mathbf{r} \int d\mathbf{u} \int d\mathbf{u}' V^{\text{seg-seg}}(\mathbf{u}, \mathbf{u}') \phi(\mathbf{r}, \mathbf{u}) \phi(\mathbf{r}, \mathbf{u}')
\]
\[
+ \frac{2}{V} \int d\mathbf{r} d\mathbf{u} d\mathbf{u}' V^{\text{end-seg}}(\mathbf{u}, \mathbf{u}') \hat{\phi}(\mathbf{r}, \mathbf{u}) \left[ \hat{\psi}(\mathbf{r}, \mathbf{u}', t = 0) + \hat{\psi}(\mathbf{r}, \mathbf{u}', t = 1) \right]
\]

(2.164)

which is related to the total interaction energy, Eq. (2.74) by

\[
\frac{\beta^2}{2} V \langle V^{SF}(\mathbf{u}, \mathbf{u}') \rangle = \beta W(\{\mathbf{r}(t), \mathbf{u}(t)\}, n).
\]

(2.165)
Eq. (2.163) is known as the Parsons and Lee decoupling approximation. The orientational degrees of freedom are contained in the term $\beta F_{\text{int}}$, which has the form of the two-body second virial approximation. The higher virial corrections to the positional degrees of freedom are contained in the term $J(\eta)$. The terminology “decoupling approximation” refers to the fact that (2.163) has the simple form of a product of a factor depending on the positional degrees of freedom and a term depending on the orientational degrees of freedom. This method has been previously used in density functional theories [39–41, 75] on nematic and smectic-A ordering of rigid spherocylinders.

Applying the decoupling approximation simply amounts to modifying the external fields in the second virial approximation, Eqs. (2.85) and (2.87) with

$$
    w(r, u) \to J(\eta) w(r, u)
$$

$$
    w_q(r, u) \to J(\eta) w_q(r, u)
$$

and modifying the initial condition in the Fokker-Planck equation, (2.97)

$$
    q(r, u, t \to 0) = \exp(w_q(r, u)) \to \exp(-J(\eta) w_q(r, u)).
$$

A possible further development of the decoupling approximation involves using a positionally dependent rescaling factor $J(\eta(r))$, where the local packing fraction $\eta(r)$ could be derived in terms of the contour averaged segment density, $\phi(r, u)$. This would leave the free energy in the nematic phase unchanged but would have an effect on the free energy in the smectic phase. This approach has not been developed sufficiently for presentation in this Thesis; however, a preliminary calculation discussed in Section 3.6 gives a promising
result.

2.12 Obtaining the equilibrium free energy

One of the main purposes in this work is to obtain the phase diagram in the $\eta$ (packing fraction) vs. $L/D$ plane for the I, N and SmA phases. This is done by comparing the Helmholtz free energies per unit volume, denoted in this Section by

$$ f = \frac{\beta F}{V}, $$

(2.168)

of each respective phase. Before this can be done, the free energy in the SmA phase has to be minimized with respect to the smectic period, $\lambda$.

The isotropic free energy, independent of positions and orientations, is easiest to calculate and can be given analytically as follows:

$$ f = J(\eta)\left(\frac{\pi C^2 \eta}{4} + 2CC_2\right) + C \log (C) - C \log (4\pi), $$

(2.169)

where $C_2$ and $C$ are given by Eqs. (2.121) and (2.123)

$$ C = \rho DL^2, \quad C_2 = \frac{\pi}{2} \rho D^2 L. $$

(2.170)

Additive constants in Eq. (2.169) are omitted since they do not affect the calculation of the phase boundaries. $J(\eta)$ is the Parsons-Lee rescaling factor from Section 2.11, Eq. (2.162). The nematic and smectic-A free energy densities in terms of the mean-field densities and
fields Eqs. (2.115-2.117,2.120) and (2.122) are given by:

\[
f = -2\pi C \int_0^\lambda dz \int_0^1 du_z \{ w(z, u_z) \phi(z, u_z) + w_q(z, u_z) [\psi(z, u_z, 0) + \psi(z, u_z, 1)] \} - C \log \left(\frac{Q}{V}\right) + C \log C. \\
(2.171)
\]

The above is solved using the numerical methods of Appendix 2.10.

Generally the free energy has an isotropic solution at all packing fractions, \( \eta \), while the nematic solution does not appear until some finite value of \( \eta \) where it branches from the isotropic solution as shown in Fig. 2.13. Similarly, the smectic-A solution doesn’t appear until an even higher \( \eta \) where it branches from the nematic solution. During phase separation [76] the phase-separated state of total packing fraction, \( \eta_0 \), segregates into two regions having packing fraction, \( \eta_1 \) (with fraction \( x \)) and \( \eta_2 \) (with fraction \( 1 - x \)). The quantity \( x \) is determined from the lever rule

\[
\eta_0 = x\eta_1 + (1 - x) \eta_2. \\
(2.172)
\]

The free energy per unit volume, \( \bar{f} \), for the phase-separated state is to be minimized. The homogeneous state is the limit \( \eta_1 = \eta_2 \). The quantity, \( \bar{f} \) is given by

\[
\bar{f} = x f(\eta_1) + (1 - x) f(\eta_2). \\
(2.173)
\]

This has to be minimized subject to the constraint in Eq. (2.172). This constraint is
Figure 2.13: Free energy density $f = \beta F/V$, versus packing fraction $\eta$, in the vicinity of the I-N and N-SmA transitions. The phase with higher order branches off from a point from the phase with lower order. The smectic-A branch from the nematic is much less prominent than the nematic branch from the isotropic. Data taken for $\zeta = 10$ and $L/D = 4.30$. 
implemented by introducing the Lagrange multiplier $m$ and minimizing the quantity

$$A = xf(\eta_1) + (1 - x)f(\eta_2) - m [x\eta_1 + (1 - x)\eta_2 - \eta_0].$$

(2.174)

This gives the equations

$$
\begin{align*}
\frac{\partial A}{\partial x} &= f(\eta_1) - f(\eta_2) - m [\eta_1 - \eta_2] = 0, \\
\frac{\partial A}{\partial \eta_1} &= x f'(\eta_1) - m x = 0, \\
\frac{\partial A}{\partial \eta_2} &= (1 - x) f'(\eta_2) - m (1 - x) = 0, \\
\frac{\partial A}{\partial m} &= x \eta_1 + (1 - x) \eta_2 - \eta_0,
\end{align*}
$$

(2.175)

where the prime indicates differentiation with respect to the argument variable, either $\eta_1$ or $\eta_2$. The first three equations yield

$$m = \frac{f'(\eta_1) - f'(\eta_2)}{\eta_1 - \eta_2} = f'(\eta_1) = f'(\eta_2).$$

(2.176)

This is referred to as Maxwell’s double-tangent construction and is valid for arbitrary functional forms of the Helmholtz free energy. This is shown schematically in Fig. 2.14 for the type of system in this Thesis. The phase separated state given by Eq. (2.176) appears on the phase diagram as a boundary with finite width with the coexisting phases having the packing fractions $\eta_1$ and $\eta_2$. The transition associated with this boundary is commonly called a first-order or discontinuous transition. Since there are two branch points in the free energy there will be two-phase coexistence regions, denoted $(\eta_{iso}, \eta_{nem})$ and $(\eta_{nem}, \eta_{smA})$. It is possible for the two branch points to be close enough so that the phase coexistence
Figure 2.14: Schematic of the double-tangent construction of the free energy density. The red curve is the free energy of the higher symmetry state, while the black curve is the free energy of the lower symmetry, branching off the red curve. The coexistence packing fractions, $\eta_1$ and $\eta_2$, are given by where the common tangent touches the free energy curves. In this work the curves are typically much closer (ex: Fig. 2.13).

regions overlap and the middle phase, nematic in this case, will not be present, which gives rise to a direct I-SmA phase coexistence. The point at which this occurs is called the triple point, where the three phases coexist and is analogous to the liquid-vapour-solid triple point in water. For a transition in which there is no phase coexistence there is a smooth transition from one phase to the other. This is called a second-order or continuous transition. The critical location of the packing fraction, $\eta_{\text{crit}}$, at which the continuous transition takes place occurs when the order parameter approaches zero.
2.12.1 Algorithm for the double tangent construction

The coexisting packing fractions, \( \eta_1 \) and \( \eta_2 \) cannot be found analytically since the nematic and smectic free energies do not have an analytical representation. The numerical algorithm to achieve this, developed in this work, involves the simplest type of derivative of the free energy. The free energies are evaluated at successive values of \( \eta \) differing by a constant amount, \( \eta_{i+1} - \eta_i \), (\( \sim 10^{-4} \) in this work), and over a range of packing fractions \( \{ \eta_{i_{\text{min}}}, \eta_{i_{\text{max}}} \} \) and \( \{ \eta_{j_{\text{min}}}, \eta_{j_{\text{max}}} \} \). The superscript 1 denotes the set of packing fractions for the higher symmetry phase, and the superscript 2 denotes the set of packing fractions for the lower symmetry phase. For example, to examine the N-SmA transition, 1 refers to the N phase and 2 to the SmA phase. Given the two successive free energies, \( f(\eta_i) \) and \( f(\eta_{i+1}) \), the derivative at the midpoint is given by:

\[
f'(\eta_{i+1/2}) = \frac{f(\eta_{i+1}) - f(\eta_i)}{\eta_{i+1} - \eta_i}.
\] (2.177)

The algorithm employs two sets of iterations, indexed \( i \) and \( j \). It is given as follows:

1. Start with \( f'(\eta_{i_{\text{min}}+1/2}) \).
2. Scan (through \( j \)) the set \( \{ f'(\eta_{j_{1+1/2}}) \} \) to find the closest \( f'(\eta_{j_{1+1/2}}) \) to \( f'(\eta_{i_{\text{min}}+1/2}) \).
3. Calculate the slope, \( m_{i_{\text{min}}+1/2} = \frac{f'(\eta_{i_{\text{min}}+1/2}) - f'(\eta_{j_{1+1/2}})}{\eta_{i_{\text{min}}+1/2} - \eta_{j_{1+1/2}}} \).
4. Compare \( m_{i_{\text{min}}+1/2} \) to \( f'(\eta_{i_{\text{min}}+1/2}) \).
5. Repeat steps 1-4 for increasing \( i \) to find the pair, \( m_{i+1/2} \) and \( f'(\eta_{i+1/2}) \), closest to each other.

\[
(2.178)
\]
Figure 2.15: Representative data ($\xi = 1$, $L/D = 17.00$) of the double tangent construction for the I-N transition. Black is the slope, $m$ at each grid point $i + 1/2$, from (2.178). Red is the derivative of the free energy of the N (lower symmetry) phase, denoted $f'(\eta^{(2)})$ at each grid point $i + 1/2$. The N phase boundary occurs at the value of $\eta$ where the data for $m$ crosses the data for $f'(\eta^{(2)})$. The I phase boundary is not shown, but corresponds to $f'(\eta^{(1)\eta_{1/2}})$ from (2.178).

The pair, $m_{i+1/2}$ and $f'(\eta_{i+1/2}^{(2)})$, corresponds to the coexisting packing fractions to within the numerical precision, which is dictated mainly by the choice of $\eta_{i+1} - \eta_i$. This is illustrated in Fig. 2.15 where the two curves intersect. In practice one can save the two pairs which bracket the true solution. One pair is greater and one pair is less than the true solution. These can be input into a quick linear interpolation routine to improve the precision.
Chapter 3

Results

In this Chapter the validation of the numerical method is first examined. Since these calculations for the smectic phase are rather cumbersome, it is necessary to chose enough grid points in a particular dimension such that the propagators, \( q(\mathbf{r}, \mathbf{u}, t) \), and distributions, \( \phi(\mathbf{r}, \mathbf{u}) \) and \( \psi(\mathbf{r}, \mathbf{u}, t) \), are accurately described. At the same time, if one uses too many grid points, the computation will take too long. Section 3.1 looks at the effect on the free energy and the phase boundaries of varying the grid sizes of the orientation \( \mathbf{u} \), position \( \mathbf{r} \) and contour index \( t \) on the free energy. In Section 3.2 some calculations using the Crank-Nicolson method are compared to the results obtained by the spherical harmonic expansion [2], in the second-virial approximation by Hidalgo et al.

The new results begin in Section 3.3: the phase transitions are analyzed by looking at the critical behaviour of the SmA order parameter and the phase diagrams, which are compared to experiments and Monte Carlo simulations. Section 3.4 focuses on nematic ordering in both the N and SmA phases, while looking at positional-orientational coupling.
in the SmA phase. In Section 3.5 the SmA ordering is examined in more detail by looking at surface plots of the $t$-segment distributions, $\psi(z, u_z, t)$ and contour averaged segment distribution, $\phi(z, u_z)$. The high density smectic region and equilibrium smectic period width are also examined. Non-equilibrium ordering, i.e., states that possess a smectic period $\lambda$ away from the equilibrium smectic period, $\lambda_{equ}$ is then analyzed along with an estimation on the required numerical precision in obtaining equilibrium quantities that were impossible to achieve in this work. The last examination is a brief preliminary calculation making use of a position-dependent Parsons-Lee rescaling factor on the N-SmA phase boundary. This results in behaviour that is qualitatively closer to that of Monte-Carlo simulations and experiments than the position-independent rescaling.

### 3.1 Effect of the grid Space width

The dependence of the free energy density, $F/V$ and the smectic-A order parameter, $O_{smA}$, on the number of grid points $u_{max}$ between the half interval $-1 \leq u_z \leq 0$ ($u_z = \cos \theta$) is given in Fig. 3.1. In Section 2.10 it is shown that only $-1 \leq u_z \leq 0$ is needed due to the symmetry of the system. The grid size, which is constant in this work, is then given by

$$du_z = d\cos(\theta) = \frac{1}{u_{max}}$$

(3.1)

and a Simpson rule integration scheme is used to calculate all integrals. A large range of $u_{max}$ between 400 and 5600 is examined and the relative change in $F/V$ is only about $4 \times 10^{-3}$ % over that range. For high $u_{max}$, a limiting value of $F/V$ appears to be obtained easily for most of the upper range ($u_{max} \geq 1800$). For $O_{smA}$ the relative change over the
Figure 3.1: Effect of orientational grid spacing, $1/u_{\text{max}}$, on the free energy, $F$, and smectic-A order parameter, $O_{\text{smA}}$. This data is for the semiflexible chain with bending rigidity, $\xi = 10$, shape parameter $L/D = 6.00$, and packing fraction $\eta = 0.4570$. The grid size used in this work is $u_{\text{max}} = 1200$.

The examined range of $u_{\text{max}}$ is only about $5 \times 10^{-2}$ % and the limiting value is also obtained easily over most of the upper range ($u_{\text{max}} \geq 1800$). However, for both quantities, there is a more rapid variation with respect to $u_{\text{max}}$ for $u_{\text{max}} \leq 1200$.

The orientational grid spacing in this work is chosen to be $u_{\text{max}} = 1200$, which is just beyond the steep variation of $F/V$ and $O_{\text{smA}}$ in Fig. 3.1. The algorithm has linear time complexity ($O(u_{\text{max}})$) in $u_{\text{max}}$ so there is some freedom in choosing $u_{\text{max}}$ to be larger. This choice gives a relative difference in $F/V$ of $5 \times 10^{-6}$ compared to the most precise at $u_{\text{max}} = 5600$; about an order of magnitude better than the least precise at $u_{\text{max}} = 400$ and
more than an order of magnitude less than the precision of the algorithm, $\epsilon = 10^{-4}$ (see Appendix D).

Now it is shown how $u_{\text{max}}$ affects the location and width of the coexistence region (see Section 3.3), $(\eta_{\text{nem}}, \eta_{\text{smA}})$, in Table 3.1, for $L/D = 6.00$, $\xi = 10$, $\lambda/z_{\text{max}} = 1/25$ which is the position grid size, $1/t_{\text{max}} = 1/300$, the segment contour grid size. There is barely an effect here, similar to the free energy calculations. There is a very small variation in $O_{\text{smA}}$ and the equilibrium smectic period, $\lambda_{\text{equ}}$, for lower $u_{\text{max}}$. So with the chosen value of $u_{\text{max}} = 1200$ the precision of the calculations is quite good. This analysis was done only for the parameter values, $L/D = 6.00$ and $\xi = 10$ as it takes a long time to perform, but the grid size is assumed to be a good value since the precision of the calculations is quite higher than the algorithm precision, $\epsilon = 10^{-4}$.

Next, the dependence on the one-dimensional position grid size is shown in Table 3.2. The number of grid points is given by $z_{\text{max}}$, giving a grid size of:

$$dz = \lambda/z_{\text{max}}. \quad (3.2)$$

Only three values of $z_{\text{max}}$ are looked at here, $z_{\text{max}} = 25, 33$ and 65. Since the computation time scales as $O\left((z_{\text{max}})^3\right)$, it is much more advantageous here to have $z_{\text{max}}$ as low as possible. For the calculations $z_{\text{max}}$ is chosen to be 25, and lower $z_{\text{max}}$ has not been investigated since I believe that a lower $z_{\text{max}}$ may risk giving insufficient spatial resolution. And it turns out that in analyzing the depletion zones in Section 3.5, a lower value of $z_{\text{max}}$ may make this difficult. A sure test of an optimal $z_{\text{max}}$ for the phase boundaries would take rather long, since searching for the low accuracy cut-off of $z_{\text{max}}$ is over a vast range of the
Table 3.1: Phase boundary $\eta_{nem}$, $\eta_{smA}$, phase coexistence gap $\Delta \eta$, and order parameter $O_{smA}$ at coexistence, equilibrium smectic period $\lambda_{equ}$, for varying number of grid points. Increasing the grid points $u_{max}$, corresponds to a finer grid size $1/u_{max}$. These results used $z_{max} = 25$ and $t_{max} = 300$ for the semiflexible chain with bending rigidity, $\xi = 10$, shape parameter $L/D = 6.00$, and packing fraction $\eta = 0.4570$.

<table>
<thead>
<tr>
<th>$u_{max}$</th>
<th>$\eta_{nem}, \eta_{smA}$</th>
<th>$\Delta \eta$</th>
<th>$O_{smA}$</th>
<th>$\lambda_{equ}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.44855, 0.45130</td>
<td>0.00270</td>
<td>0.10304</td>
<td>1.218</td>
</tr>
<tr>
<td>600</td>
<td>0.44859, 0.45159</td>
<td>0.00270</td>
<td>0.10599</td>
<td>1.213</td>
</tr>
<tr>
<td>800</td>
<td>0.44858, 0.45127</td>
<td>0.00270</td>
<td>0.10342</td>
<td>1.217</td>
</tr>
<tr>
<td>1200</td>
<td>0.44858, 0.45127</td>
<td>0.00268</td>
<td>0.10340</td>
<td>1.217</td>
</tr>
<tr>
<td>1800</td>
<td>0.44859, 0.45127</td>
<td>0.00268</td>
<td>0.10594</td>
<td>1.214</td>
</tr>
<tr>
<td>2400</td>
<td>0.44859, 0.45127</td>
<td>0.00270</td>
<td>0.10339</td>
<td>1.217</td>
</tr>
<tr>
<td>3000</td>
<td>0.44859, 0.45127</td>
<td>0.00270</td>
<td>0.10339</td>
<td>1.217</td>
</tr>
<tr>
<td>4500</td>
<td>0.44863, 0.45129</td>
<td>0.00266</td>
<td>0.10338</td>
<td>1.217</td>
</tr>
<tr>
<td>5600</td>
<td>0.44863, 0.45129</td>
<td>0.00266</td>
<td>0.10338</td>
<td>1.217</td>
</tr>
</tbody>
</table>
Table 3.2: Phase boundary $\eta_{nem}, \eta_{smA}$, phase coexistence gap $\Delta \eta$ and order parameter $O_{smA}$ at coexistence, equilibrium smectic period $\lambda_{equ}$, for varying number of positional grid points, $z_{max}$. Increasing the number of grid points $z_{max}$ corresponds to a finer grid size $\lambda/z_{max}$. These results used $u_{max} = 1200$ and $t_{max} = 300$ for the semiflexible chain with bending rigidity, $\xi = 10$, shape parameter $L/D = 6.00$, and packing fraction $\eta = 0.4570$.

<table>
<thead>
<tr>
<th>$z_{max}$</th>
<th>$\eta_{nem}, \eta_{smA}$</th>
<th>$\Delta \eta$</th>
<th>$O_{smA}$</th>
<th>$\lambda_{equ}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.44858, 0.45127</td>
<td>0.00272</td>
<td>0.10340</td>
<td>1.217</td>
</tr>
<tr>
<td>33</td>
<td>0.44628, 0.45191</td>
<td>0.00300</td>
<td>0.10599</td>
<td>1.213</td>
</tr>
<tr>
<td>65</td>
<td>0.44793, 0.45171</td>
<td>0.00378</td>
<td>0.11171</td>
<td>1.217</td>
</tr>
</tbody>
</table>

parameter space with respect to $\xi, L/D, \eta$ and $\lambda$. So, as in the case of $u_{max}$, a low enough $z_{max}$ is picked that still compares very closely for the phase boundary locations to the most accurate value examined, $z_{max} = 65$. However, there is some noticeable variation on the width of the phase boundary which results from the fact that the N-SmA phase width is very small—a common property of many systems exhibiting the N-SmA transition [8, 12]. Also, the nematic boundary, $\eta_{nem}$ shows more variation than the smectic boundary with respect to $z_{max}$, which may seem odd given that the N phase does not depend on position, while the smectic phase does. However, the double tangent construction for the phase boundaries, described in Section 2.12, takes into account both the smectic and nematic free energies at the same time so a change in the smectic free energy can indeed affect the coexisting nematic packing fraction, $\eta_{nem}$. It is difficult to say why $\eta_{nem}$ is affected more than $\eta_{smA}$, though.
Table 3.3: Phase boundary $\eta_{nem}, \eta_{smA}$, phase coexistence gap $\Delta \eta$ and order parameter $O_{smA}$ at coexistence, equilibrium smectic period $\lambda_{equ}$, for varying number of segment grid points, $t_{max}$. These results used $u_{max} = 1200$ and $z_{max} = 25$ for the semiflexible chain with bending rigidity, $\xi = 10$, shape parameter $L/D = 6.00$, and packing fraction $\eta = 0.4570$.

<table>
<thead>
<tr>
<th>$t_{max}$</th>
<th>$\eta_{nem}, \eta_{smA}$</th>
<th>$\Delta \eta$</th>
<th>$O_{smA}$</th>
<th>$\lambda_{equ}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.44858, 0.45127</td>
<td>0.00272</td>
<td>0.10340</td>
<td>1.217</td>
</tr>
<tr>
<td>600</td>
<td>0.44855, 0.45122</td>
<td>0.00267</td>
<td>0.10488</td>
<td>1.216</td>
</tr>
</tbody>
</table>

Finally, the dependence on segment grid size is shown in Table 3.3. The number of grid points is $t_{max} + 1$ which gives a segment grid size of:

$$dt = 1/t_{max}. \quad (3.3)$$

Only two values of $t_{max}$ are considered here, $t_{max} = 300$ and 600, and the coexistence packing fractions and boundary width differ by a very small amount. Since the computation time scales linearly as $O(t_{max})$, one can get away with using a relatively large value of $t_{max}$, which is chosen at 300.

In conclusion, the phase boundaries are most affected by the position grid spacing, $dz = 1/z_{max}$. Within the examined ranges, this affects the phase boundary widths by about an order of magnitude more than $du = 1/u_{max}$ and $dt = 1/t_{max}$. The changes induced on the phase boundary width $\Delta \eta = \eta_{smA} - \eta_{nem}$ are large relative to the boundary width itself, but unfortunately obtaining a more precise boundary width with our algorithm would require much more computation time.
Table 3.4: Comparison of the I-N phases boundaries for $\xi = 10$ of select $L/D$ in the second-virial approximation. i.e., $J(\eta) = 1$.

<table>
<thead>
<tr>
<th>$\xi = 10$</th>
<th>Hidalgo et al. [2]</th>
<th>This Work, $J(\eta) = 1$</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L/D$</td>
<td>$\eta_{iso}$</td>
<td>$\eta_{nem}$</td>
<td>$\eta_{iso}$</td>
</tr>
<tr>
<td>6.0</td>
<td>0.6928</td>
<td>0.7277</td>
<td>6.0</td>
</tr>
<tr>
<td>8.0</td>
<td>0.5060</td>
<td>0.5494</td>
<td>8.0</td>
</tr>
<tr>
<td>10.0</td>
<td>0.4000</td>
<td>0.4415</td>
<td>10.0</td>
</tr>
</tbody>
</table>

3.2 Comparison of Crank-Nicolson method to previous results

Some selected results of the Crank-Nicolson method from the present work are compared to the spherical harmonic representation of the previous work of Hidalgo et al. [2]. In order to do this the second virial approximation must be used and this amounts to setting the Parsons-Lee rescaling factor in our theory to

$$J(\eta) = 1,$$  \hspace{1cm} (3.4)

discussed in Section 2.11. In Table 3.4 the calculated I-N transition for some values of $L/D$ at $\xi = 10$ are compared and the agreement is quite good, differing by no more than 2.5 %. The higher value of 2.5 % at $L/D = 10.0$ may be related to the claim by Hidalgo
Figure 3.2: Order-parameter behaviour close to the N-SmA critical point of rigid rods, \( \xi = 9000 \), for \( L/D = 7.50 \). A comparison with the numerical algorithm in this Thesis in the second virial approximation \((J(\eta) = 1)\) to the results by Hidalgo et al. [2] et al. that the numerical calculation does not converge well, i.e. the solution cannot be obtained by the algorithm for \( L/D > 10 \) [2]. Thus, calculations close to \( L/D = 10 \) in the method of Hidalgo et al. could possibly be less precise.

The last comparison is the behaviour of the smectic-A order parameter, \( O_{\text{smA}} \), vs. \( \eta \) as \( \eta \) approaches the critical value, \( \eta_{\text{crit}} \) for a continuous transition. This is shown in Fig. 3.2 for the rigid-rod case, \( \xi = 9000 \) for \( L/D = 7.50 \) and the location of the N-SmA transition differs by about 0.014, which is about 2%.
3.3 The phase transitions

First, the phase boundaries of the model are examined in the $\eta$ vs. $L/D$ plane for different values of $\xi$. These are found by holding $L/D$ constant while calculating $\beta F/V$ for successively lower values of $\eta$ until the higher symmetry phase is reached. The I-N phase boundary is found to exhibit phase coexistence at all values of $L/D$ and $\xi$ examined. Phase coexistence regions of first-order phase transitions are found from the double-tangent method discussed in Section 2.12 on the curves of free energy per volume $\beta F/V$.

For the I-N transition the reduced number density parameter is examined, $C$ from Table 2.1, which in terms of $\eta$ and $L/D$ can be shown to be:

$$C = \frac{4\eta(L/D)}{\pi} \left[ 1 + \frac{2}{3(L/D)} \right]^{-1}. \quad (3.5)$$

This parameter was originally introduced in Onsager’s theory of rigid rods [17] in the second virial approximation and approaches a constant in the asymptotic limit, $L/D \to \infty$, in which Eq. (3.5) gives the shape of the I-N coexistence curve. Onsager calculated $C$ at the isotropic and nematic boundaries, $C_{iso}$ and $C_{nem}$, to be 4.253 and 5.714 respectively using an artificially imposed trial function. Table 3.5 shows the more precise SCFT results in the second virial approximation from Chen [1], Hidalgo et al. [2] and in this work. The work by Chen is in the analytic limit $L/D \to \infty$ while in this work $L/D = 10^6$. Hidalgo et al. [2] do not report how large $L/D$ is in their calculation. Fig. 3.3 shows that the reduced density approaches the asymptotic value at around $L/D \sim 10^3$, indicating that the second virial approximation requires a very high shape anisotropy to be accurate. Our agreement with the other two works for $C$ at the I-N transition, $(C_{iso}, C_{nem})$, is quite good,
Figure 3.3: Asymptotic limit of the reduced densities $C$, Eq. (3.5), at the I-N phase boundary for rigidity, $\xi = 1$ (black), 10 (red), 9000 (blue). The lower curves correspond to the isotropic boundary and the upper curves to the nematic.

Table 3.5: Asymptotic ($L/D \to \infty$) isotropic-nematic coexistence reduced densities, $(C_{iso}, C_{nem})$ for several values of the relative rigidity, $\xi$. Ref. [1]: asymptotic $L/D \to \infty$. Ref. [2]: Large (unreported) $L/D$, and Present work: $L/D = 10^6$.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_{iso}$</td>
<td>$C_{nem}$</td>
<td>$C_{iso}$</td>
</tr>
<tr>
<td>$\infty$</td>
<td>4.19</td>
<td>5.33</td>
<td>4.18</td>
</tr>
<tr>
<td>10</td>
<td>4.74</td>
<td>5.54</td>
<td>4.78</td>
</tr>
<tr>
<td>1</td>
<td>9.69</td>
<td>10.39</td>
<td>9.61</td>
</tr>
</tbody>
</table>
especially for the more rigid cases, $\xi = 10$ and 9000. For the semiflexible case, $\xi = 1$, there is much better agreement with Chen’s [1] calculation than Hidalgo et al. [2]. It is hard to comment on the disagreement with Ref. [2] but it may be due to them simply not having a high enough $L/D$.

For the N-SmA transition there are regions where there are second-order transitions (no phase coexistence) as well as first-order transitions. The location of the second-order transition occurs when $O_{smA}$ approaches zero as the packing fraction $\eta$ reaches its critical (or threshold) value $\eta_{crit}$, again while keeping $L/D$ constant (see Section 2.12). This is shown for the semiflexible ($\xi = 1$) and rigid chain ($\xi = 9000$) for several values of $L/D$ in Fig. 3.4. Because SCFT is a mean-field theory, at a second-order transition, $O_{smA}$ should vanish according to a power-law decay,

$$O_{smA} \sim (\eta - \eta_{crit})^{\frac{1}{2}}.$$ \hspace{1cm} (3.6)

Logarithmic fits are shown in Fig 3.4 for $O_{smA}$ vs. separation from the transition point, $(\eta - \eta_{crit})$, where a power law behaviour is satisfied but the exponent in Eq. (3.6) differs from the mean-field prediction of $\frac{1}{2}$. The exponent $\nu$ in almost all cases differs significantly from $\frac{1}{2}$ and is shown in Fig. 3.4. The fits are pretty good for high $(\eta - \eta_{crit})$ but there is some deviation from this for lower values. This arises due to the difficulty in calculating the free energies close to the transition point, $\eta_{crit}$, but by increasing the numerical precision $\epsilon$, down to as small as $10^{-6}$ the $O_{smA}$ can be calculated more reliably closer to 0. This requires more computation time however, as discussed more at the end of Section 3.5, and requires more care to implement systematically, which should be looked at in future
Figure 3.4: The left column shows the SmA order parameter, $O_{smA}$, vs. packing fraction $\eta$ for a range of $L/D$ at rigidities $\xi = 9000$ (a) and 1 (b). The right column shows the corresponding log-log plots of $O_{smA}$ vs. the distance to the critical point, $(\eta - \eta_{crit})$. The points are the calculated data which are fitted by the lines. The fitted critical exponent, $\nu$, and its uncertainty are shown.
work. The discrepancy of the exponents, \( \nu \), from the mean-field value of \( \frac{1}{2} \) is not unique to this work. My analysis for \( O_{smA} \) on the data by Hidalgo et al. [2] with \( \xi = 9000 \) and \( L/D = 7.50 \), see Fig. 3.2, gives the power law exponent to be \( 0.428 \pm 0.006 \).

Next are the phase diagrams, shown in Fig’s. 3.5-3.8. The solid double lines indicate the phase coexistence region for first-order transitions, while the dotted single line indicates the location of the critical packing fraction, \( \eta_{crit} \) for continuous transitions. The phase diagrams obtained are qualitatively similar to that of Hidalgo et al. [2] (see Fig. 1.7). However, this work has made two significant improvements. The phase boundaries in [2] occur at packing fractions that are too high, in some cases even higher than the close-packed limit \( \sim 0.91 \). This is corrected here using the rescaling method of Parsons and Lee [28, 38], and is described in Section 2.11. The second improvement is that phase boundaries can be calculated for \( L/D > 10 \), which was unattainable in [2], using the improved Crank-Nicolson numerical algorithm, described in Section 2.10.

Consider first the rigid rod case, \( \xi = 9000 \). For low \( \eta \) there is a first-order I-N transition for \( L/D > 4.3 \), which has been calculated up to \( L/D = 10^6 \). At \( L/D = 4.3 \) the transition occurs at \( (\eta_{iso}, \eta_{nem}) = (0.4350, 0.4524) \) then slowly decreases asymptotically to \( \eta = 0 \) as \( L/D \) increases. The coexistence width, \( \Delta \eta = \eta_{nem} - \eta_{iso} \), slowly decreases to zero as \( L/D \to \infty \), in accordance with Eq. (3.5). Fig. 3.5 (a) plots \( L/D < 53 \) but the trend is apparent. The onset of nematic ordering with increasing \( \eta \) is understood as a competition between translational and orientational entropy of anisotropic molecules. For low enough concentration, the rigid rod molecules are free to move through space as well as orient themselves in any direction. For higher concentration there is less space to move around,
Figure 3.5: Phase diagrams for systems of different rigidities with $3.6 < L/D < 53.0$ plotted on log scale to show a wide range. (a) $\xi = 9000$, (b) 10 and (c) 1. The solid lines define the coexistence regions of first-order phase transitions. The dashed line defines the critical packing fraction, $\eta_c$ for the second-order transition.
but the molecules can form an oriented nematic and gain translational entropy at the expense of some orientational entropy [78]. This gain in entropy is more prominent for higher shape anisotropy, which then lowers $\eta$ of the I-N transition for higher $L/D$.

From Fig. 3.6, the tricritical point for the N-SmA boundary is predicted at $L/D = 4.3$ above which, is a continuous N-SmA boundary. Below this is phase coexistence of the I and SmA phases with no prediction of N-SmA coexistence and therefore no triple point is predicted, within the uncertainty of our the calculation. This is different than what is obtained by Hidalgo et al. [2] in that for $4.2 < L/D < 5.0$ there is N-SmA coexistence and for $L < 4.2$ there is I-SmA coexistence, so the triple point occurs at $L/D = 4.2$. Their tricritical point is at $L/D = 5$. In my analysis of the free energy, there is a tiny region
where N-SmA boundary exists for $4.2 < L/D < 4.3$ but this is within the I-SmA boundary and therefore does not indicate the equilibrium nematic phase there.

The Monte Carlo simulations of rigid spherocylinders by Bolhuis and Frenkel [12], Fig. 1.4, found the triple point to be at $L/D = 3.7$, while an extension to that study by Polson and Frenkel [32] predicts that the N-SmA boundary is first-order at all $L/D$, i.e. no tricritical point. As for the packing fraction for the I-SmA phase boundary, our result is surprisingly close to that obtained from the Monte Carlo simulations of van Roij and Frenkel [77]. For example, [77] predicts the N-SmA phase boundary at $L/D = 3.8$ to occur at $(\eta_{nem}, \eta_{smA}) = (0.50, 0.52)$ which is right above their calculated I-N coexistence at $(\eta_{iso}, \eta_{nem}) = (0.47, 0.49)$. For $L/D = 3.80$ this work predicts that the nematic phase is pre-empted by the direct I-SmA transition at $(\eta_{iso}, \eta_{smA}) = (0.4597, 0.5001)$. Aside from the absence of the nematic phase, our co-existence boundary is very close to van Roij et al. [77] and Bolhuis and Frenkel [12]. The comparison is shown in Fig. 3.6.

For $L/D \sim 32$ the continuous N-SmA phase boundary suddenly has a more rapid decrease, and the trend continues up to the highest calculated $L/D = 53$, while the smectic ordering remains relatively high. There is a steady increase of the smectic period $\lambda$ as well and preliminary calculations for $L/D$ up to 65 show that the trend may continue. The sudden drop in the phase boundary indicating increased SmA stability is not observed in the Monte Carlo simulations ([12], see Fig. 1.4), as they do not have much data in that region. The SmA phase is stabilized by the end-segment interaction, $V_{end-seg} \propto LD^2$, discussed in Section 2.6.4 and this interaction is expected to have less effect than the segment-segment interaction, $V_{seg-seg} \propto L^2D$, for higher $L/D$. So the SmA phase would
be expected to be less stable for higher $L/D$. However the measurements on fd virus particles, $L/D = 133$ [14] (see Fig. 1.2), and M13 with also very high $L/D$ [15] observe the SmA phase, which is consistent with our rigid rod phase diagram. In Section 3.4 where nematic ordering is discussed in more detail, a possible explanation of this is given based on a scaling argument, as well as the saturation of the nematic order parameter ($O_{nem} \sim 1$) which occurs for $L/D$ greater than $\sim 30$ for the rigid rod (see Fig. 3.10).

Next the semiflexible chain is shown in Fig. 3.7 with $\xi = 10$. The phase boundaries shift to slightly higher packing fractions while the order of the transition has clearly shifted from second-order to first-order for all $L/D$ examined with no tricritical point. This is in contrast to Hidalgo et al. where the transition is second-order for $L/D > 9$ (tricritical point at $L/D = 9$), but is the same behaviour as the Monte Carlo simulation by Polson [32] for rigid spherocylinders. The triple point here occurs at $L/D = 4.30$ which is the same as [2], to within numerical accuracy.

A significant feature in Fig. 3.5 (b) is that for $L/D$ increasing, the packing fraction at the N-SmA transition, $(\eta_{nem}, \eta_{smA})$, starts to change from decreasing to increasing at around $L/D = 16$. This was not observed in the phase diagram of Hidalgo et al. [2], which only examines $L/D < 10$, nor in the rigid chain in this work where the transition actually drops faster. The Monte Carlo simulation does not investigate the semiflexible chain for this range of $L/D$. This feature is consistent with the interaction, $V_{end-seg}$, becoming weaker than $V_{seg-seg}$ for high $L/D$, discussed above. At around $L/D = 40.0$, the numerical algorithm begins to take much longer and calculations have not been obtained for higher $L/D$ than this for the N-SmA boundary, but at this point the trend is apparent. More
data on $O_{smA}$ is needed to see the change in smectic ordering with respect to flexibility at high $L/D$. For high $L/D$ the SmA phase thus appears to be destabilized by flexibility, of which there is but a small amount present for $\xi = 10$. However small flexibilities are enough to affect the N-SmA coexistence boundary as seen in Fig. 3.5. Also see Refs [2],[14] and [36] for this point. This effect is discussed further for $\xi = 1$.

The last phase diagram is for the semiflexible case $\xi = 1$. A further increase in the transition packing fraction is predicted as well as a shift in the tricritical point to higher $L/D$. This implies that the N-SmA transition for a given $L/D$ can be preempted by a direct I-SmA transition for an increase in flexibility. Also, for this flexibility, the N-SmA boundary behaves more similarly to that of $\xi = 9000$ rather than $\xi = 10$: the tricritical point is again equal to the onset of I-SmA coexistence, within numerical uncertainties,
occurring at $L/D = 6.78$. Like the rigid rod, this point is very close to the prediction of the triple point by Hidalgo et al. $L/D = 6.7$. This reversal of the phase transition from continuous at $\xi = 9000$ to discontinuous at $\xi = 10$ back to continuous at $\xi = 1$ is unexpected and different from the other theoretical predictions of Hidalgo et al. [2], Tkachenko, [35] and van der Schoot [4], which predict that the transition only becomes more and more discontinuous with increasing flexibility. N-SmA phase boundaries for rigidities intermediate to $\xi = 1, 10$ and 9000 have not been investigated fully so it is not quite understood what causes the boundaries to behave this way. In Section 3.6, a non-uniform rescaling factor of the interaction free energy $J(\eta(z))$, is briefly examined and, in that case, the phase boundary for $\xi = 1$ behaves more in accord with the theoretical predictions and virus particle measurements [14].
With further increase in $L/D$ the N-SmA transition occurs at roughly constant $\eta$ until around $\sim 16.5$ in Fig. 3.8 at which point the transition increases slightly while the smectic ordering $O_{smA}$ starts to decrease significantly. Also at $L/D \sim 17$, slightly above the N-SmA boundary, $O_{smA}$ actually begins to decrease with increasing $\eta$ until a re-entrant nematic phase forms at higher enough $\eta$. By around $L/D \sim 17.50$ the smectic phase completely destabilizes with respect to the nematic phase, which is similar behaviour to the destabilization of the SmA phase previously mentioned for $\xi = 10$ for high $L/D$ but much more drastic. On the phase diagram this appears as a nose-shaped continuous SmA-N phase boundary, which was possible to calculate back to $L/D = 15.50$ (thick dotted line above N-SmA boundary) after which the computation does not converge at the higher packing fractions. This may be due to the tendency of the system to form a solid phase at high enough packing fractions, which cannot be analyzed using this theory. So it appears that flexibility, which tends to disorganize the positions of the terminal end segments, does indeed destabilize the smectic phase. The disordering of the end segments for higher flexibility is illustrated in the surface plots of $\psi(z, u_z, t = 0)$ and $\psi(z, u_z, t = 1)$ in Figs. 3.14 (a), (e) where $\xi = 1$ and Figs. 3.15 (a), (e) where $\xi = 9000$. For the semiflexible chain, $\xi = 1$ the relative probability of the end segment possessing orientational order, $u_z \sim 1$, at the edge of the smectic layer, $z/\lambda = 0$ or 1, is much less than that for the rigid chain, $\xi = 9000$.

The effects of flexibility can be stated as follows: Rigid chains exhibit a SmA phase for all calculated $L/D$ which becomes more stable with increasing $L/D$. The stability at high $L/D$ is rather delicate though; a small amount of flexibility destroys the smectic ordering.
Figure 3.9: The N-SmA transition ($\eta$ vs $1/\xi$) for $L/D = 6.00$ given by the red squares with line of fit. In the case of first-order transitions, the values above represent $(\eta_{nem} + \eta_{smA})/2$. The dashed curve represents the simulation results by Bladon and Frenkel [3], the dotted curve describes asymptotic results of [4] and the straight line the SCFT results by [2]. This plot, without the present results, is taken from [2].

In Fig. 3.9 our results (red squares), which include extra calculation at rigidities $\xi = 3, 5$ and 8, for the N-SmA transition in terms of $\eta$ vs. $1/\xi$ at $L/D = 6.00$ are compared to some other works. In this figure, the dashed line represents the Monte Carlo simulation results
obtained by Bladon and Frenkel [3] for a model of jointed spherocylinders with the same $L/D$ value (fitted to the equation proposed by van der Schoot [4], so it is actually drawn over a wider range of $1/\xi$ values than examined in [3]). The plots of van der Schoot [4] and Hidalgo et al. [2] are well above those of the simulations [3] which is expected due to their use of the second virial approximation. The present results have better agreement with the simulations with excellent agreement for the rigid chain, $\xi = 9000$, however the discrepancy with the simulations increases with increasing flexibility. A curious phenomenon is that the slope for all three previous results, Refs. [2–4], are parallel while the present calculation is outside of this trend with a more gradual slope. The rigid rod calculation is in great agreement with the Monte Carlo simulations but they observe less SmA stability as the flexibility increases.

### 3.4 Nematic ordering in the smectic phase

From the disordered isotropic phase the first symmetry breaking is the orientational nematic, presented here. For high orientational ordering the distribution, $\phi(z,u_z)$, has very sharp peaks at $u_z = \pm 1$ so to calculate $O_{nem}$, Simpson rule integration is used, based on quadratic interpolation.

In Fig. 3.10, $O_{nem}$ is shown at the I, N and SmA phase boundaries. At the I-N boundary for the rigid rod case, $O_{nem}$ varies from 0.66 at low $L/D$ to 0.78 for $L/D = 10^6$. Flexibility lowers $O_{nem}$ at this transition quite noticeably even for a seemingly small amount of flexibility, $\xi = 10$ where $O_{nem}$ drops by $\sim 0.1$. This, combined with the fact that higher flexibility raises the I-N transition packing fraction (see Section 3.3) indicates that flexibility
Figure 3.10: Value of the nematic order parameter at the I-N and N-SmA phase boundaries for a wide range of $L/D$ and the three rigidities $\xi = 1, 10$ and 9000. The two red lines are for $\xi = 10$ correspond to $O_{nem}$ on the higher and lower coexistence lines of the phase boundary. The uncertainty in $O_{nem}$ is unnoticeable on the graph so the error bars are omitted.

also lowers the nematic ordering. The variation in $O_{nem}$ over all $L/D$ is gradual for all rigidities, especially at higher flexibility. The origin of the decrease in $O_{nem}$ for increasing flexibility is because flexibility leads to higher orientational disorder of the segments in the flexible chain. $O_{nem}$ for the N-SmA transition could only be found up to a certain $L/D$ shown in Fig. 3.10, just like the phase diagrams in Fig. 3.5. At the N-SmA boundary $O_{nem}$ is higher than at the I-N boundary and decreases with flexibility. There is also more variation: a sharp dip in $O_{nem}$ occurs for very low $L/D$ at the tricritical point (Section
3.3) for $\xi = 9000$ and 1 and is a result of the SmA boundary dropping to lower packing fraction, see Figs. 3.6 and 3.8. For $\xi = 10$, the N-SmA boundary is a lot smoother because there is no sharp drop in the SmA boundary in this case (see Fig. 3.7). The rigid case saturates to almost perfect nematic ordering, $O_{nem} \sim 1$, at the SmA boundary for high $L/D$, while for the semiflexible cases $O_{nem}$ is noticeably less than 1 for the ranges that could be calculated. Once again, the seemingly small amount of flexibility for $\xi = 10$ produces a noticeable change in the phase behaviour.

It appears that the saturated nematic ordering for the rigid rod at higher $L/D$ is consistent with the increased tendency to form the SmA phase, while the lowered nematic ordering for the semiflexible chain correlates with the destabilization of the SmA phase, as observed in Section 3.3. An attempt to qualitatively explain this is given here. In our model the end-segment interaction, $V_{\text{end-seg}} = \frac{\pi LD^2}{2}$ responsible for smectic ordering, is independent of orientation so smectic ordering should not be affected by the relative orientation of the ends and segments, contrary to what is expected in a model where the end-segment interaction does depend on orientation. This means that the mechanism for smectic ordering is present and always has the same strength, for a given $(\eta, L/D)$, even when the rods are completely parallel. At high enough $L/D$, once the rigid rods are highly parallel, the nematic-inducing segment-segment interaction, $V_{\text{seg-seg}} = L^2D|u \times u'|$, becomes $\sim 0$ and cannot decrease further. The ratio $\frac{V_{\text{seg-seg}}}{V_{\text{end-seg}}} = \frac{L}{D}|u \times u'|$ can become large for large $L/D$ in the semiflexible case where the nematic order parameter is always unsaturated, $O_{nem} < 0$. The interaction $V_{\text{end-seg}}$ is insignificant and SmA ordering is suppressed. But for the rigid rod case, this ratio can become small for large $L/D$ due
to the saturated nematic order parameter and $V_{end-seg}$ can become significant leading to increased SmA stability. This is consistent with the phase diagrams, Fig. 3.5 (a)-(c), in which the N-SmA boundary for rigid rods drops quicker at around $L/D = 30$-very close to where $O_{nem} \sim 1$ occurs. But the N-SmA boundary for the semiflexible case, $\xi = 1$ and 10 where $O_{nem}$ never saturates, always goes up for high $L/D$. Therefore it appears that increased flexibility can lead to complete destabilization of the SmA phase at high $L/D$. However, a more quantitative investigation of these effects is warranted to be sure. It would be desirable to examine rigidities between $\xi = 10$ and 9000 to detect a reversal of the N-SmA boundary from a sudden drop to an increase in packing fraction, $\eta$.

The SmA phase is now examined in more detail. First, the position profile for the chains averaged over the orientations is given:

$$\bar{\phi}(z) = \langle \phi(z, u) \rangle_{\mu} = \int d\mu \phi(z, u), \quad (3.7)$$

describing the density of chains vs. position $z$ and $\phi(r, u)$ is the contour averaged segment distribution. The quantity in Eq. (3.7), $\bar{\phi}(z)$, will be called the chain density which is normalized as follows over one smectic period, $\lambda$:

$$\frac{1}{\lambda} \int_{0}^{\lambda} dz \bar{\phi}(z) = 1. \quad (3.8)$$

The above follows directly from the normalization condition on $\phi(r, u)$ from Eq. (2.59). Fig. 3.11 shows graphically the effect of changing the flexibility, $1/\xi$, while holding $L/D$ and $\eta$ constant. The effect of increasing flexibility is seen to lower the smectic ordering as well as lowering the equilibrium smectic period from $\lambda_{eq}/L = 1.257$ to 1.116. This can be
understood by considering that the flexibility tends to disrupt the organization of the chain ends. The interaction, $V_{\text{end-seg}}$, repels the ends from the segments, and it is expected that it will entropically favour the ends to segregate from the segments, giving rise to smectic ordering. Therefore disorganization of the chain ends would be expected to lower smectic ordering.

The dependence of the orientational ordering on the position within the smectic layer...
Figure 3.12: Nematic ordering in the smectic phase. The dotted line is the orientationally averaged contour-averaged segment density (or the chain density), \( \bar{\phi}(z) = \langle \phi(z, u) \rangle_{u_z} = \int d\mathbf{u} \phi(z, \mathbf{u}) \) vs. reduced position, \( z/\lambda \), where \( \lambda \) is the smectic period. The solid line with crosses is the local order parameter, \( S_2(z) \) given by Eq. (3.9). The solid line is the local orientation order per number of chains, \( \bar{P}_2(z/\lambda) \), in the vicinity of \( z \), defined in Eq. (3.10). For (a), \( O_{nem} = 0.8301 \) and \( O_{smA} = 0.1991 \) and in (b), \( O_{nem} = 0.5758 \) and \( O_{smA} = 0.2604 \).

is investigated here. The local order parameter:

\[
S_2(z) = \int d\mathbf{u} P_2(\cos \theta) \phi(z, \mathbf{u}), \tag{3.9}
\]
gives the amount of nematic ordering in the vicinity of the position \( z \). The \( z \)-dependent local orientational order parameter, \( \bar{P}_2(z) \), where the order parameters of degree \( l \) are defined \([33]\) by the following

\[
\bar{P}_l(z) = \frac{\int d\mathbf{u} P_l(\cos \theta) \phi(z, \mathbf{u})}{\int d\mathbf{u} \phi(z, \mathbf{u})} = \frac{S_l(z)}{\bar{\phi}(z)} \tag{3.10}
\]

and \( S_l(z) = \int d\mathbf{u} P_l(\cos \theta) \phi(z, \mathbf{u}) \). The above expression for \( l = 2 \), \( \bar{P}_l(z) \), gives the amount of local nematic ordering at position \( z \), per number of chains \([33]\) and the variation of this with respect to \( z \) indicates the amount of positional-orientational coupling. Finally, to
examine the strength of the positional-orientational coupling the quantity, $Q$, is defined by the difference between the maximum of $\bar{P}_2(z)$, $\bar{P}_2^{\text{max}}$ and the minimum, $\bar{P}_2^{\text{min}}$.

$$Q = \frac{\bar{P}_2^{\text{max}} - \bar{P}_2^{\text{min}}}{\bar{P}_2^{\text{ave}}},$$  \hspace{1cm} (3.11)

where $\bar{P}_2^{\text{ave}}$ is the average over the smectic period.

In Fig. 3.12 (a) $P_2(z)$, is presented alongside the chain density for the rigid rod, $\xi = 9000$, with $L/D = 3.8$ and $\eta = 0.5007$, just above the SmA phase boundary (see Fig. 3.6). $O_{\text{nem}} = 0.8301$ here and $\bar{P}_2(z)$ has a very small variation with $Q = 0.03$, indicating very weak positional-orientational coupling. Also shown, in Fig. 3.12 (b), is the semiflexible, $\xi = 1$, case for $L/D = 6.00$ and $\eta = 0.5400$, with less nematic ordering, $O_{\text{nem}} = 0.5758$. Here $Q = 0.35$, much greater than in Fig. 3.12 (a), with higher orientation in the middle of the smectic layer, while the chains are more disorganized in between the smectic layers. These two cases demonstrate the effect of flexibility on the positional-orientational coupling. Even though the system in Fig. 3.12 (b) has higher smectic ordering with $O_{\text{smA}} = 0.2604$ compared to $O_{\text{smA}} = 0.1991$ for the system in Fig. 3.12 (a), the nematic order is notably less. Note also that for this case the effects of greater $L/D$ and $\eta$ than in the rigid case, Fig. 3.12 (a), which tend to favour nematic ordering, are overcome by the chain flexibility resulting in reduced nematic ordering.

In Fig. 3.13 the general behaviour of the positional-orientational coupling is shown with respect to the rigidities, $\xi = 1, 10$ and 9000 and over all calculated $L/D$. However, the dependence on the packing fraction $\eta$, is not shown. $Q$ increases monotonically with respect to $\eta$ and a wide range of $\eta$’s were calculated for each $(\xi, L/D)$ above the N-SmA
transition, just like for the smectic order parameter $O_{smA}$, in Fig. 3.4. So for simplicity only the maximum $Q$ is shown from each range of values. The positional-orientational coupling clearly increases with higher flexibility and lower $L/D$.

Again the comparison to the Monte Carlo simulations of van Roij and Frenkel [77] can be made at $L/D = 3.8$ just above the SmA phase boundary. In [77] this is at $\eta$ slightly higher at 0.527. The calculations of this Thesis were not able to obtain a solution at this packing fraction with the highest satisfactory value at $\eta = 0.5007$ and corresponding data in Fig. 3.12 (a). They observed that $S_2(z)$ varied from a maximum of 0.894 in the middle of the smectic layer to 0.052 in between the smectic layers, along with large positional-orientational coupling. This is rather different than our result of $0.421 < S_2(z) < 1.025$.
with very weak positional-orientational coupling. They observe it to change approximately by a factor of ten from the maximum to the minimum, where we have that the variation in the number density (proportional to number density) is around a factor of 2. The discrepancy here between our mean-field calculations and the Monte Carlo simulations is not a big surprise considering that for rigid chains, where the interpenetration between adjacent chains is quite low, the MFA is less valid than for flexible chains. Comparisons to [77] will be looked at furthermore in Section 3.5.

### 3.5 The smectic layer width and depletion zone

The smectic-A phase is now examined in more detail. Figs. 3.14 and 3.15 show the distribution functions, $\psi(z, u_z, t)$ and $\phi(z, u_z)$, which give detailed indication of which structure is present. $\psi(z, u_z, t)$ is the probability that a given segment, $t$, of any chain is located at position $z$, with orientation $u_z$, while $\phi(z, u_z) = \int_0^1 dt \psi(z, u_z, t)$ is the probability that any chain segments are located at $z$ with orientation $u_z$.

Two examples of these are shown in Figs. 3.14 and 3.15 for several segment values, $t$, for $\xi = 1$, $L/D = 7.00$, $\eta = 0.5100$, and $\xi = 9000$, $L/D = 6.90$, $\eta = 0.4470$. The origin of the $z$ axis (in units of chain length, $L$) is taken to be in the middle of adjacent smectic layers where the minimum of $\phi(z, u_z)$ or $\psi(z, u_z, t = 0.5)$ occurs. The symmetry relation for $q(z, u_z, t)$, see Eq. (2.101), was used in producing these figures. Fig. 3.14 shows a relatively weak smectic-A phase with equilibrium smectic period (see Section 2.12), $\lambda = 1.055$ with definite peaks at orientations $u_z = \pm 1$, indicative of nematic ordering, and periodicity in the $z$ direction, indicative of smectic ordering. It is also seen that the minima
Figure 3.14: The t-segment distribution function, $\psi(z, \cos(\theta), t)$, in the SmA phase at segment indices $t = 0, 0.25, 0.5, 0.75$ and 1; see Figs. (a), (b), (c), (d) and (e), respectively. Plots are for the semiflexible chain ($\xi = 1$) with $L/D = 7.00$ and $\eta = 0.5100$ exhibiting weak smectic ordering, $O_{smA} = 9.543 \times 10^{-2}$. $z/\lambda$ is the position within the smectic layer in units of $\lambda$ and $u_z = \cos(\theta)$ is the $z$-component of the orientation, $\mathbf{u}$. The contour averaged segment distribution, $\phi(z, u_z) = \int_0^1 \psi(z, u_z, t) dt$, is shown in (f). The equilibrium smectic period is $\lambda = 1.055L$, where $L$ is the chain length.
Figure 3.15: The t-segment distribution function, $\psi(z, \cos(\theta), t)$, in the SmA phase at segment indices $t = 0, 0.25, 0.5, 0.75$ and 1; see Figs. (a), (b), (c), (d) and (e), respectively. Plots are for the rigid chain ($\xi = 9000$) with $L/D = 6.90$ and $\eta = 0.4470$ exhibiting stronger smectic ordering, $O_{smA} = 1.768 \times 10^{-1}$, than in Fig. 3.14. $z/\lambda$ is the position within the smectic layer in units of $\lambda$ and $u_z = \cos(\theta)$ is the $z$-component of the orientation, $\mathbf{u}$. The contour averaged segment distribution, $\phi(z, u_z) = \int_0^1 dt \psi(z, u_z, t)$ is shown in (f). The equilibrium smectic period is $\lambda = 1.248L$, where $L$ is the chain length, which is noticeably wider than for the semiflexible chain in Fig. 3.14.
of $\psi(z, u_z, t = 0.5)$ are located in the vicinity of where $\psi(z, u_z, t = 0)$ and $\psi(z, u_z, t = 1)$ are maximum, and that the distance between these maximum locations can be interpreted as the width of the high density smectic region which is defined, as in Hidalgo et al. [2], by the formula

$$d_{smA} = |r[\psi(z, u_z = \pm 1, t = 0)_{max}] - r[\psi(z, u_z = \pm 1, t = 1)_{max}]|.$$  \hspace{1cm} (3.12)

In the above, $r[\psi(z, u_z, t)_{max}]$ denotes the position where the segment indexed by $t$ has the highest probability of occurring for the most probable orientation, which is $u_z = \pm 1$, parallel to the nematic director. The numerical uncertainty $\Delta d_{smA}$ of $d_{smA}$ is equal to

$$\Delta d_{smA} = \frac{2}{z_{max}} \lambda = 0.08 \lambda$$ \hspace{1cm} (3.13)

where $2/z_{max} = 0.08$ is equal to twice the position grid spacing, $dz_{amax}$ and the factor of $\lambda$ arises because the position $z$ is in units of $\lambda$. The region outside of this is interpreted as the width of the depletion zone between higher density smectic layers defined by

$$d_{depl} = \lambda - d_{smA},$$ \hspace{1cm} (3.14)

easily seen to be the difference between the smectic period, $\lambda$, and the high density region. The uncertainty of $d_{depl}$ is the same as $d_{smA}$. The high density region for the weaker smectic in Fig. 3.14 has thickness of $d_{smA} = 0.844L \pm 0.042L$ with a corresponding depletion zone width of $d_{depl} = 0.211L \pm 0.042L$. Fig. 3.15 shows a smectic phase with notably wider equilibrium smectic period $\lambda = 1.248L$, and a corresponding high density smectic region and depletion zone of $d_{smA} = 0.948L \pm 0.050L$ and $d_{depl} = 0.300L \pm 0.050L$, respectively.
Figure 3.16: The equilibrium width of the high density region, $d_{_{\text{smA}}}/L$ in units of $L$ for selected values of $L/D$ for $\xi = 9000$ (blue), 10 (red) and 1 (black). More than one point is often shown at each $L/D$ corresponding to a selected set of packing fractions, $\eta$.

In Fig 3.16 the high density width, $d_{_{\text{smA}}}/L$ vs. $L/D$ is plotted for rigidities, $\xi = 1, 10$ and 9000. There are 42 data points here taken from a range of $(\xi, L/D$ and $\eta)$, with the error bars from Eq. (3.13) displayed. The variation of $d_{_{\text{smA}}}/L$ with respect to the packing fraction $\eta$ as it approaches the N-SmA phase boundary is quite small and within the uncertainty, $dz/\lambda$. Our calculations cover only a small range of $\eta$, typically no more than $\sim 0.01$ and the data is rather noisy with respect to $\eta$ so therefore the dependence on $\eta$ is not examined. This could be looked at in future works with a lower uncertainty.
in $dz/\lambda = 1/z_{max}$ by increasing $z_{max}$. Or, possibly the numerical precision ($\epsilon = 10^{-4}$ for these calculations, see Appendix D) can be feasibly increased, as discussed more at the end of this Section. Another possibility, not discussed yet, is to use Fourier basis functions to model the position dependence, a very common technique in SCFT [44]. The structure is examined well into the smectic phase, where $O_{smA}$ is greater than around 0.05, because it is often hard to obtain the SmA solution very close to the N-SmA transition. There is noticeable dependence of $d_{smA}/L$ on $\xi$, becoming lower for increasing flexibility, with $d_{smA}/L \sim 0.85$ for much of $\xi = 1$ and $d_{smA}/L$ closer to one for much of $\xi = 10$ and 9000. Within the uncertainty there is no noticeable dependence on $L/D$.

In Fig. 3.17 the equilibrium smectic period, denoted $\lambda_{equ}$, vs. $L/D$ is plotted for different rigidities. Again, the data is taken at packing fractions, $\eta$, sufficiently above the N-SmA phase boundary such that the regions of high uncertainty in $\lambda_{equ}$ are avoided. Each data point consists of the average of $\lambda_{equ}$ over the set of $\eta$ at given $(\xi, L/D)$ and the error bars denote the standard deviation of that set, of which there are anywhere from 15 to more than 50 points. A general trend for all $\xi$ is the initial increase of $\lambda_{equ}$ as $L/D$ increases from its minimum value; however, each case has different behaviour for higher $L/D$. The curve for $\xi = 1$ plateaus at around $\lambda_{equ} \sim 1.12$ for $L/D \sim 17.5$ where the SmA phase destabilizes with respect to the N phase (see Section 3.3). $\xi = 10$ also plateaus at around $\lambda_{equ} \sim 1.2$ and stays close to this up until $L/D = 40$ where the SmA phase is less stable. The rigid chain is very different, exhibiting a mostly steady increase in $\lambda_{equ}$ for all calculated $L/D$. This is consistent with the steady lowering of the N-SmA boundary, see Fig. 3.5 (a) in Section 3.3, and further indicates an increasing stability of the SmA phase.
Both Figs 3.16 and 3.17 for the rigid rod indicate that due to the constant width, $d_{smA}$, of the high density region and the steady increase of the SmA period, with increasing $L/D$, the low density depletion zone width, $d_{depl}$, steadily increases.

There is a clear dependence of $\lambda_{eq}$ on the rigidity as well - an increase in flexibility lowers the smectic period, which is consistent with measurements on virus suspensions [14] by Dogic and Fraden as well as computer simulations [3] by Bladon and Frenkel.
Interestingly enough, the semiflexible chain $\xi = 1$, has a smectic period with $\lambda_{equ} < L$, while Hidalgo et al. [2] report the lowest $L/D$ for this case to be 6.00, with $\lambda_{equ} = 1.04L$. The point at which $\lambda_{equ}$ becomes less than $L$ is between $L/D = 4.65$ and 5.00. To our knowledge $\lambda_{equ} < L$ has not been observed experimentally; however, fd virus particles have been measured with $\lambda_{equ}$ as low as 1.03$L$ [14]. From this result, virus measurements with $\lambda_{equ} < L$ may be expected though, considering that the commonly studied ones such as fd, TMV and M13 have relative large anisotropy, $L/D > 17$, and as shown in Fig. 3.17, for increasing $L/D$, $\lambda_{equ}$ tends to increase.

The lowest $L/D$ obtained is 4.20 with $\lambda_{equ} = 0.97$ and below this, the numerical algorithm does not converge. This may not indicate a deficiency of the algorithm, however, and may be due to the limitation of our theory, which has been developed only to describe fluid type phases. The Monte Carlo simulations [12] for rigid spherocylinders predict the SmA fluid phase to destabilize at $L/D = 3.1$, where a solid phase arises. A SCFT that accounts for the solid phase would be needed.

The system is also examined away from equilibrium, away from where it attains minimum free energy, with respect to the smectic period, where attention is focused on the order parameters, $O_{smA}$ and $O_{nem}$ (Figs. 3.18 and 3.19). It is expected that $O_{nem}$ is maximized at equilibrium by considering the segment-segment interaction, $V_{seg-seg}$, of the theory which favours parallel alignment of the chains. A similar argument applies to the maximization of $O_{smA}$ at equilibrium, where the interaction, $V_{end-seg}$ favours the separation of the terminal end segments from the segments away from the ends, leading to increased smectic ordering. Two cases for this are shown for the semiflexible chain in Figs.
Figure 3.18: The free energy density $F/V$ (black points, left axis), vs. smectic period in units of $L$ plotted on top of the order parameters, (a) $O_{nem}$ (red points, right axis) and (b) $O_{smA}$ (blue points, right axis) for $\xi = 10$ and $L/D = 4.50$.

Figure 3.19: The free energy density $F/V$ (black points, left axis), vs. smectic period in units of $L$ plotted on top of the order parameters, (a) $O_{nem}$ (red points, right axis) and (b) $O_{smA}$ (blue points, right axis) for $\xi = 1$ and $L/D = 7.00$.

3.18 ($\xi = 10, L/D = 4.50$) and 3.19 ($\xi = 1, L/D = 7.00$) well into the smectic phase. The equilibrium ($F/V = \text{minimum}$) order parameters are offset from their maximum value only very slightly, if at all. This is also observed for a few other cases as well, including
variations in the packing fraction, $\eta$, which are not shown, which is consistent with what is expected. However, even though the concave behaviour of $O_{nem}$ and $O_{smA}$ can be seen, it turns out that the exact values of $\lambda$ for where $O_{nem}$ and $O_{smA}$ are maximum are unfortunately not precise enough due to the numerical precision of the free energy, $F/V$ (see Appendix D), having a relative value $\epsilon = 10^{-4}$. An analysis of the data in Fig. 3.18 shows that for $\epsilon = 10^{-4}$, which is used in the previous works on semiflexible polymers [2, 33], $\lambda$ can range from 1.13 to 1.22-an uncertainty of $\delta \lambda \sim 0.09$, most of the plotted range. For higher precision, $\epsilon = 10^{-6}$, used in much of the other SCFT work, the analysis indicates that the uncertainty is lowered to $\delta \lambda \sim 0.007$ and for $\epsilon = 10^{-7}$ the analysis indicates it is lowered to $\delta \lambda \sim 0.002$, only a couple of grid points wide on Fig. 3.18. Even though much of the system can be described well using a numerical precision of $\epsilon = 10^{-4}$, $\epsilon$ needs to be smaller to examine off equilibrium effect in better detail.

The precise determination of $\lambda_{equ}$ is fundamental to obtaining other equilibrium properties such as the high density smectic width, $d_{smA}$ (Eq. (3.12)) and the depletion zone width, $d_{depl}$ (Eq. (3.14)). The dependences of these with respect to packing fraction $\eta$ are not shown, essentially because $\lambda_{equ}$ lacks the required precision, and instead error bars have been used to depict the spread of $\eta$ over its average value. In future work it would be desirable to develop an efficient enough numerical algorithm which can address this.
3.6 Position-dependent rescaling of the interaction: Preliminary result

A main goal of this work was to go beyond the second virial approximation, which was accomplished by using the method of Parsons and Lee [28, 38]. While this method has had success for uniform phases (I and N) and non-uniform phases (SmA and SmC) [39] where the positionally dependent local density is taken into account, in this Thesis the simplest approach is employed which rescales the interaction term for the non-uniform SmA phase to that of a uniform system of hard spheres (see Section 2.11).

A preliminary calculation using the positionally dependent rescaling factor

$$J(\eta(z)) = \left(1 - \frac{3\eta(z)}{4}\right) \left(1 - \eta(z)\right)^2$$ \hspace{1cm} (3.15)

is looked at here. The local packing fraction, \(\eta(z)\) from Eq. (3.15), is directly proportional to the chain density, Eq. (3.7):

$$\eta(z) = \eta \tilde{\phi}(z) .$$ \hspace{1cm} (3.16)

Just one result is shown, the N-SmA phase boundary in the vicinity of the tricritical point and triple point for the semiflexible case \(\xi = 1\), in Fig. 3.20 (b). In this case there is N-SmA coexistence which gives the triple point at \(L/D = 7.3\) and the tricritical point at \(L/D = 7.7\), which was not present using the position-independent rescaling factor, \(J(\eta)\), from Fig. 3.8 and shown again in Fig. 3.20 (a) for comparison. This result is now more in agreement with the virus particle experiments [14] which show stronger first-order behaviour with increasing flexibility. This also looks very similar to the phase diagram of
Figure 3.20: (a) The phase diagram for $\xi = 1$ using the position-independent rescaling, $J(\eta)$, from Section 3.3. (b) Same phase diagram as (a) calculated using the position-dependent rescaling, $J(\eta(z))$.

Hidalgo et al. [2] with the triple point at $L/D = 6.7$ and the tricritical point at 9 (see Fig. 1.7). Lower values of the smectic period are also predicted using this method.
Chapter 4

Conclusion

In this work the behaviour of semiflexible liquid crystalline polymers was studied using Onsager’s excluded volume interaction for wormlike cylindrical segments and the terminal end segments in the context of SCFT.

A new numerical algorithm based on the Crank Nicolson finite difference method was developed which is able to describe the SmA phase for finite length to diameter ratio, $L/D$ greater than 10 which had not been performed before, to our knowledge. The Parsons-Lee rescaling of the interaction free energy is used which goes beyond the second virial approximation and obtains phase transitions that are well within the close-packed volume limit, overcoming difficulties encountered in previous theories. Our phase diagram for the rigid chain is quite close to that produced by hybrid Monte Carlo/molecular dynamics computer simulations. In particular the SmA phase boundary at $L/D = 3.8$ is in great agreement. However while the computer simulations exhibit a weak first-order N-SmA transition for all $L/D$ and Hidalgo et al. predict the same for lower $L/D$, in this work a second-order transition is found at all $L/D$. Our results also disagree with Hidalgo
et al. for the semiflexible case, however for slight flexibility $\xi = 10$, they are consistent with the computer simulations for rigid rods. The equilibrium smectic period is expected to increase with increasing $L/D$ for the rigid rods while it plateaus to a constant value for the semiflexible chain before the SmA phase destabilizes. The prediction that the equilibrium smectic period increases with higher rigidity is consistent with measurements on virus particles by Dogic et al. For flexible enough chains, calculations indicate the equilibrium period can be smaller than the chain length, which has not been observed in computer simulations or experiments, to the author’s knowledge. The presence of positional orientational coupling is also apparent which increases in strength with higher flexibility and is much smaller for the rigid case. The high density smectic region in the middle of the smectic layer is found to stay constant for increasing $L/D$ which implies that the depletion zone (low density smectic region between smectic layers) is expected to increase for increasing $L/D$ as well. The high density smectic region is found to increase very slightly for increasing rigidity.

The stability of rigid rods in the SmA phase is expected to increase with increasing $L/D$. However this stability is rather delicate since it is lost for only a small amount of flexibility, somewhere in the region of $\xi > 10$. The destabilization of the SmA phase was analyzed by considering the relative strengths of the segment-segment excluded volume interaction and the end-segment excluded volume as the flexibility is varied. For rigid rods at high enough $L/D$, the system is in a regime of highly saturated nematic ordering where the SmA inducing end-segment interaction becomes significant compared to the segment-segment interaction. The semiflexible chains with $\xi = 1$ and 10 do not inhabit
this regime.

Future work will make use of the positionally dependent Parsons-Lee rescaling of the interaction free energy that takes into account the local packing fraction, as opposed the packing fraction of the whole system. Preliminary calculations demonstrated that this predicts N-SmA coexistence for the semiflexible chain $\xi = 1$. This is consistent with other theories and is observed in both computer simulations and experiments on virus particles, in addition to a triple point and a lower smectic layer width. Yet another possible extension would be to include the local orientational order with its corresponding effect on the excluded volume. This may have an effect on the local packing fraction as well. An interaction that was ignored in this work, significant for lower $L/D$, was the end-end excluded volume which repels the chain ends and tends to destabilize the SmA phase in favour of the nematic or perhaps the SmC phase. This could provide better agreement with computer simulations in the lower $L/D$ region and for higher flexibility.

Because this work was purely in the mean-field regime fluctuations were ignored, which are important when the system approaches the continuous phase transition. The phase boundaries for the I-N and N-SmA coexistence regions in experiments and simulations are typically weakly first-order so the inclusion of fluctuations in the theory may be important for first-order transitions as well. Another issue is that the mean-field approximation is less valid for chains of higher rigidity, as discussed at the beginning of Chapter 2, due to less overlap of the segments. In the above situations, the behaviour of the system is not entirely dominated by the mean-field configuration and field configurations close to and possibly far from the saddle point can make important contributions. These field fluctuation effects
are rather well developed for polymers in the Gaussian limit, but the SCFT for semiflexible chains this area needs more development.

It is also be desirable to feasibly increase the numerical precision from $\epsilon = 10^{-4}$, used here and in previous similar work, to $10^{-6}$ or even $10^{-7}$. Higher precision is required for calculating the SmA phase close to the critical packing fraction, which was quite difficult to access as well as having very long computation time. Algorithms of higher sophistication should be developed as well. For example some preliminary work with a parabolic interpolation scheme has been done and an adaptive grid for the packing fraction may be useful for approaching the critical packing fraction from above. An issue with the numerical algorithm is that it scales poorly with the number of spatial grid points $z_{max}$, scaling as $O(z_{max}^3)$. To get better resolution of the positional ordering, it may be possible to use a relatively small set of Fourier basis functions to model the sinusoidal density variation.

The model developed in this Thesis simulates homogenous polymers but it is straightforward to extend this model to diblock or $n$-block systems. Confinement type studies could be performed as well, for example, by modifying the boundary conditions of the existing numerical model. An extension to the SmC phase would be possible too, but the only feasible approach would be a perturbation scheme since the extra orientational degree of freedom would increase computation time drastically.
Appendix A

Calculations For The Wormlike Chain

A.1 Derivation of the Fokker-Planck equation in the absence of an external field

In this Section, the Fokker-Planck equation, (2.52), is derived from Eq. (2.51), where the latter equation is

\[ p_0 (r + u \Delta t, u, t + \Delta t) = \int d(\Delta u) \Phi (\Delta u; r, u - \Delta u) p_0 (r, u - \Delta u, t). \]  

(A.1)

Expanding the left side of this integral equation to first order in \( \Delta t \) and the right side to second order in \( \Delta u \) gives

\[
\Delta t \left[ \frac{\partial}{\partial t} + u \cdot \nabla_r \right] p_0 (r, u, t) + O (\Delta t^2) = - \nabla_u \cdot [(\Delta u) \Phi p_0 (r, u, t)] \\
+ \frac{1}{2!} \nabla_u \nabla_u : [(\Delta u) \Phi p_0 (r, u, t)] \\
+ O (\langle \Delta u \Delta u \Delta u \rangle \Phi p_0)
\]

(A.2)
where $\nabla_r$ and $\nabla_u$ denote the gradient with respect to position $r$ and orientation $u$ respectively. The exact meaning of the shorthand term, $\nabla_u \nabla_u$: $[\langle \Delta u \Delta u \rangle \Phi p_0 (r, u, t)]$, for the $O (\Delta u^2)$ term is discussed in Appendix A.2. Also the average of a quantity $f (\Delta u)$ with respect to the transition probability is given by

$$\langle f (\Delta u) \rangle \Phi = \int d(\Delta u) f (\Delta u) \Phi (\Delta u; r, u).$$  \quad \text{(A.3)}$$

The transition probability $\Phi (\Delta u; r, u)$ turns out to be a Gaussian distribution [37] with the first and second moments given by (see Appendix A.2)

$$\langle \Delta u \rangle \Phi = 0$$

$$\nabla_u \nabla_u: \langle \Delta u \Delta u \rangle \Phi = \frac{\Delta t}{\xi} \nabla_u^2.$$  \quad \text{(A.4)}$$

Substituting these into Eq. (A.2) leads to the desired Fokker-Planck equation

$$\frac{\partial}{\partial t} p_0 (r, u, t) = -u \cdot \nabla_r p_0 (r, u, t) + \frac{1}{2\xi} \nabla_u^2 p_0 (r, u, t),$$  \quad \text{(A.5)}$$

where $\nabla_u^2$ is the Laplacian operator on the unit sphere

$$\nabla_u^2 f \equiv \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial f}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 f}{\partial \varphi^2}.$$  \quad \text{(A.6)}$$

where $\theta$ is the polar angle and $\varphi$ is the azimuthal angle.

### A.2 Evaluation of averages with respect to the transitional probabilities in spherical coordinates

The averages listed in Eq. (A.4) are now evaluated. The explicit form of the transition probability $\Phi (\Delta u; r, u)$ for the wormlike chain is first examined, which is proportional
to $\exp(-\beta U_0)$. The quantity $\beta U_0(\{r, u\}) = \frac{\xi}{2} \int_0^1 dt \left| \frac{du(t)}{dt} \right|^2$ is discretized with respect to small displacements on the unit sphere so it is convenient to examine Fig. A.1. A small displacement along the unit vectors $e_\theta$ and $e_\varphi$ is given by $\Delta u = (\Delta \theta, \sin \theta \Delta \varphi)$ which gives the following for the bending energy of an individual small displacement

$$\beta U_0 = \frac{\xi}{2\Delta t} \left[ (\Delta \theta)^2 + (\sin \theta \Delta \varphi)^2 \right]. \quad (A.7)$$

The transition probability is thus a Gaussian distribution with the first moment having the form

$$\langle \Delta u \rangle_\varphi = \int d(\Delta \theta) \int d(\Delta \varphi \sin \theta) (\Delta \theta, \Delta \varphi \sin \theta) \exp[-\beta U_0(\{r, u\})]. \quad (A.8)$$
Both integration limits are understood to be over symmetric intervals centred at 0 and the integrand consists of a product of an even and odd function, which gives

$$\langle \Delta u \rangle_\phi = 0 \quad (A.9)$$

which gives a zero contribution for the term first order in the orientational derivative in Eq. (A.4).

The second order orientational derivative term in (A.4), $\nabla_u \nabla_u : \langle \Delta u \Delta u \rangle_\phi$, is more involved. There are four terms in this expression, two of which contain cross terms of the form, $\langle (\Delta \theta) (\sin \theta \Delta \phi) \rangle_\phi$, and the other two terms are the squared terms $\langle (\Delta \theta)^2 \rangle_\phi$ and $\langle (\sin \theta \Delta \phi)^2 \rangle_\phi$. The cross terms will vanish for the same reason as in Eq. (A.9). The squared terms are given by the second moment of the Gaussian distribution given by the standard result:

$$\langle \Delta u_\alpha \Delta u_\beta \rangle = \delta_{\alpha, \beta} \frac{\Delta t}{\xi}, \text{ where } \alpha \text{ and } \beta = \theta \text{ or } \varphi. \quad (A.10)$$

The $\langle (\Delta \theta)^2 \rangle_\phi$ term multiplies the double derivative in the $\theta$ direction while the $\langle (\sin \theta \Delta \varphi)^2 \rangle_\phi$ term multiplies the double derivative in the $\varphi$ direction. This will give

$$\nabla_u \nabla_u : \langle \Delta u \Delta u \rangle_\phi p_0 (r, \mathbf{u}, t) = \frac{\Delta t}{\xi} \nabla_u \cdot \nabla_u p_0 (r, \mathbf{u}, t) \quad (A.11)$$

$$= \frac{\Delta t}{\xi} \nabla_u^2 p_0 (r, \mathbf{u}, t)$$

$$= \frac{\Delta t}{\xi} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] p_0 (r, \mathbf{u}, t)$$

where $\nabla_u^2$ is the Laplacian operator in spherical harmonics for the unit sphere. A subtle point here is the presence of the scale factors $\sin \theta$ which appears left of the first operation of $\frac{\partial}{\partial \theta}$ on $p_0 (r, \mathbf{u}, t)$ and $\frac{1}{\sin \theta}$ which appears left of the second operation of $\frac{\partial}{\partial \theta}$ on $p_0 (r, \mathbf{u}, t)$.
This shows that one should be careful when doing a Taylor expansion in a non-Cartesian coordinate system. One way to see that the above formula is true is by doing the Taylor expansion to arrive at the Laplacian in Cartesian coordinates. Then simply replace this term by the Laplacian in spherical coordinates, which is valid since this quantity is a scalar and thus does not depend on the chosen coordinate system. The Laplacian of a scalar quantity $V$ in any orthogonal curvilinear coordinate system can be found by using the following conversion formula

$$\nabla^2 V = \frac{1}{h_1 h_2 h_3} \left[ \frac{\partial}{\partial m_1} \left( \frac{h_2 h_3}{h_1} \frac{\partial V}{\partial m_1} \right) + \frac{\partial}{\partial m_2} \left( \frac{h_3 h_1}{h_2} \frac{\partial V}{\partial m_2} \right) + \frac{\partial}{\partial m_3} \left( \frac{h_1 h_2}{h_3} \frac{\partial V}{\partial m_3} \right) \right]$$  \hspace{1cm} (A.12)

where the Cartesian coordinates are

$$x = x(m_1, m_2, m_3), \quad y = y(m_1, m_2, m_3), \quad z = z(m_1, m_2, m_3)$$  \hspace{1cm} (A.13)

and the curvilinear coordinates are

$$m_1 = m_1(x, y, z), \quad m_1 = m_2(x, y, z), \quad m_1 = m_3(x, y, z).$$  \hspace{1cm} (A.14)

The scale factors are given by

$$h_1 = \left| \frac{\partial \mathbf{r}}{\partial m_1} \right|, \quad h_2 = \left| \frac{\partial \mathbf{r}}{\partial m_2} \right|, \quad h_3 = \left| \frac{\partial \mathbf{r}}{\partial m_3} \right|$$  \hspace{1cm} (A.15)

where $\mathbf{r} = (x, y, z)$ [79].
A.3 Derivation of the propagator equation for a wormlike chain in an external field

In the following it is assumed that the external fields, \( w(r, u) \) and \( w_q(r, u) \) act only on the \( 1/\Delta t \) segments that join each monomer of the polymer chain, not on the monomers. Each segment, \( t \), is acted on by \( w(r(t), u(t)) \). The end segments are acted on by both \( w(r(t), u(t)) \) and \( w_q(r(t), u(t)) \) for \( t = 0 \) or \( t = 1 \).

The external field partition function, Eq. (2.84), for a single wormlike chain is given by

\[
Q = \int \mathcal{D}r \int \mathcal{D}u \prod_{t=0}^{t=1} \left[ \delta \left( u(t) - \frac{dr(t)}{dt} \right) \delta \left( |u(t)| - 1 \right) \right] \times \exp \left( -\frac{\xi}{2} \int_0^1 \left[ \frac{du(t)}{dt} \right]^2 - w_q(r(0), u(0)) - \int_0^1 dt w(r(t), u(t)) - w_q(r(1), u(1)) \right),
\]

(A.16)

and can be refactorized in the following way:

\[
Q = \int dr(t) du(t) \exp \left\{ -dt w(r(t), u(t)) \right\} \times \int D_1 \{ \cdot \}_{t' < t} \exp \left\{ -w_q(r(0), u(0)) - \int_{t < t'} dt' w(r(t'), u(t')) \right\} \times \int D_1 \{ \cdot \}_{t' > t} \exp \left\{ -\int_{t > t'} dt' w(r(t'), u(t')) - w_q(r(1), u(1)) \right\}
\]

(A.17)

where

\[
\int D \{ \cdot \}_{t' < t} = \int d(-\Delta r(t')) d(-\Delta u(t')) P \{ r, u; [0, t-dt] \},
\]

\[
\int D \{ \cdot \}_{t' > t} = \int d(\Delta r(t')) d(\Delta u(t')) P \{ r, u; [t + dt, 1] \}.
\]

(A.18)

In the above, \( \Delta r(t) = r(t) - r(t - dt) \) and \( \Delta u(t) = u(t) - u(t - dt) \). To think about Eq.
(A.16), start by performing the \( \int d\mathbf{r}(t) \, d\mathbf{u}(t) \) integral. Then do each of the \( t' > t \) integrals successively following this all the way to \( t' = 1 \), since the \( \Delta\mathbf{r} \) and \( \Delta\mathbf{u} \) terms link each integral to the previous one. The analogous operation is done for the \( t' < t \) integrals all the way to \( t' = 0 \). The notation \( d(-\Delta\mathbf{r}) \) and \( d(-\Delta\mathbf{u}) \) in the first integral of Eq. (A.18) illustrate backwards along the chain. Eq. (A.17) can be rewritten as

\[
Q = \int d\mathbf{r} d\mathbf{u} q(\mathbf{r}, \mathbf{u}, t) \exp \{ dt \, w(\mathbf{r}(t), \mathbf{u}(t)) \} \, q(\mathbf{r}, -\mathbf{u}, 1 - t),
\]  

(A.19)

note the plus sign on the exponential. Taking the limit \( dt \to 0 \), will give

\[
Q = \int d\mathbf{r} d\mathbf{u} q(\mathbf{r}, \mathbf{u}, t) \, q^\dagger(\mathbf{r}, \mathbf{u}, t)
\]  

(A.20)

where \( q(\mathbf{r}, \mathbf{u}, t) \) and \( q^\dagger(\mathbf{r}, \mathbf{u}, t) \) are called the propagators, defined for \( 0 < t < 1 \) by:

\[
q(\mathbf{r}, \mathbf{u}, t) = \int D_1 \{ \cdot \}_{t'<t} \exp \left\{ -w_q(\mathbf{r}(0), \mathbf{u}(0)) - \int_{t'<t} dt' \, w(\mathbf{r}(t'), \mathbf{u}(t')) \right\}
\]  

(A.21)

\[
q^\dagger(\mathbf{r}, \mathbf{u}, t) = \int D_1 \{ \cdot \}_{t'>t} \exp \left\{ -\int_{t'>t} dt' \, w(\mathbf{r}(t'), \mathbf{u}(t')) - w_q(\mathbf{r}(1), \mathbf{u}(1)) \right\},
\]  

(A.22)

where \( q^\dagger(\mathbf{r}, \mathbf{u}, t) = q(\mathbf{r}, -\mathbf{u}, 1 - t) \). From Eqs (A.19-A.22) one can think of the propagator, \( q(\mathbf{r}, \mathbf{u}, t) \), for a segment indexed by \( t \), at position \( \mathbf{r} \) and with orientation \( \mathbf{u} \) as the sum over paths from \( t' = 0 \) forward to \( t \). Therefore \( q(\mathbf{r}, -\mathbf{u}, 1 - t) \) is the sum over paths for the same segment but summed over from the opposite end, \( t' = 1 \), backwards (hence the sign change \( \mathbf{u} \to -\mathbf{u} \)) to \( t' = t \).

The Fokker-Planck equation satisfied by Eqs. (A.21) and (A.22) can be deduced in a similar way to Eq. (2.46) using a stochastic process approach similar to how \( p_0(\mathbf{r}, \mathbf{u}, t) \) was handled for the field free case. The corresponding Chapman-Kolmogorov equation for
where \( \Psi (\mathbf{r} - \mathbf{r}', \mathbf{u} - \mathbf{u}') \) serves the same purpose here as Eq. (2.47). The limit \( t \to 0 \) for Eqs. (A.21), (A.22) gives:

\[
q (\mathbf{r}, \mathbf{u}, t \to 0) = \exp \{-w_q (\mathbf{r} (0), \mathbf{u} (0)) - dt w (\mathbf{r} (0), \mathbf{u} (0))\} \\
q^\dagger (\mathbf{r}, \mathbf{u}, t \to 1) = \exp \{-w_q (\mathbf{r} (1), \mathbf{u} (1)) - dt w (\mathbf{r} (1), \mathbf{u} (1))\},
\]

and the limit \( dt \to 0 \) gives:

\[
q (\mathbf{r}, \mathbf{u}, t \to 0) = \exp \{-w_q (\mathbf{r} (0), \mathbf{u} (0))\} \\
q^\dagger (\mathbf{r}, \mathbf{u}, t \to 1) = \exp \{-w_q (\mathbf{r} (1), \mathbf{u} (1))\}.
\]

It is easy to see how the initial condition, \( q (\mathbf{r}, \mathbf{u}, 0) = 1 \) for the field free case (Eq. (2.48)) can be recovered from the above.

Taylor expanding Eq. (A.23) to first order in \( \Delta t \) on the left hand side and second order in \( \Delta \mathbf{u} \) and the exponential term to first order on the left hand side gives the following expression

\[
q (\mathbf{r}, \mathbf{u}, t) + \Delta t \left[ \frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla \right] q (\mathbf{r}, \mathbf{u}, t) + O (\Delta t^2) = (1 - \Delta tw (\mathbf{r}, \mathbf{u}) + O (\Delta t^2)) \times \\
\left[ q (\mathbf{r}, \mathbf{u}, t) - \nabla \cdot (\langle \Delta \mathbf{u} \rangle_\phi q (\mathbf{r}, \mathbf{u}, t) \\
+ \frac{1}{2} \nabla \cdot \langle \Delta \mathbf{u} \Delta \mathbf{u} \rangle_\phi q (\mathbf{r}, \mathbf{u}, t) + O (\langle \Delta \mathbf{u} \Delta \mathbf{u} \rangle_\phi) \right].
\]

It should be noted that \( \langle \Delta \mathbf{u} \Delta \mathbf{u} \rangle_\phi = O (\Delta t) \) according to the first line of Eq. (A.11) so
both sides of the equation are effectively being expanded to $O(\Delta t)$. Simplifying the above according to results in Appendix A.2 the desired Fokker-Planck equation for a single chain in the presence of an external field is given by:

$$\frac{\partial}{\partial t} q(r, u, t) = \left[ -u \cdot \nabla_r + \frac{1}{2\xi} \nabla^2_u - w(r, u) \right] q(r, u, t). \quad (A.27)$$

The Fokker-Planck equation for $q^\dagger(r, u, t)$ can be found by substituting $t \to 1 - t$ and $u \to -u$ into the above then replacing $q^\dagger(r, u, t) = q(r, -u, 1 - t)$. The time derivative and $-u \cdot \nabla_r$ term both change sign, while the Laplacian term, $\nabla^2_u$ doesn’t. The “source” term does not change sign due the symmetry properties discussed at the beginning of Section 2.9. For $q^\dagger(r, u, t)$, the Fokker-Planck equation is

$$\frac{\partial}{\partial t} q^\dagger(r, u, t) = \left[ -u \cdot \nabla_r - \frac{1}{2\xi} \nabla^2_u + w(r, u) \right] q^\dagger(r, u, t). \quad (A.28)$$
Appendix B

The Second Virial Approximation

It is well known that real gases and fluids exhibit deviations from ideal behaviour as the particle density is increased or the temperature is lowered. While there are many empirical and semi-empirical equations of state that describe this non-ideal behaviour, the virial equation of state has the most sound theoretical foundation of these [80]. However, an exact treatment of the virial equation of state is typically intractable, so in this Appendix the second virial approximation to the virial equation of state will be developed.

In this discussion *intra*-particle interactions due to the internal degrees of freedom, such as the bending energy of polymer chains are ignored. While these interactions affect the statistics of polymer chain conformations (see Section 2.4), this will not affect the conclusion of this section. The goal here is to find the deviation from ideal behaviour due to this approximation using an excluded volume interaction, such as that from Section 2.6.

The virial expansion of interacting particles is an expansion of the pressure in a power
series of the density, $\rho = n/V$

\[ \beta P = \rho + B_2(T) \rho^2 + B_3(T) \rho^3 + \ldots \] (B.1)

where $\beta = 1/(kT)$ and $B_j$ are known as the virial coefficients, which depend on temperature. A useful way to derive the virial coefficients is by using the grand canonical ensemble. The second virial approximation assumes that the terms involving the third virial coefficient $B_3(T)$ and higher are negligible, and it is generally valid only in the limit of very small solute concentration, or equivalently, $\rho$ [81].

Eq. (B.1) up to first order in $\rho$ is simply the ideal gas law and depends upon only the “one-body” term which describes $n$ particles. Deviations from the ideal gas are accounted for by the higher order coefficients $B_j$. $B_2$ accounts for non-additive two-body interactions, $B_3$ for non-additive three-body and two-body interactions and so on [82].

The second virial approximation is now invoked, eliminating terms $O(\rho^3)$ and higher:

\[ \beta P \simeq \rho + B_2(T) \rho^2 \] (B.2)

where $P_{\text{ideal}}$ is the ideal gas pressure, and $P_{\text{int}}$ is the deviation in pressure due to interactions between 2 particles. Integrating Eq. (B.2) with respect to the volume, $V$, gives the free energy $F$

\[ \beta F = \beta F_{\text{ideal}} + \beta F_{\text{int}} \] (B.3)

\[ = \beta F_{\text{ideal}} + VB_2(T) \rho^2. \]

where $F_{\text{int}}$ is the free energy deviation from ideal behaviour. The second virial coefficient
in the classical limit for a given pairwise potential \( u(r_1, r_2) \) between two particles located at positions \( r_1 \) and \( r_2 \) is

\[
B_2(T) = -\frac{1}{2V} \int \int d\mathbf{r}_1 d\mathbf{r}_2 \left[ e^{-\beta u(r_{12})} - 1 \right]
\]  

(B.4)

where \( e^{-\beta u(r_{12})} - 1 \) is the well known Mayer function with \( r_{12} = |\mathbf{r}_2 - \mathbf{r}_1| \) the interparticle distance [80]. The deviation from ideal behaviour due to the second virial approximation is present in Eq. (B.3) in the form of an extra term, \( \beta F_{\text{int}} \), which is proportional to the second virial coefficient. In particular the theory makes use of hard core interactions between two finite volume particles of convex shape (i.e., containing no indents).

In this Thesis the excluded volume interaction (Section 2.6) between two finite volume particles of convex shape (i.e., containing no indents) is used. This has the hard core potential

\[
u(r) = \infty, \text{ if there is volume overlap} \\
u(r) = 0, \text{ if there is no volume overlap.}
\]

(B.5)

There is no attractive part to this potential, but it does simulate the steep repulsive part of realistic potentials. Performing the integral in Eq. (B.4) using the potential (B.5) gives

\[
B_2(T) = \frac{1}{2} V_{\text{excluded}}.
\]

(B.6)

\( V_{\text{excluded}} \) is the volume that is inaccessible to particle 1 due to the presence of particle 2 and is in fact independent of temperature. For this interaction \( \beta F_{\text{int}} \) from Eq. (B.3) is now

\[
\beta F_{\text{int}} = \frac{VV_{\text{excluded}}}{2} \rho^2.
\]

(B.7)
This is the desired result. The free energy of a system of particles exhibiting hard core excluded volume interactions differs from the ideal free energy $F_{\text{ideal}}$ simply by an extra term that is proportional to the excluded volume between two particles. While the internal degrees of freedom affect chain conformation statistics they do not affect the form of $\beta F$, which can be seen by following the derivations in Section 2.8. This will not be shown rigorously here. The usefulness of this form of the free energy (B.3) is that it allows the partition function, Eq. (2.78) in Section 2.8 to be factored the way it is.

The validity of the second virial approximation for flexible spherocylinders is difficult to assess but the virial coefficients for rigid spherocylinders have been looked at. From Section 2.6 it was seen that to evaluate the two-body excluded volume, and hence the second virial coefficient, the molecular arrangements must be considered. In the case of Section 2.6 this was given by the relative orientation, $\gamma$, of two rods. Therefore it is expected that the virial coefficients depend on whether the system is in the I, N or SmA phase. The relative virial coefficients, $B_n/B_2^{n-1}$, are used as a measure of the importance of each viral term in the free energy, which can be written as:

$$\frac{\beta F}{n} = \frac{\beta F_{\text{ideal}}}{n} + B_2\rho + \frac{B_3}{2B_2^2}(B_2\rho)^2 + \frac{B_4}{3B_2^3}(B_2\rho)^3 + ... \quad \text{(B.8)}$$

Starting with the I phase, Table B.1 shows the relative virial coefficients $B_3/B_2^2$, $B_4/B_2^3$ and $B_3/B_2^4$ for a wide range of spherocylinder lengths, calculated by Frenkel [78] using the method of Ree and Hoover [85]. Indeed for large enough $L/D$, the second virial approximation becomes more and more exact. However for low enough $L/D$ this is definitely not the case.
Table B.1: Virial coefficients of hard Spherocylinders in the I phase. Taken from [78, 83, 84].

\[
\begin{array}{cccc}
L/D & B_3/B_2^2 & B_4/B_2^3 & B_5/B_2^4 \\
0 & 0.625 & 0.28695 & 0.11025 \\
5 & 0.4194 (3) & 0.0528 (4) & 0.0110 (7) \\
10 & 0.3133 (3) & -0.0157 (4) & 0.0229 (7) \\
10^2 & 0.0698 (1) & -0.0291 (2) & 0.0325 (5) \\
10^3 & 0.01060 (5) & -0.00450 (7) & 0.0051 (2) \\
10^4 & 0.00145 (2) & -0.00050 (2) & 0.00061 (6) \\
10^5 & 0.000172 (7) & -0.000049 (7) & 0.00003 (1) \\
10^6 & 0.000021 (2) & -0.000005 (2) & 0.000011 (6) \\
\end{array}
\]

In the N phase the behaviour of the virial coefficients for spherocylinders with respect to the nematic order parameter, \(O_{\text{nem}}\), has been looked at by Velasco et al. [86] and shown in Fig. B.1. The magnitudes of the relative virial coefficients increase with increasing \(O_{\text{nem}}\), indicating that the second virial approximation is less valid toward the N-SmA transition than it is at the I-N transition. This can be understood by an argument [86], which considers a system of perfectly oriented hard ellipsoids. This system scales exactly to a corresponding fluid of hard spheres, whose virial expansion is known to have a poor convergence [87, 88].

To my knowledge, the higher virial coefficients for the SmA phase have not been examined as extensively as for the I and N phase. But as Table B.1 and Fig B.1 show, it has low accuracy for the isotropic and nematic ordering for \(L/D\) less than \(\sim 100\), necessitating extensions beyond this.
Figure B.1: Dependence of the scaled third, fourth and fifth virial coefficients $B_3/B_2^2$, $B_4/B_3^2$ and $B_5/B_4^2$ on the nematic order parameter for three different elongations: (a) $L/D = 10$, (b) $L/D = 10^2$, (c) $L/D = 10^3$. Full line, third virial coefficient; dashed line, fourth virial coefficient; and dotted line, fifth virial coefficient. From [86].
Appendix C

Notes on The Order Parameters

C.1 The order parameters as given by McMillan

The following development is essentially that of McMillan [63, 89] but taken from Chapter 7 of the review by Priestley [8].

The distribution for the SmA phase is written in terms of the following spectral decomposition:

\[ \phi(z, u) = \sum \sum_{i \text{ (even)}}^{\infty} d_{i,j} Y_{i,0}(u) \cos \left( \frac{2\pi j z}{\lambda} \right), \]  

(C.1)

where for this phase only the even Fourier coefficients are needed. The standard spherical harmonics, \( Y_{l,m} \), are defined by [90]:

\[ Y_{l,m}(u) = (-i)^m \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P^m_l(\cos \theta) e^{im\phi} \]  

(C.2)

where \( i \) is the imaginary unit and \( P^m_l(x) \) is the associated Legendre polynomial:

\[ P^m_l(x) = (-1)^m (1 - x^2)^{m/2} \frac{d^m}{dx^m}(P_l(x)) \]  

(C.3)
and \( P_l(x) \) is the Legendre polynomial, that may be expressed as:

\[
P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} \left( (x^2 - 1)^l \right). \tag{C.4}
\]

For the SmA phase, specializing to even \( l \) and \( m = 0 \):

\[
Y_{l,0}(u) = \sqrt{\frac{(2l + 1)}{4\pi}} P_l(\cos \theta). \tag{C.5}
\]

\( Y_{l,m}(u) \) also satisfy the orthogonality relations:

\[
\int du \, Y_{l,m}(u) Y_{l',m'}(u) = \delta_{l,m} \delta_{l',m'}. \tag{C.6}
\]

The Fourier series basis functions also satisfy the following orthogonality relations:

\[
\frac{1}{\lambda} \int_0^\lambda dz \cos \left( \frac{2\pi iz}{\lambda} \right) \cos \left( \frac{2\pi i'z}{\lambda} \right) = 1, \quad i = i' = 0 \quad \Rightarrow \quad \delta_{i,i'} = 1
\]

\[
= \frac{1}{2}, \quad i = i' \geq 1
\]

\[
= 0, \quad i \neq i'. \tag{C.7}
\]

The coefficients \( d_{i,j} \) are found by multiplying both sides of Eq. (C.1) by \( Y_{l',0}(u) \) \( \cos \left( \frac{2\pi i'z}{\lambda} \right) \), integrating and using the definition of averages:

\[
\langle X \rangle = \frac{1}{\lambda} \int_0^\lambda dz \int du \, X(z,u). \tag{C.8}
\]

The \( d_{i,j} \)'s are typically designated to be proportional to the various order parameters.
These terms are

\[ d_{0,0} = \frac{1}{4\pi} \]

\[ d_{0,j} = 2\langle \cos (2\pi jz/\lambda) \rangle, \quad j \geq 1 \]  

\[ d_{i,0} = \langle Y_{i,0} (u) \rangle, \quad i \geq 2 \]  

\[ d_{i,j} = 2\langle Y_{i,0} (u) \cos (2\pi jz/\lambda) \rangle, \quad i \geq 2, \quad j \geq 1, \]  

where the result for \( d_{0,0} \) comes from the fact that \( Y_{0,0} = 1/\sqrt{4\pi} \). In addition to the purely orientational and translational order parameters, \( \langle Y_{i,0} (u) \rangle \) and \( \langle \cos (2\pi jz/\lambda) \rangle \), there are also the mixed order parameters \( \langle Y_{i,0} (u) \cos (2\pi jz/\lambda) \rangle \). These describe the correlation, or coupling, between the degrees of orientational order and translational order. In much of the published theories \([8, 63, 89]\) the three lowest order parameters are given the special symbols \( \eta \equiv \langle P_2 (\cos \theta) \rangle, \tau \equiv \langle \cos (2\pi jz/\lambda) \rangle \) and \( \sigma \equiv \langle P_2 (\cos \theta) \cos (2\pi jz/\lambda) \rangle \). This convention is not used in this thesis, however. The order parameter \( \tau \), proportional to the lowest Fourier amplitude, is often used to describe smectic ordering but in this work a different quantity is used (see Appendix C.2). The mixed order parameter, \( \sigma \), is not considered here.

From Eq. (C.9), this Thesis makes use of the lowest non-vanishing, non-trivial spherical harmonic amplitude, \( d_{2,0} \), to denote the nematic order parameter. The symbol \( \eta \) is not used, as this is already used for the packing fraction. The nematic order parameter is as
follows:

\[ O_{\text{nem}} = \sqrt{\frac{4\pi}{5}} \langle Y_{2,0}(u) \rangle \]
\[ = \langle P_2(\cos \theta) \rangle, \text{ nematic order parameter.} \]  

(C.10)

C.2 The smectic order parameter used by Hidalgo et al.

In the work by Hidalgo et al. [2] the smectic order parameter, \( O_{\text{smA}} \), for the one-dimensional SmA phase is defined as

\[ O_{\text{smA}} = \left[ \frac{1}{\lambda} \int_0^\lambda dz \left( \sqrt{4\pi \phi_0(z)} - 1 \right)^2 \right]^{\frac{1}{2}}. \]  

(C.11)

In the above, \( \lambda \) is the smectic period, \( z \) is the one-dimensional position and \( \phi_0(z) \) is the isotropic contribution to the orientation dependence, \( \mathbf{u} \), in the spherical harmonic expansion of \( \phi(z, \mathbf{u}) \) [90]:

\[ \phi(z, \mathbf{u}) = \sum_{l \text{ (even)}} \phi_l(z) Y_{l,0}(\mathbf{u}). \]  

(C.12)

For the SmA phase, only the uniaxial case is considered where \( l \) is even and \( m = 0 \). Therefore, the subscript \( m \) is suppressed on \( \phi_l \). It is noted that in Eq. (C.11), \( \sqrt{4\pi \phi_0(z)} = \int d\mathbf{u} \phi(z, \mathbf{u}) \), so \( O_{\text{smA}} \) can be replaced by the following definition which is that used in this thesis:

\[ O_{\text{smA}} = \left[ \frac{1}{\lambda} \int_0^\lambda dz \left( \int d\mathbf{u} \phi(z, \mathbf{u}) - 1 \right)^2 \right]^{\frac{1}{2}}, \text{ Smectic order parameter.} \]  

(C.13)

\( O_{\text{smA}} \) as defined in Eq. (C.13) relates to the purely translational spectral coefficients,
$d_{0,i}$ from Appendix C.1, of $\phi(z, u)$. The spectral decomposition (C.1) of $\phi(z, u)$ is rewritten in a more compact form:

$$\phi(z, u) = \sum_{i \text{ (even)}} \sum_{j} d_{i,j} Y_{i,0}(u) f_j(z)$$

(C.14)

where

$$f_i = \cos\left(\frac{2\pi i z}{\lambda}\right).$$

(C.15)

Substituting this to the innermost bracketed term in Eq. (C.11) or (C.13) gives:

$$\sqrt{4\pi} \phi_0(z) - 1 = \int d\mathbf{u} \phi(z, u) - 1 = \sqrt{4\pi} \sum_{i=0}^{\infty} d_{0,i} f_i(z) - 1,$$

(C.16)

where the fact that $Y_{0,0} = 1/\sqrt{4\pi}$ is used. Squaring the above will give:

$$\left[\int d\mathbf{u} \phi(z, u) - 1\right]^2 = \sum_{i \geq 0} 4\pi d_{0,i}^2 f_i^2(z) + \sum_{i \neq j} 4\pi d_{0,i} d_{0,j} f_i(z) f_j(z) - 2\sqrt{4\pi} \sum_{i} d_{0,i} f_i(z) + 1.$$

(C.17)

To perform the positional average, $\frac{1}{\lambda} \int_0^\lambda dz$ on Eq. (C.17) each term will be looked at, individually. The terms $4\pi d_{0,i}^2 f_i^2(z)$ are handled by using the orthogonality relations given in Eq. (C.7), which will give

$$\frac{1}{\lambda} \int_0^\lambda dz 4\pi \sum_{i \geq 0} d_{0,i}^2 f_i^2(z) = 1 + 2\pi \sum_{i \geq 1} d_{0,i}^2.$$

(C.18)

The unity term corresponding to $i = 0$ comes from the relation $d_{0,0} = 1/\sqrt{4\pi}$, from Eq. (C.9). The terms $4\pi d_{0,i} d_{0,j} f_i(z) f_j(z)$ with $i \neq j$ will give zero contribution, since they are orthogonal functions. The terms $-2\sqrt{4\pi} \sum_i d_{0,i} f_i(z)$ will all vanish as well, except for the
$i = 0$ term, which gives:

$$- 2 \frac{1}{\lambda} \int_0^\lambda dz \sqrt{4\pi} \sum_{i \geq 0} d_{0,i} f_i(z) = -2,$$  \hfill (C.19)

and leads to the following simple expression

$$\frac{1}{\lambda} \int_0^\lambda dz \left[ \sqrt{4\pi} \phi_0(z) - 1 \right]^2 = 1 + 2\pi \sum_{i \geq 1} d_{0,i}^2 - 2 + 1$$  \hfill (C.20)

$$= 2\pi \sum_{i \geq 1} d_{0,i}^2.$$

Therefore the smectic order parameter can be written as:

$$O_{smA} = \sqrt{2\pi} \left[ \sum_{i \geq 1} d_{0,i}^2 \right]^{\frac{1}{2}}.$$  \hfill (C.21)

This result, which uses information from all the non-trivial purely translational spectral coefficients, is different from Appendix C.1, which uses only the lowest purely translational spectral coefficient.
Appendix D

Mixing Method for The Fields

In section 2.9.1 the importance of mixing the external fields from previous iterations for converging the solution is discussed. This procedure is discussed here. First the input external field at a given iteration, $i$, is written as a vector instead of scalar, $w_{in,i}$. Each component of the vector, $w_{in,i}^j$, corresponds to a given value of $r$ and $u$. The output external field at iteration $i$ is $w_{out,i}$. Next, the residual vector is defined as

$$R_i = w_{out,i} - w_{in,i}. \quad (D.1)$$

The input external field for the next iteration, $i + 1$, is given by

$$w_{in,i+1} = w_{in,i} + \beta_i R_i \quad (D.2)$$

where $\beta_i$ is the so-called mixing parameter. The field $w_{in,i}$ is calculated iteratively until the root mean square of the difference in the components, $w_{in,i+1}^j - w_{in,i}^j$, is below a set tolerance, $\epsilon$. 

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A constant value for $\beta_i$ is used, typically set to $\beta_i = 0.05$, which seems to work as well as other choices. The work by Duch [91] also uses constant $\beta$ for SCFT of the semiflexible chain, however a variable $\beta_i$ is used in other aspects of that work. For variable $\beta_i$ the following recipe is used

$$\beta_i = \sqrt{\frac{\sum_j (w_{in,i}^j - w_{in,i-1}^j)^2}{\sum_j (R_i^j - R_{i-1}^j)^2}}. \quad (D.3)$$

If $\beta_i$ as calculated above falls outside a preset interval $[\beta_{\text{min}}, \beta_{\text{max}}]$, it is set to the closest boundary of that interval. The above recipe is similar to a more general scheme known as Anderson mixing, in which $\beta_i$ can be calculated for the last $n$ steps [92, 93]. The tolerance, $\epsilon$ used in this work is $10^{-4}$. For relatively low $L/D$ a smaller tolerance can be used, say $\epsilon \sim 10^{-5}$, but for larger $L/D$, greater than around 9 or 10, the iteration process starts to take longer. Therefore $\epsilon = 10^{-4}$ was used throughout for the N-SmA transition.

The number of iterations depends on how much the parameters for the input guess solution differ from those of the calculation. The nematic solutions are generally very quick to obtain. However for the SmA phase a single calculation takes typically from a few minutes to an hour or more if close to the N-SmA transition for a change in packing fraction $\eta$, of 0.0001. Higher $L/D$ generally takes longer too.

The mixing routine was provided by Raul Cruz Hidalgo, one of the authors of Ref. [2].
References


