TOPICAL REVIEW

Understanding the properties of liquid-crystalline polymers by computational modeling

Kurt Binder¹, Sergei A Egorov², Andrey Milchev³ and Arash Nikoubashman⁴

1 Institute of Physics, Johannes Gutenberg University Mainz, Staudingerweg 7, 55128 Mainz, Germany
2 Department of Chemistry, University of Virginia, Charlottesville, VA 22901, United States of America
3 Institute for Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
E-mail: anikouba@uni-mainz.de

Keywords: semiflexible polymers, liquid crystals, nematic liquids, computer simulations, density functional theory, lyotropic solutions

Abstract

A topical review of recent theoretical work on the properties of lyotropic solutions and melts containing semiflexible polymers in thermal equilibrium is given, with a focus on the liquid-crystalline and smectic order of these systems in the bulk and under confinement. Starting with a discussion of single chain properties in terms of the Kratky-Porod worm-like chain model and its limitations, extensions along the lines of Onsager’s theory for the isotropic-nematic transition of solutions of hard rods are briefly reviewed. This discussion is followed by a review of recent Molecular Dynamics simulations and classical Density Functional Theory calculations. It is argued that, even in the simplest case of athermal solutions, coarse-grained polymer models must include three lengths: the contour length \( L \), the persistence length \( \ell_p \), and the effective chain thickness \( D \). The discussion is then extended to semiflexible polymers in solutions with thermally driven transitions, where the isotropic-isotropic phase separation competes with the isotropic-nematic transition. Basic physical phenomena due to confinement of these systems in thin films with either repulsive or attractive walls are briefly reviewed, and conditions for the formation of strongly ordered surface layers are identified.

1. Introduction

Semiflexible polymers are of great interest as constituents of materials in a variety of contexts: due to their liquid-crystalline phases they are of basic interest for applications such as displays and other devices [1–5]. While various other materials formed from small anisotropic molecules are also available for these purposes [4, 5], polymeric liquid crystals have various practical advantages, such as controlling some of their Frank elastic constants [4–6] by suitably chosen molecular weight, and also their production may be cheaper etc. Other applications of liquid-crystalline polymers include the production of fibers with ultrahigh strength [2]. Finally, we state that liquid crystallinity of polymers may also play a role in biological contexts [7, 8], but this aspect and other applications are beyond the scope of the present topical review.

We focus here on the understanding of phase diagrams of semiflexible polymers in lyotropic solutions and in corresponding melts, and discuss the properties of such systems both in the bulk and confinement, from the perspective of theory and computer simulation. In principle, the theoretical physics of materials aims to explain the structure-property relationships, starting with the chemical structure [9]. However, for liquid-crystalline polymers, such an approach building a quantitative bridge from the chemistry to macroscopic properties is still in its infancy. Unlike the simulation approaches for liquid-crystalline materials formed from small molecules [10, 11], a chemically realistic model development shall not be dealt with here. Disregarding side-chain liquid-crystalline polymers [12] completely, we focus on a coarse-grained description of main-chain liquid-crystalline polymers in terms of mesoscopic parameters, such as their diameter \( D \), persistence length \( \ell_p \), and contour length \( L \). Furthermore, solvent molecules are not included explicitly in the models discussed here, to facilitate the theoretical description and to expedite the simulations. With such an implicit description, the solvent quality can be controlled by the reduced strength
deals with phase diagrams and properties of bulk homogeneous phases of discusses a few examples where phase separation into coexisting describes inhomogeneities in the structure of we have summarized some frequently used symbols and their contains a brief summary. provides schematic illustrations of some of the models that have been used for the range from 1 to 2 nm (apart from biopolymers such as F-actin), that the lack of small-angle bending deformations implied by such models means that physics, which is that the study of topological defects in nematics through numerical methods based on approaches for coarse-grained models starting from the molecular scale. Numerical modeling on outset we would like to point out that by 'Computational Modeling' in this review we mean numerical methods such as Self-Consistent Field Theory \[\text{SCT}\] and Density Functional Theory \[\text{DFT}\] \[\text{a}^{25}\text{–}45\]. At the outset we would like to point out that by 'Computational Modeling’ in this review we mean numerical approaches for coarse-grained models starting from the molecular scale. Numerical modeling on macroscopic scales, such as the study of topological defects in nematics through numerical methods based on the Landau–de Gennes free energy density \[\text{b}^{22}\], lies beyond its scope. Also, simulations addressing phenomena on mesoscopic scales, where molecular information is introduced in a field-theoretic approach \[\text{a}^{23,24}\], are out of consideration here. Such hybrid approaches promise great potential for the future, but they have been applied only occasionally in the contexts discussed here. Any simplified molecular-level model of the considered semiflexible polymers must allow for two length scales that are both large and independent from each other, i.e. the persistence length \(\ell_p\) and the contour length \(L\). Figure 1 provides schematic illustrations of some of the models that have been used for the simulation of semiflexible polymers. In Table 2 we have summarized some frequently used symbols and their physical meaning for improving readability.

2. Models and theoretical methods

The properties of semiflexible polymers can be studied using a wide range of numerical techniques, like Monte Carlo (MC) or Molecular Dynamics (MD) simulation methods \[\text{b}^{17,18}\] as well as analytic theoretical methods such as Self-Consistent Field Theory \[\text{b}^{19}\] and Density Functional Theory (DFT) \[\text{b}^{20,21}\]. In section 2, we shall briefly characterize models and methods, on which the results reviewed in the later sections are based. Section 3 deals with phase diagrams and properties of bulk homogeneous phases of athermal systems, while section 4 discusses a few examples where phase separation into coexisting phases occurs in solvents of varying quality. Section 5 describes inhomogeneities in the structure of liquid-crystalline polymeric systems arising from confinement by planar walls, considering both purely repulsive and attractive surfaces. Finally, section 6 contains a brief summary.

2.1. Lattice models

In early work, for simplicity and computational efficiency, lattice models such as the self-avoiding walk on square and simple cubic lattices (see figure 1(a)) have been very popular (e.g. references \[\text{b}^{25–45}\]). Chain stiffness was typically introduced through a bond-bending potential that reduces to some extent the number of 90° kinks on the lattice. The attractive feature of these particularly simple models is that contour lengths up to \(L = 80000\) lattice spacings were accessible for simulations of single chains. However, it must be noted that the lack of small-angle bending deformations implied by such models means that physics, which is

| Polymer                          | Solvent          | \(\ell_p\) (nm) | \(D\) (nm) |
|---------------------------------|------------------|----------------|----------|
| F-actin                         | water            | 17,000         | 8        |
| schizophyllan                   | water            | 200            | 1.52–2.6 |
| poly (γ-benzyl-L-glutamate)[PBLG]| dimethylformamide| 150            | 1–1.7    |
| ds-DNA                          | water + salt     | 50             | 2–20     |
| poly (n-hexyl isocyanate)[PHIC] | toluene          | 37             | 1.15–1.6 |
| poly (n-hexyl isocyanate)[PHIC] | dichloromethane  | 21             | 0.95–1.25|
| poly (p-phenylene terephthalimde)| sulfuric acid    | 18             | 0.51–0.60|
| poly (yne)-Pr [PYPt]            | trichloroethane  | 13             | 1.08–1.2 |
| (hydroxypropyl)cellulose [HPC] | dimethylacetamide| 6.5            | 1.13–1.28|
| (acetoxypropyl)cellulose [APC]  | dibutylphthalate | 5.9            | 1.19     |
| cellulose triacetate             | trifluoroacetic acid | 5.3      | 0.95     |

\(a\) Spread of numbers refers to estimations using different experimental techniques.

\(b\) The value of \(D\) depends strongly on the salt concentration. The smallest value is the limiting value for a saturated solution, the largest refers to 5 mM salt, as quoted by Reisner et al \[\text{16}\].

\(\epsilon/(k_B T)\) of some effective potential acting between the coarse-grained repeat units, with Boltzmann’s constant \(k_B\) and temperature \(T\). This implicit treatment of solvent effects is possible, since the dynamic response of the considered systems (viscosity, behavior under shear deformation, etc) is completely disregarded here, although we are well aware that these aspects are important for the processing of such materials. Finally, we consider only polymers with linear chemical architecture, disregarding semiflexible ring polymers \[\text{13}\], as well as branched polymers such as bottle-brush polymers, dendronized polymers, etc. To give an overview over the wide variety of naturally occurring and synthetic semiflexible polymers, table 1 provides examples of estimates for \(\ell_p\) and \(D\) (taken from references \[\text{14, 15}\]). While \(D\) is typically in the range from 1 to 2 nm (apart from biopolymers such as F-actin), \(\ell_p\) varies over a wide range.

\[\text{Table 1. Persistence lengths } \ell_p\text{ and effective diameters } D\text{ of selected semiflexible polymers in good solvents.}\]
important under certain circumstances, is missed. For instance, chains confined by walls \([43, 44]\) do not exhibit fluctuations on the scale of the deflection length \([46–49]\), but can only exhibit propagation along straight lines over distances of the order of \(\ell_p\) or larger \([43]\). Similarly, the lattice model predicts that adsorption of stiff polymers at planar surfaces occurs already for very small adsorption energy of order \(e_{\text{ads}}^{\text{crit}} / (k_B T) \propto \ell_p^{-1}\) \([26, 32, 45]\), while treatments based on the Kratky-Porod (KP) \([50]\) worm-like chain model yield \(e_{\text{ads}}^{\text{crit}} / (k_B T) \propto \ell_p^{1/3}\) instead \([51–53]\).

While the majority of previous studies focused on the single chain behavior \([26, 30–32, 34–45]\), it is clear that in multi-chain systems even worse lattice artifacts must occur. For example, the director of nematic order is constrained to be oriented along one of the lattice axes. Thus the character of this order is of the Ising type \([54]\) in \(d = 2\) dimensions or of 3-state Potts type \([55]\) in \(d = 3\). Also generalizations of this lattice model where smaller bond angles are admitted, such as the well-known bond fluctuation model \([56, 57]\) augmented by a bond-angle potential \([37, 58–62]\), still suffer from the same unphysical description of the nematic phase. Despite these inherent limitations, such lattice models have some attractive features: ‘layering’ of effective monomers near hard walls is qualitatively described \([60–62]\); large system sizes (such as films bounded by hard walls at distances \(L_z = 200\) to \(500\) lattice spacings apart, with lateral linear dimensions up to \(150\) lattice spacings) allow a rather accurate estimation of the phase diagram for ‘capillary nematization’ \([63]\) for such liquid crystal forming polymers \([60–62]\).

### 2.2. Tangent hard spheres and related models

Alternative approaches that avoid the artifacts of lattice models and are also well-suited for both analytic methods and for MC simulations are based on hard particles in the continuum. Just as a system of hard spheres is a standard model for dense fluids \([64, 65]\), small molecule fluids forming nematic and smectic phases can be modeled by systems of hard ellipsoids or hard spherocylinders, etc \([66, 67]\). One can proceed from such models of nematogens to models of liquid-crystalline polymers in several ways, e.g. tangent hard spheres with a bond bending potential \([68]\), or joining hard spherocylinders with an elastic bending potential \([69]\). In their pioneering work \([69]\) (we shall discuss some of their results in section 3) Dijkstra and Frenkel used spherocylinders of length \(l_p\) and diameter \(D\) with aspect ratio of \(l_p/D = 4\) and a bending energy

\[
U_{\text{bend}}(\theta_{l_p}) = \frac{1}{2} C l_p \theta_{l_p}^2 ,
\]

where \(\theta_{l_p}\) is the angle between the unit vectors along the axes of subsequent spherocylindrical segments. Here \(C\) is an elastic bending constant which can be chosen very large so that the system approaches the hard rod limit. However, the crossover to the behavior of fully flexible polymers, that could be easily studied with the generalized self-avoiding walk model \([38, 39]\), is less conveniently addressed with this model. A two-dimensional variant of this model was studied in the range of persistence lengths \(\ell_p = C / (k_B T)\) from 2 to 120 \(\text{(choosing } l_p = 1 \text{ as the unit of length)}\) \([70]\), providing evidence for a continuous transition from the isotropic phase to quasi long-range orientational order.

### 2.3. Onsager theory and its extensions

For analytical methods, such as DFT, the tangent hard sphere model is a convenient starting point, and follows closely the classical work of Onsager describing the isotropic-nematic transition in solutions of long
thin hard rods [71] (which is a reasonable model for, e.g., solutions of the tobacco mosaic virus). For homogeneous systems, the molecular density \( \rho_{\text{mol}}(r, \omega) \) is written as a product of the molecular orientational distribution function, \( f(\omega) \), and the spatial density distribution, \( \rho_{\text{mol}} = N^*/V \). Here, \( \omega \) is an abbreviation for the two polar angles \((\theta, \phi)\) characterizing the orientation of a molecule, and \( N^* \) is the number of rods (of length \( L \) and diameter \( D \)) in a system with volume \( V \). Note that this ansatz disregards any non-uniformity of the particle density (unlike DFT of simple liquids [20]), but rather considers only the non-uniformity of molecular orientations. In the isotropic phase, \( f(\omega) \) is independent of the molecular orientation, and is simply given by \( f_{\text{iso}} = 1/(4\pi) \) in \( d = 3 \). The Helmholtz free energy per molecule can then be written as the sum of ideal and excess terms:

\[
F_{\text{id}}/(Nk_B T) = \ln(\rho_{\text{mol}}) - 1 + \int d\omega f(\omega) \ln[4\pi f(\omega)],
\]

(2)

\[
F_{\text{exc}}/(Nk_B T) = \rho_{\text{mol}} \int d\omega \int d\omega' f(\omega)f(\omega')V_{\text{exc}}(\omega, \omega'),
\]

(3)

where \( V_{\text{exc}}(\omega, \omega') \) is the excluded volume for two rods with orientations \( \omega \) and \( \omega' \), respectively, when only the second virial coefficient is taken into account. Noting that \( V_{\text{exc}} \propto DL^2 \sin \gamma \), where \( \gamma \) is the angle between them, one finds that the excess term, equation (3), scales proportionally to \( \rho_{\text{mol}}L^2D \) (or \( \rho D^2L \), respectively, when we consider a rod as a straight chain of \( N = LD \) tangent spheres of diameter \( D \), at monomer density \( \rho = N^*/V \)). Since \( F_{\text{id}}/(Nk_B T) \) in equation (2) is of order unity in the isotropic phase, the onset of the nematic order occurs when the excess term becomes of order unity as well, i.e. for \( \rho D^3 \propto D/L \). Thus, for long enough rods the transition occurs at a very small density, and hence the approximations made are well justified.

Note that the isotropic-nematic transition must be of first order due to general symmetry arguments based on Landau theory [6], which is born out by explicit calculation [71, 72]. So in terms of the dimensionless variable \( e = (\pi/4)\ell_p D^2 \rho \), one finds that the isotropic phase is stable for \( e < c_i = (\pi/4)\ell_p D^2 \rho_i \), while the nematic phase is stable for \( e > c_n \), and the region \( c_i < e < c_n \) is a two-phase coexistence region. We have replaced here the contour length \( L \) by \( \ell_p \) (with the understanding that \( \ell_p \sim L \) for strictly rigid rods), because then the variable \( c \) defined here can be used for the case of solutions of semiflexible polymer as it stands. Unfortunately, one can not compute either \( c_i, c_n \) or the distribution function in the nematic phase, \( f_n(\omega) \), exactly by analytical methods, but must resort to numerical methods instead [72]. However, a plausible approximation for \( f_n(\omega) \) [73], that is also useful for describing nematic phases of semiflexible polymers, is

\[
f_n(\omega) \propto \exp \left( -\frac{\alpha \theta^2}{2} \right),
\]

(4)

where \( \theta \) is the angle between a rod and the ‘director’ [6] that characterizes the ordering in the nematic phase. The parameter \( \alpha \) controls the amount of bond orientational fluctuations in the liquid crystal. Minimizing the total free energy with respect to \( \alpha \) yields

\[
\alpha \approx 4e^{2/3}/\pi^{1/3} = (4\pi)^{1/3}(D^2\ell_p D^2)^{2/3}.
\]

(5)
One can then show that [72]
\[ c_i \approx 3.451, c_n \approx 5.122, S_n \approx 0.91, \]
where \( S_n \) being the nematic order parameter at \( c = c_n \). Here we recall that orientational order is described by the traceless tensor
\[ \mathbf{Q}^{\alpha\beta} = \frac{1}{2} \left( 3 \left( \mathbf{u}_i^\alpha \mathbf{u}_i^\beta \right) - \delta^{\alpha\beta} \right), \alpha, \beta = x, y, z, \]
where the index \( i \) labels the rods which are aligned along unit vectors \( \mathbf{u}_i \). In the nematic phase, the three eigenvalues of \( \mathbf{Q}^{\alpha\beta} \) are \( \Lambda_1 = S, \Lambda_2 = \Lambda_3 = -S/2 \), respectively.

This approach describing the isotropic-nematic transition for an athermal solution of very thin long hard rods has been generalized by Khokhlov and Semenov [74–76], Odijk [73], and Chen [77] to semiflexible polymers, which were described by the KP worm-like chain model [50]. In the continuum version of this model (see figure 1(c)), a semiflexible polymer is described by a space curve \( \mathbf{r}(s) \) where \( s \) is a coordinate along this curve, from one chain end at \( s = 0 \) to the other chain end at \( s = L \). The Hamiltonian of this model is
\[ H_{\text{KP}} = \frac{k_B T}{2} \ell_p \int_0^L ds \left( \frac{\partial^2 \mathbf{r}(s)}{\partial s^2} \right)^2, \]
i.e. the potential energy is due to an integral of the local curvature of the polymer along the chain. From equation (8) one can show that tangent unit vectors \( \mathbf{u}(s) \) along the chain lose their orientation over the persistence length
\[ C(s) = \langle \mathbf{u}(s') \cdot \mathbf{u}(s' + s) \rangle = \exp(-s/\ell_p), \]
with bond orientational autocorrelation function, \( C(s) \). From equation (9) it is straightforward to derive the mean-square distance between monomeric units a distance \( s \) apart (note that \( \mathbf{R}(s) = \int_0^s \mathbf{u}(s' + s) ds' \mathbf{u}(s' + s) \)) as
\[ \langle \mathbf{R}^2(s) \rangle = 2\ell_p s \left[ 1 - \ell_p (1 - \exp(-s/\ell_p))/s \right]. \]

The basic idea to combine this description with Onsager’s [71] theory is to divide the chain for \( L \gg \ell_p \) into pieces of length \( \ell_p \) (in the opposite limit, \( L \ll \ell_p \), the chain molecule is rod-like anyway). So the analog of the ideal gas term, equation (2), is then an ideal gas of persistent segments, which can reorient independently of each other, \( F_{\text{id}}/(Nk_B T) \propto L/\ell_p \). The translational part is still \( \ln(\rho_{\text{mol}}) \), as in equation (2). The excess part then is the product of the density of persistent segments \( \rho_D/\ell_p \) times the number of persistent segments per chain \( N/\ell_p \) times the excluded volume between the two persistent segments, which is of order \( D^2\ell_p^2 \).

This rough order of magnitude argument (which is substantiated by explicit calculations [73–77]) yields \( F_{\text{exc}}/(Nk_B T) \propto \rho_D LD^2. \) The isotropic-nematic transition occurs when \( F_{\text{exc}} \) is of the same order as \( F_{\text{id}}^\text{mol} \), i.e. for \( \rho_D \propto (D^2\ell_p^2)^{-1} \). The explicit calculation can then describe the full crossover from the Onsager rod limit to this result in terms of a function \( f(L/\ell_p) \) as [73–77]
\[ D^3\rho_D \ell_p^2 = f(L/\ell_p), \]
with \( f(x \gg 1) = \text{const} \) and \( f(x \ll 1) \propto 1/x \).

### 2.4. Going beyond the 2nd virial coefficient

A key problem of the treatment based on the second virial coefficient is that it is expected to be accurate only for \( \ell_p/D \gg 1 \); otherwise, higher order virial coefficients come into play as well. However, there is no unique way to extend Onsager-style theory [73–77], and one can find many attempts to do this in the literature (e.g. references [14, 78, 79]). Here we shall focus on the most recent approach [80, 81], which finds support from the accompanying MD simulations (we shall describe this methodology briefly below). Egorov et al [80, 81] simply rescaled the prefactor of the excluded volume term, so that instead of \( \rho_{\text{mol}} \) in equation (3) one uses a rescaled density \( \rho_{\text{mol}} a_{\text{resc}} \). Following Parsons [82] and Lee [83], one bases the choice of \( a_{\text{resc}} \) on the Carnahan-Starling (CS) equation of state [84] of a hard sphere fluid of \( N \) unconnected spherical monomers:
\[ a_{\text{resc}}^{\text{PL}} = \frac{4 - 3\eta}{4(1 - \eta)^2}, \]
where \( \eta = \rho(\pi D^3/6) \) is the monomer packing fraction. The DFT results based on equation (12) henceforth will be termed DFT-CS. In the low density limit \( \eta \to 0 \), the Onsager-style results [77] are exactly recovered, since \( a_{\text{resc}}^{\text{PL}} \to 1 \).
One could argue that the CS equation of state is inappropriate for describing a dense polymeric fluid, since the chain connectivity is completely disregarded in $\Phi^{PL}_{exc}$. To test for potential issues of this description, Egorov et al [80, 81] proposed an alternative rescaling of the prefactor $\rho_{mol}$ in equation (3), based on the Generalized Flory Dimer (GFD) equation of state [85]. The resulting version of the DFT will be termed DFT-GFD. We emphasize that this approximation is expected to be good only for moderately stiff chains, so that we have an isotropic polymeric fluid still as the stable phase at rather high monomer densities. But one finds that this approximation does not reduce to the Onsager form in the low density limit.

A further difficulty concerns the explicit form of $V_{exc}^{\omega}(\omega, \omega')$ which is known for hard rods and also for infinitely stiff hard sphere chains (i.e. the ‘shish-kebab’ model [86]), but not for semiflexible polymers. Accordingly, Egorov et al [80, 81] used an empirical expression for $V_{exc}^{\omega}(\omega, \omega')$ due to Fynnewer and Yethiraj [87] obtained from fitting MC simulation results for two chains interacting with each other, for various choices of chain lengths and stiffnesses. Thus, the semiflexible chains can be regarded as pseudo rods with mutual excluded volume adjusted to account for the bending degrees of freedom of the chains. The order parameter $S$ resulting from these DFT calculations hence characterizes the order of the whole chains, different from the order parameter defined in equation (7) referring to individual bond vectors [88]. In view of these approximations, it is clear that the DFT results of Egorov et al [80, 81] for semiflexible polymers are much less rigorous than DFT results available for simple fluids (e.g. references [89, 90]). Nevertheless, we include those results here because their usefulness has been established by extensive comparisons with MD simulation results.

A further caveat needs to be made that equations (2)–(12) all refer to $d = 3$ dimensions only. One can formulate an Onsager-style theory for hard rods in $d = 2$ dimensions as well, but readily finds that using only the second virial coefficient never becomes self-consistent [91]. In fact, MC studies of corresponding models have revealed Kosterlitz-Thouless [92] type continuous transitions and an algebraic decay of orientational correlation functions rather than true long-range nematic order [93, 94]. An interesting aspect needs also to be noted when the KP model, equation (8), is used in $d = 2$: while in $d = 3$ there are two transverse directions to the tangent vector $\mathbf{u}(s)$, there is only a single one in $d = 2$. As a consequence, orientational correlations in $d = 2$ decay slower than in $d = 3$, and equation (9) needs to be replaced by $C(s) = \exp[-s/(2\ell_p)]$ when one keeps the meaning of $\ell_p$ as defined in $d = 3$. Then in equation (10) $\ell_p$ needs to be replaced by $2\ell_p$ throughout as well.

### 2.5. Molecular dynamics (MD) simulation methods

One of the most powerful simulation techniques for soft matter systems, and in particular polymers [17, 18, 65], is based on the numerical integration of the Newtonian equations of motion for the considered many-body systems. While for the tangent hard sphere model mentioned in section 2.2 above this technique would be difficult to apply, it can be used for the slightly modified ‘rattling spheres’ model [95]. In that model, the internal molecular motion consists of bonded atoms ‘rattling’ in their (narrow) confining potentials, with the number and tolerance of bonding constraints controlling the flexibility of the chain. In that first MD simulation of a liquid-crystal forming system of short semiflexible polymers, the three phases – isotropic, nematic, and smectic A—could be identified, at least qualitatively. In more recent work (e.g. references [80, 81, 96–102]) bead-spring models are mostly used. In the case of lyotropic solutions, the effective pair potential between the polymer beads, $U_{MM}$, is often modeled as a purely repulsive pair potential $U_R$:

$$U_R(r) = \begin{cases} U_{11}(r) + \varepsilon & \text{for } r \leq 2^{1/6}\sigma \\ 0 & \text{for } r > 2^{1/6}\sigma \end{cases} \quad (13)$$

where $r$ is the distance between two beads, and $U_{11}(r)$ is the standard Lennard-Jones (LJ) potential:

$$U_{11}(r) = 4\varepsilon \left[ (\sigma/r)^{12} - (\sigma/r)^{6} \right] \quad (14)$$

with interaction strength $\varepsilon$ and bead diameter $\sigma$, which are often chosen as the MD units of energy and length, respectively. Equation (13) holds both between bonded and non-bonded beads, and the resulting interaction describes polymers dissolved in a good solvent (recall that the solvent molecules are accounted for only implicitly).

In MD simulations, monomers are typically not bonded via rigid constraints, but rather through (harmonic) springs. Many studies [80, 81, 97, 101, 102] use the finitely extensible non-linear elastic (FENE) potential [103]

$$U_b(r) = \begin{cases} -\frac{1}{2}kr_0^2 \ln \left( 1 - \frac{r^2}{r_0^2} \right) & r \leq r_0 \\ \infty, & r > r_0 \end{cases} \quad (15)$$
with spring constant \( k = 30 \varepsilon/\sigma^2 \) and maximum bond length \( r_0 = 1.5 \sigma \), to prevent unphysical bond crossing [104, 105]. This choice for the parameters leads to an effective bond length \( \ell_p = 0.97 \sigma \approx \sigma \) between nearest neighbors along the chain. Thus, the model resembles the tangent hard sphere chain model of DFT, but with smooth rather than hard repulsive potentials. When one is interested in smectic phases at large monomer densities [98–100], it may be preferable to replace equation (15) by a simple harmonic potential

\[
U_{\text{harm}}(r) = \frac{1}{2} k'(r - \ell_b)^2
\]  

with a large spring constant \( k' \gg k_B T/\sigma^2 \), and an equilibrium bond length of \( \ell_b < \sigma \). Alternatively, one can also introduce rigid constraints to fix the distance between consecutive beads [98]. In either case, excluded volume interactions between the nearest- and/or next-nearest neighbors along the chain are typically turned off, leading to chains of strongly overlapping spheres with a smoother surface compared to a bead-spring polymer with FENE bonds. For example, in references [99, 100] a value of \( \ell_b = 0.5 \sigma \) was employed for \( U_{\text{harm}} \), while in reference [98] rigid bonds with \( \ell_b = 0.6 \sigma \) were utilized.

When one wishes to consider variable solvent quality, one may use instead of equation (13) a potential of the form

\[
U_{\text{MM}}(r) = U_b(r) + U_s(r) / T_{\text{eff}},
\]

where \( U_b(r) \) is an attractive contribution of the form [106]

\[
U_b(r) = \begin{cases} 
-\varepsilon & \text{for } r \leq 2^{1/6}\sigma \\
U_L(r) & \text{for } 2^{1/6}\sigma < r \leq r_c \\ 0 & \text{for } r > r_c
\end{cases}
\]  

with cutoff radius \( r_c \). The parameter \( T_{\text{eff}} \) controls the effective temperature of the system (or equivalently the quality of the implicit solvent). The advantage of varying \( T_{\text{eff}} \) over the thermodynamic temperature, \( T \), is that \( T_{\text{eff}} \) only affects the strength of the attractive monomer-monomer interaction, \( U_s \), while leaving the strength of the bond and bending interactions (and thus \( \ell_p \)) unchanged. This model then leads to phase separation into a polymer-rich and a solvent-rich phase, both in the case of fully flexible polymers, and when a bond-bending potential is added to describe stiff chains [106].

A standard choice for this bond-bending potential is [80, 81, 97, 101, 102]

\[
U_{\text{bend}}(\theta_{ijk}) = \varepsilon_b [1 - \cos(\theta_{ijk})],
\]

where \( \varepsilon_b \) controls the chain stiffness, and \( \theta_{ijk} \) is the angle between two subsequent bond vectors, \( \mathbf{a}_i = \mathbf{r}_j - \mathbf{r}_i \) and \( \mathbf{a}_j = \mathbf{r}_k - \mathbf{r}_j \), with \( \mathbf{r}_i, \mathbf{r}_j, \) and \( \mathbf{r}_k \) indicating the positions of the three subsequent beads of the chain (see figure 1(d)). The bending potential \( U_{\text{bend}}(\theta_{ijk}) \) is minimized for an angle of \( \theta_{ijk} = 0 \), which corresponds to the three monomers \( i, j, \) and \( k \) lying on a straight line. For sufficiently large \( \varepsilon_b \gg k_B T \), this potential is approximately harmonic in \( \theta_{ijk} \), i.e., \( U_{\text{bend}}(\theta_{ijk}) \approx \varepsilon_b \theta_{ijk}^2/2 \), similar to equation (1). However, equation (18) is preferred when one wishes to study the crossover to fully flexible chains where large bond angles (up to almost \( \theta_{ijk} \approx \pi \)) can occur. When the potential \( U_{\text{MM}}(r) \) is only applied to nearest neighbors along the chain, the excluded volume interaction between the beads is essentially shut off, and the resulting model can be viewed as a discretization of the KP model (equation (8)) when \( \varepsilon_b \) is large. Such discrete versions of the KP model have been considered in the context of the adsorption of single semiflexible chains [107], and related somewhat different models have been studied in this context as well (e.g., references [108–110]). An estimate of the persistence length, \( \ell_p \), can then be obtained from

\[
\ell_p / \ell_b = -1 / \ln \left( \cos \theta_{ijk} \right) \approx 2 / \left( \theta_{ijk}^2 \right).
\]

For \( \kappa \equiv \varepsilon_p/(k_B T) \gtrsim 2 \), the expression for \( \ell_p \) can be approximated by \( \ell_p / \ell_b \approx \kappa \) in \( d = 3 \) dimensions. For \( d = 2 \), the persistence length \( \ell_p \) (computed from equation (19)) would be twice as large. As a caveat, we mention that chains adsorbed on a surface still retain some three-dimensional character [107, 111]. In that case, \( \ell_p / \ell_b = \kappa \) still holds for nearest neighbor bonds, and only when larger distances \( s \) along the chain are considered, a crossover of the effective persistence length, \( \ell_{p,\text{eff}} \), from \( \ell_p \) to \( 2\ell_p \) can be observed with increasing \( s \) [107, 111], provided that \( \kappa > 1 \) so that excluded volume for the considered distances \( s \) does not yet matter.

If not stated otherwise explicitly, the parameters \( \varepsilon \) and \( \sigma \) of equation (13) have been chosen as the MD units of energy and length, respectively. Further, all simulations have been conducted at \( T = 1 \) unless stated otherwise. With monomer (unit) mass, \( m \), we define \( T_{\text{MD}} = \sqrt{m \sigma^2 / \varepsilon} \) as the intrinsic MD unit of time. As a final note, we emphasize that we consider here cases where the bond length, \( \ell_b \), and the effective thickness of the cylindrical worm-like polymer (\( D \approx \sigma \) in our case) are of the same order. When one considers worm-like chains with a complicated chemical architecture, such as bottlebrush polymers [112–114] or dendronized polymers [115–117], also the case \( D \approx \ell_p \gg \ell_b \) can occur: these polymers then behave like coarse-grained...
fully flexible polymers on length scales exceeding \(\ell_p\), while equation (9) can apply for \(s \ll \ell_p\) [117]. Thus, a very rich and diverse physical behavior can be captured even in the framework of the simple coarse-grained model description via equations (13)–(18) by appropriate choice of parameters.

2.6. Monte Carlo (MC) simulation methods

When one considers the properties of single chains, often specialized Monte Carlo (MC) algorithms are the method of choice, as they allow for highly efficient moves that generate trial configurations within the desired statistical mechanics ensemble [17, 18]. MC methods have been routinely employed for reliably estimating the equilibrium properties of very long chains, e.g. the data shown in figure 2(c) was obtained in this way. For systems containing many chains, it depends on the details of the system one wishes to study and on the conditions of interest, whether MC or MD methods are preferable.

MC simulations for semidilute solutions or melts of long semiflexible polymers are possible if the standard MC move, where small random displacements of randomly chosen monomers are attempted, is complemented by the so-called ‘slithering snake’ move. Here, one randomly chooses an end monomer of a randomly chosen chain, cuts it off, and attempts a transfer to the opposite end of the same chain, where it is added if the Metropolis test [17, 18] is successfully passed. To obtain a reasonable acceptance rate, it is advisable to choose the new bond length and bond angle by the force bias algorithm [97]. A similar method has been applied recently to a model with a soft monomeric repulsion [118, 119], for studying the elastic constants of a melt of semiflexible polymers.

MC methods have the principle advantage that one can use the grandcanonical ensemble of statistical mechanics, where the chemical potential \(\mu\) rather than the thermodynamically conjugate variable, i.e. the particle number \(N\), is used as a control variable in the simulation. Alternatively, MC simulations can be carried out in the so-called Gibbs ensemble [120, 121], where two boxes, which can exchange both chains and volume, are simulated together to avoid the problem of finite size interfacial effects. For polymeric systems, such MC simulations involve moves where whole chains are inserted into the system or deleted from it. Such techniques are of interest when phase equilibria are studied, such as the phase separation in a dilute polymer solution under poor solvent conditions [122–124], and also for the isotropic-nematic phase transition of semiflexible polymers under good solvent conditions [68, 87]. Unfortunately, the Metropolis acceptance rate for inserting long chains is extremely small [17, 18], which limits the practicability of these techniques to only rather short chains, typically in the order of few tens of monomers. Further, no dynamical information can be extracted from traditional MC methods, thus restricting them to the analysis of static equilibrium properties.

2.7. Outlook on other models and approaches

At this point we stress that nematic order in solutions and melts of the polymers modeled by equations (13)–(18) arises only from the interplay of polymer stiffness (described by a sufficiently large persistence length \(\ell_p\)) and an isotropic bead-bead interaction, such as equation (13). There are, however, many models where anisotropic pairwise interactions are chosen, which lead to liquid-crystalline order in polymeric systems: e.g. generalizations of the Gay-Berne model [125] for particles with ellipsoidal shape have been used for a model where elongated mesogenic elements are connected to each other by flexible spacers [126]. On a more coarse-grained level (in the spirit of the Maier-Saupe [127] description), one may use a local coupling between neighboring unit vectors \(\mathbf{u}_{mn}, \mathbf{u}_{n'n}\) of neighboring chains \(n\) and \(n'\) [23, 24, 128, 129]. Many of these studies of semiflexible polymers in thermotropic solution yield valuable insight on the properties of specific polymers, for example poly(3-hexylthiophene) (P3HT) [128]. Such studies are interesting in their own right, but far from the expertise of the present authors. Further, the limited space available for the present topical review has made restrictions on its scope inevitable, and hence all those studies (and related ones) shall not be discussed further. We only note that with such models nematic order may arise already for rather small values of \(\ell_p/\ell_b\approx 3\) [129], while for models with isotropic repulsive interactions (equation (13)) distinctly stiffer chains are required (e.g. \(\ell_p/\ell_b \gtrsim 8\)).

3. Phase diagrams and properties of bulk homogeneous phases

3.1. Single Chains and Dilute Solutions

For stiff polymers under good solvent conditions, the properties of the solution will still reflect the properties of single isolated polymers when the concentration (or the related density \(\rho\) of the effective monomeric units, respectively) is small enough so that no coil overlap occurs. To estimate the overlap concentration [130, 131], the radii of individual polymer coils must be known. For semiflexible chains with short enough contour lengths \(L\), excluded volume can be neglected and hence (in \(d = 3\) dimensions) equation (10) with \(s = L\) then yields the mean-square end-to-end distance describing the crossover from rod-like behavior, \(\langle R^2(L)\rangle \approx L^2\),
to Gaussian coils, $\langle R^2(L) \rangle \approx 2\ell_p L$, where $2\ell_p$ can be considered as the ‘Kuhn length’ of the chain [131]. A similar result holds for the mean-square gyration radius [132]:

$$
\frac{3 \langle R^2 \rangle}{\ell_p L} = 1 - \frac{3}{n_p} + \frac{6}{n_p^2} \left[ 1 - \exp(-n_p) \right],
$$

(20)

where $n_p = L/\ell_p$ is the number of stiff segments. However, equation (20) is true for an arbitrary large $L$ only for ‘phantom chains’ without excluded volume. Already, from simple Flory arguments [133, 134], one can show that equation (20) breaks down when $L$ exceeds $L^* = \ell_p n_p^* = \ell_p^3 / D^2$. Then both $\langle R^2 \rangle$ and $\langle R_\phi^2 \rangle$ scale as

$$
\langle R^2 \rangle \propto \langle R^2 \phi \rangle \propto R^2 \left( \frac{n_p^*}{n_p} \right)^{2\nu} \propto (\ell_p D)^{2/5} L^{6/5},
$$

(21)

where $R^*$ is the radius of a ‘blob’ containing $n_p^*$ segments of length $\ell_p$. Note that equation (21) has been derived using the approximate Flory exponent $\nu = 3/5$ instead of the more accurate value of $\nu \approx 0.588$ [130, 131], but this slight difference will be disregarded here. While the rod to coil crossover simply occurs for $n_p \approx 1$, the crossover from Gaussian to swollen coils depends on the polymer diameter, $n_p \approx n_p^* = (\ell_p / D)^2$. This result shows explicitly that for $\ell_p \approx D$ no regime of Gaussian behavior is expected, as anticipated above. In figure 2, this crossover scaling description is also extended to the single chain structure factor $S(q)$ [45], with wave vector $q$ [130, 131]. $S(q)$ is defined as

$$
S(q) = \frac{1}{N^2} \left\{ \sum_{j=1}^N \sum_{k=1}^N \exp[iq \cdot (\mathbf{r}_j - \mathbf{r}_k)] \right\}
$$

(22)

and it is, at least in principle, accessible experimentally via small angle neutron scattering (SANS). Observing the crossover at $q_0 \ell_p \approx 1$ can be invoked as an experimental method to estimate $\ell_p$, but the accuracy of this method to estimate $\ell_p$ (as well as other methods based on various dynamic quantities and their theoretical interpretation [135]) is somewhat doubtful, and often the estimates obtained for $\ell_p$ for nominally the same polymer by different methods disagree up to a factor of 2. An important experimental problem often is polydispersity. On the theoretical side, the computation of $S(q)$ for single semiflexible chains by analytical methods is a formidable problem, even if one restricts the task to the use of the KP model without excluded volume [136]. Thus, figure 2(b) is completely hypothetical, as there are no monodisperse polymers for which $S(q)$ could be accurately measured over 6 decades in $q$. Even large scale MC simulations for semiflexible self-avoiding walks on a lattice could verify the description contained in figure 2 only by combining data for a broad range of stiffnesses [41]. As reviewed by Hsu et al [41], the analytical description of $S(q)$ for semiflexible polymers is a long-standing and complicated problem.

The crossover from Gaussian to swollen chains, showing up in the behavior of the chain radii and in $S(q)$, has also consequences for the decay of the bond orientational autocorrelation function, $C(s)$, equation (9). The exponential decay is expected in the regime $s < \ell_p$, but for $s > \ell_p$, it is replaced by a power law behavior. In the regime $s > L^*$, where excluded volume is fully operative, we have [138]

$$
C(s) \propto s^{-\beta}, \quad \beta = 2(1 - \nu)
$$

(23)

This universal behavior has been verified for the semiflexible self-avoiding walk model [38], with $\beta \approx 0.824$ ($\beta = 4/5$ according to Flory theory). In the intermediate regime, $\ell_p < s < L^*$, a gradual crossover from the exponential decay to the power law, equation (23), was observed.

The smallness of the 2nd virial coefficient between a pair of segments of length $\ell_p$ and diameter $D$, which we have already invoked in the context of the Onsager-Khokhlov-Odijk-Chen theory discussed in sections 2.3 and 2.4, shows up also in the osmotic equation of state of the polymer solution [130, 131]. This problem was already considered by Khokhlov [139] who predicted that for monomer concentrations $\rho$ above the overlap concentration $\rho^*$ and in the good solvent regime the osmotic pressure $p_{osm}$ scales as

$$
p_{osm}/(k_B T) \propto \rho^{3/4} (\ell_p / D)^{3/4},
$$

(24)

while for $\rho < \rho^*$ one simply has an ideal-gas like behavior, $p_{osm}/(k_B T) = \rho / N$. Scaling considerations [130, 131] imply that for $\rho = \rho^*$ the density of monomers inside a coil agrees with the overall density, and hence equation (21) yields

$$
\rho^* D^3 \propto (L / D)^{-4/5} (\ell_p / D)^{-3/5}
$$

(25)
Figure 2. (a) Schematic log-log plot of the normalized mean square end-to-end distance $\langle R^2 \rangle / (2L_p L)$ vs $n_p = L / L_p$. The Kratky-Porod model [50] describes the crossover from rods to Gaussian coils, as indicated. At $n_p = n_p^*$ a smooth crossover from Gaussian to swollen coils occurs. Note that prefactors of order unity have been ignored throughout for simplicity. (b) Schematic Kratky plot $q L S(q)$ of the single chain structure factor plotted vs the scaled wavenumber $q L$ on log-log scales. Four regimes occur: at small $q$ the so-called Guinier regime, $S(q) = 1 - q^2 \langle R^2_g \rangle / 3$; for $q > q_{max}$, the location of the maximum in this plot, one has a power law $S(q) \propto q^{-1 / \nu}$, characteristic of swollen coils, crossing over at $q_R^* \approx 1$ to a second power-law $S(q) \propto q^{-2}$, characteristic of Gaussian coils. For $q \ell_p \approx 1$ another smooth crossover occurs to scattering from rod-like objects, $S(q) \approx \pi / (L q)$. Only the last two regimes are described accurately by the Kratky-Porod model. Reprinted (adapted) with permission from reference [45]. Copyright (2013) American Chemical Society. (c) Log-log plot of normalized gyration radius square $\langle R_g^2 \rangle / (L_p^2)$ vs the number of Kuhn segments, for the range $30 \leq n_k \leq 3000$. Chains of widely varying stiffness are shown ($q_b = 0.4, 0.2, 0.05, 0.02,$ and 0.005 correspond to $\ell_p / \ell_b = 1.12, 1.18, 5.7, 13.35$ and 51, respectively). (d) Same as (c) but showing corresponding experimental data, taken from Norisuye and Fujita [137], as redrawn in reference [41]. In that experimental work, the persistence length was denoted by $\rho$ and the mean square gyration radius as $\langle S^2 \rangle$. Broken straight lines are power law fits with effective exponents, while the full straight line is the Kratky-Porod model. Adapted and reprinted from reference [41], with the permission of AIP Publishing.

For $\rho > \rho^*$ it is implied that excluded volume is effective only for length scales less than a screening length (or correlation length, respectively) $\xi$ and the chain can be considered as a random walk of blobs of radius $\xi \propto \ell_p^{1/5} D^{3/5} \ell_b^{8/5}$, containing $g$ monomers. However, this picture only makes sense if $g$ by far exceeds $L^* / \ell_p$, and hence $\xi$ exceeds $R^* = \ell_p \sqrt{\rho \ell_b}$, cf equation (21). Since the blobs are space filling, we have $\rho \propto g / \xi^3$ and thus the condition $\xi = R^*$ yields a density $\rho^{**}$ above which the excluded volume is no longer felt [140], so $\rho_{osm} / (k_B T) \propto \rho^{**}$ and

$$\rho^{**} D^3 \propto (L^* / D)^{-1/2} (\ell_p / D)^{-3/2} = (\ell_p / D)^{-3}.$$  

Comparing this result to equation (11), we see that $\rho^{**}$ is a much smaller monomer density than the density $\rho_i$ where nematic order sets in.

Finally, we emphasize that the behavior in $d = 2$ dimensions (applicable for polymers confined in narrow planar slits or strongly adsorbed on planar walls) is completely different from the picture shown in figure 2. There occurs a crossover from the rod regime immediately to the self-avoiding walk regime (with $\nu = 3/4$ in $d = 2$), so equation (21) is replaced by
as soon as $L$ exceeds $\ell_p$, [39, 134, 141, 142]. This fact can be understood readily in terms of Flory arguments [134], and has been confirmed both for semiflexible self-avoiding walks and for bead-spring models by extensive simulations [39, 141, 142].

3.2. Nematic and smectic order in concentrated solutions and melts

When the osmotic equation of state is extended to larger densities and pressures, the weakly first order isotropic-nematic transition shows up in the isotherm pressure vs monomer density via a narrow two-phase coexistence region (figure 3(a)). At still larger densities, the nematic order parameter $S$, vs monomer density, $\rho$, for chains with $N = 32$ beads and 5 choices of $\kappa$, as indicated. Full curves are DFT-CS results, broken straight lines indicate the lever rule in the two-phase coexistence region. Dotted straight lines connecting the square symbols indicate the corresponding predictions from Chen’s Onsager-style theory [77]. Symbols are the MD results. Reproduced from reference [81] with permission from The Royal Society of Chemistry.

$$\langle R^2 \rangle \propto \left( \frac{R_g^2}{\ell_p^2} \right) \propto k_B T / L^{3/2}$$

(27)

as soon as $L$ exceeds $\ell_p$, [39, 134, 141, 142]. This fact can be understood readily in terms of Flory arguments [134], and has been confirmed both for semiflexible self-avoiding walks and for bead-spring models by extensive simulations [39, 141, 142].

3.2. Nematic and smectic order in concentrated solutions and melts

When the osmotic equation of state is extended to larger densities and pressures, the weakly first order isotropic-nematic transition shows up in the isotherm pressure vs monomer density via a narrow two-phase coexistence region (figure 3(a)). At still larger densities, the nematic order parameter $S$, vs monomer density, $\rho$, for chains with $N = 32$ beads and 5 choices of $\kappa$, as indicated. Full curves are DFT-CS results, broken straight lines indicate the lever rule in the two-phase coexistence region. Dotted straight lines connecting the square symbols indicate the corresponding predictions from Chen’s Onsager-style theory [77]. Symbols are the MD results. Reproduced from reference [81] with permission from The Royal Society of Chemistry.

$$\langle R^2 \rangle \propto \left( \frac{R_g^2}{\ell_p^2} \right) \propto k_B T / L^{3/2}$$

(27)
The smectic phase is characterized by a density modulation in the $z$-direction (along the nematic director), $\rho(z) \propto \cos(2\pi z/\Lambda + \phi)$. Both the wavelength $\Lambda$ and the amplitude of this modulation are of interest. For a quantitative characterization, the collective structure factor $S_{\text{coll}}(q)$ is considered:

$$S_{\text{coll}}(q) = \frac{1}{NN} \left\langle \sum_{j=1}^{NN} \exp(iq \cdot r_j) \right\rangle^2. \quad (28)$$

In principle, the smectic order parameter, $\tau$, can be defined from the amplitude of the largest peak of $S_{\text{coll}}(q)$, which is expected to occur at $q_z = 2\pi/\Lambda$. However, it was found that global order was often somewhat imperfect due to local defects (e.g. spiral disclinations). Thus, one could obtain better results by computing $\tau$ in rectangular slabs with volume $l \times l \times L_z$, with $l = 5$ or $l = 10$, instead of the entire system. The order parameter $\tau$ obtained in this way is shown in figure 6(c), as well as an order parameter $\Psi_6$ defined from

$$\langle \Psi_6 \rangle = \frac{1}{M} \left\langle \sum_{\alpha} \Psi_{6\alpha} \right\rangle, \quad \Psi_{6\alpha} = \frac{1}{n_\beta} \sum_{\beta=1}^{n_\beta} \exp(i6\phi_{\alpha\beta}), \quad (29)$$

which characterizes the transverse order in the $(xy)$-planes perpendicular to the director. Labeling the chains with index $\alpha$ in an individual smectic layer ($M$ being the number of chains in the layer), one asks whether the center of mass coordinates $\mathbf{r}^{\text{CM}}$ of the chains projected onto the $xy$-plane form a triangular lattice. In equation (29), $\phi_{\alpha\beta}$ is the angle between the vector $\mathbf{r}_{\alpha}^{\text{CM}} - \mathbf{r}_{\beta}^{\text{CM}}$ and the $x$-axis $\mathbf{r}_{\alpha}^{\text{CM}} \equiv (\mathbf{r}_{\alpha}^{\text{CM},x}, 0, 0)$. A nonzero order parameter $\langle \Psi_6 \rangle$ hence indicates that the stretched out rod-like chains form a triangular lattice in their perpendicular plane. Indeed, figure 6 provides clear evidence for a continuous nematic-smectic transition of the considered model, while the transition from the smectic phase to the crystal is clearly of first order. As a caveat, we mention that in real polymeric systems the smectic phase is easily suppressed by the polydispersity of the chains. For a description of possible crystal phases of polymeric systems, a chemically detailed description of the dense packing of the atoms will be required; while we maintain that our simplified coarse-grained model should provide a qualitatively reasonable description of nematic order, no such claim is made concerning the smectic and crystal phases at high density.

A particular advantage of MD simulations of nematic phases of semiflexible macromolecules is that one can elucidate their structure in great detail. For instance, one finds that the persistence length $\ell_p$, extracted...
Figure 5. Simulation snapshots of a system with $N = 89600$ chains of length $N = 12$ at $T = 0.5$ for $\varepsilon_b = 64$ and four different (osmotic) pressures: (a) $P = 0.6$, (b) $P = 0.7$, (c) $P = 0.8$, and (d) $P = 0.9$. Monomers are shown in green, apart from the chain ends which are shown in yellow. The edges of the simulation box are indicated by straight blue lines. In order to reduce finite size effects, the linear dimension of the simulation box in the $z$-direction (i.e. along the nematic director) was chosen about twice as large as in the $x$, $y$-directions. Case (a) shows a nematic state, cases (b) and (c) are typical smectic states, while case (d) refers to a somewhat disordered crystal. Reprinted from reference [102], Copyright (2019), with permission from Elsevier.

Figure 6. Monomer density $\rho$ and nematic order parameter $S$ plotted vs (osmotic) pressure $P$ for the case $N = 12$, $\varepsilon_b = 64$ at (a) $T = 0.5$ and (b) $T = 1.0$. (c) Order parameters $S$, $\tau$, and $\Psi_6$ vs $P$ for the same parameters as in (b). Reprinted from reference [102], Copyright (2019), with permission from Elsevier.

from the angle $\theta_{ijk}$ between subsequent bond vectors via equation (19), does not depend on the monomer density of the solution (and hence the local environment encountered by the bond vector), as long as one stays in the isotropic phase. However, the transition to the nematic phase leads to a (discontinuous) increase of $\ell_p$, and the deeper one moves into the nematic phase the more the progressive alignment of bonds along the director also has an effect of decreasing $\left< \theta_{ijk}^2 \right>$, figure 7(a).

One can also investigate the extent to which hairpin conformations are present (figure 7(b)) and test the corresponding theoretical predictions [145], which were found to be qualitatively reasonable. Another quantity of interest is the so-called ‘deflection length’ $\lambda$ defined as $\lambda = \ell_p/\alpha$ [145]. For polymers with $L \gg \ell_p$ this length describes the undulations of the local chain orientation around the director (see schematic in figure 8(a)). Figure 8(b) shows a comparison between MD and DFT results for this length, demonstrating excellent agreement between the two methods.
Figure 7. (a) Plot of persistence length $\ell_p$ normalized by its value $\ell_{p,0}$ in the dilute limit for chains with $N = 64$ plotted vs monomer density $\rho$ for three choices of $\kappa$, as indicated. Arrows show estimates for the onset of nematic order in the solution. (b) Fraction of chains $f_h$ which exhibit hairpin conformations and the corresponding nematic order parameter $S$ plotted vs monomer density $\rho$ for the case $N = 64$ and $\kappa = 32$. Adapted and reprinted from reference [101], with the permission of AIP Publishing.

Figure 8. (a) Schematic representation of a ‘ semiflexible chain’ with $L \gg \ell_p$ in the nematic phase: each chain is in a cylindrical tube of length $L$ and radius $r_\rho$ formed by its nearest neighbors (see main text for definition of $r_\rho$). However, this cylindrical tube (shaded) is not straight but bent, so that on a scale $\lambda$ a radial extension $r_{eff}$ is reached instead, and the $z$-component of the end-to-end vector is somewhat smaller than the contour length $L$. (b) Deflection length $\lambda = \ell_p/\alpha$ plotted vs $\kappa$ at the density $\rho_n$ where the isotropic-nematic coexistence ends, for four choices of $N$, as indicated. Filled symbols are MD results, while open symbols are from the DFT-CS calculation. Lines are guides to the eye only. Adapted and reprinted from reference [101], with the permission of AIP Publishing.

Also the dependence of the parameter $\alpha$ (equation (4)) which dictates the amount of bond orientational fluctuations in the nematic phase is of interest (figure 9(a)). It is seen that the corresponding theoretical prediction has the right order of magnitude, but increases with increasing density much less steeply than the simulation results. Since equation (19) implies $\langle \theta^2 \rangle = 2/\alpha$ and for large $\alpha$ hence $\langle \theta^2 \rangle$ is very small, $S = (3 \langle \cos^2 \theta \rangle - 1)/2 \approx 1 - \frac{1}{2} \langle \theta^2 \rangle$. When hairpins are neglected, the end-to-end distance is simply given by $\sqrt{\langle R^2 \rangle} \approx L(1 - \langle \theta^2 \rangle)/2$, and one can conclude that $1 - S = 3(1 - \sqrt{\langle R^2 \rangle}/L)$ in this limit. Figure 9(b) tests for deviations from this simple limiting case, and one can see that the data for $\ell_p/L \approx 1/2$ are already close to this limit. On the other hand, for $\ell_p/L > 1$ the data tend over to a straight line parallel to the ordinate (the latter would be reached in the hard rod limit $\ell_p/L \to \infty$).

We can estimate the extent to which chains are spatially correlated, by defining the radius $r_\rho$ from the condition that a (fictitious) cylindrical tube with a chain in it does not contain monomers of any other chains (see figure 8(a)). Since then the monomer density in the tube must coincide with the overall density $\rho$, $\rho = N/(L\pi r_\rho^2)$ (where $L\pi r_\rho^2$ is the tube volume), one concludes that $r_\rho = (N/(\pi L \rho))^{1/2}$. For $\ell_p/L > 1$, the typical angles $\sqrt{\langle \theta^2 \rangle}$ indicate collective fluctuations of neighboring chains that are much larger than expected from $r_\rho$. The collective orientational fluctuations are assumed to be responsible for the fact that the order parameter $S$ saturates with increasing density, according to the simulations, much slower than predicted by the DFT calculations (figure 3(b)).

In this section, we have only addressed ‘monodomain’ samples, where the nematic or smectic order is uniform, i.e. free of defects. However, defects are extremely widespread and common in experimental realizations of liquid crystalline systems (see e.g. references [146–150]). Such defects can form when the
Figure 9. (a) Parameter $\alpha$ controlling the width of the Gaussian distribution of orientational fluctuations (equation (4)) plotted vs monomer density $\rho$ for chain length $N = 32$ and three choices of $\kappa$, as indicated. Symbols connected by solid lines are MD results, while the dashed curves show the Vroege-Odijk [145] result $\alpha = (4\pi)^{1/3}(D^2\ell_p\rho)^{2/3}$, predicted for the limit $N \to \infty$.

(b) Plot of $1 - S$ vs $1 - \sqrt{\langle R^2 \rangle / L}$ for several choices of $N$ and $\kappa$, as indicated, for densities in the nematically ordered regime (the parameter that varies for each of the shown data sets is the density of the system). The dashed straight line shows the asymptotic limiting case $1 - S = 3(1 - \sqrt{\langle R^2 \rangle / L})$ reached for $L \gg \ell_p$. The opposite hard-rod limit ($\ell_p \to \infty$, $L$ finite) would correspond to the ordinate axis. Adapted and reprinted from reference [101], with the permission of AIP Publishing.

Figure 10. Schematic representation of the pure splay, pure twist, and pure bend distortion in a system with liquid-crystalline order. The spatially varying nematic director is represented by ellipses and the equilibrium director is denoted $n$. Figure by courtesy of Neal Robert Scruggs.

system did not have enough time during its preparation to develop perfect order, which can also occur in simulations as a result of improper equilibration or inappropriate starting configurations [102]. Alternatively, defects can emerge due to the influence of external fields, e.g. electromagnetic fields, mechanical stress, and/or external walls. Particularly interesting from an application point of view are walls, which can be exploited to control the local orientation of bonds near the walls through, e.g. anchoring of chains at functional surfaces. Simulations have the advantage that such external factors can be precisely controlled. For example, external walls can be easily incorporated into MD simulations or DFT calculations (see section 5), or they can be completely eliminated through the use of periodic boundary conditions. Indeed, defects and defect-related phenomena play an important role for liquid crystalline materials, but they are out of scope of the present treatment, which focuses on the intrinsic bulk properties of (perfectly) ordered systems.

3.3. The Frank elastic constants
In the nematically ordered phase, the resistance of the system to deformations of this nematic order on large length scales is described by the Frank elastic constants $K_1$, $K_2$, and $K_3$ [4, 6]. Each of these three constants represents a type of distortion of a nematic. The first represents pure splay, the second pure twist, and the third pure bend (see figure 10), and a combination of these constants can be used to represent an arbitrary deformation in a liquid crystal.

Understanding the behavior of these constants is crucial for many applications of liquid-crystalline materials, but it is rather difficult to make reliable predictions of them from either theory or simulations. The free energy density of the nematic, $f(r)$, can be described exclusively in terms of the director field $n(r)$,

$$f(r) = \frac{1}{2} \left\{ K_1 (\nabla \cdot n)^2 + K_2 [n \cdot (\nabla \times n)]^2 + K_3 [n \times (\nabla \times n)]^2 \right\}$$

(30)
One then defines the Fourier transform of the tensorial order parameter \( n \)-mers \( \bar{Q}^{\alpha \beta}(r) \) (cf equation (7)) as

\[
\bar{Q}^{\alpha \beta}(q) = \frac{\sqrt{V}}{N(N-1)} \sum_{n=1}^{N} \sum_{p=1}^{N-1} \left( \frac{3}{2} u_{n \alpha}^s u_{n \beta}^s - \frac{1}{2} \delta^{\alpha \beta} \right) \exp(iq \cdot r_{np}).
\]  

(31)

Here, \( V \) is the volume of the considered system, and the sums extend over all unit vectors from monomer at site \( r_{n,i} \) to the next monomer in the same chain (labeled by index \( n \)) at site \( r_{n,i+1} \). Equation (30) can then be used to compute \( \left\langle \left| \bar{Q}^{\alpha \beta}(q) \right|^2 \right\rangle \) which yields

\[
\frac{4}{9} \left\langle \left| \bar{Q}^{\alpha \beta}(q_1, q_2) \right|^2 \right\rangle = \frac{1}{K_2 q_1^2 + K_3 q_2^2} \left( 1 - \frac{q_1^2}{q_2^2} \right) + \frac{1}{K_2 q_2^2 + K_3 q_1^2} \frac{q_1^2}{q_2^2}, \quad \alpha = x, y,
\]  

(32)

with \( K_2^q \) being a wavevector-dependent generalization of \( K_2 \) which will not be discussed further here. Considering special orientations of \( q \), e.g. \( q = (0, q_x, q_z) \), one can separate twist-bend fluctuations from splay-bend fluctuations [101, 129]. While equation (32) seems fairly complicated, it must be realized that it is strongly simplified since only orientational fluctuations are considered while packing density fluctuations are completely disregarded. However, the latter must be included when one wishes to address the collective structure factor \( S(q) \) as it is accessible in the standard small-angle scattering of neutrons and X-rays. Kamien et al. have shown that the structure factor has the following form in the small wave vector limit [151]

\[
S(q)/(k_B T) = \frac{\rho_0 q_1^2 + (K_1 q_1^2 + K_2 q_2^2) / G}{B q_1^2 + (B/(G \rho_0)) + q_2^2 (K_1 q_1^2 + K_2 q_2^2)}
\]  

(33)

with mean areal chain packing density \( \rho_0 \), two-dimensional bulk modulus \( B \), and elastic modulus \( G = k_B T L/(2 \rho_0) \). This result has in fact been useful for both experimental X-ray scattering studies from nematic polymers [152] and for the interpretation of simulations [97, 129].

A key question is to understand how the Frank constants \( K_1 \), \( K_2 \), and \( K_3 \) depend on the chain parameters \( L \) and \( \ell_p \) and the monomer density \( \rho \). This problem is still rather controversially discussed in the literature (see reference [153] and the discussion in reference [101]). In particular, many theories (e.g. reference [154]) imply \( K_1 = 3K_2 \), but this result is derived when one takes orientational fluctuations of the bonds as the only relevant degree of freedom, disregarding the coupling between local density fluctuations and orientational fluctuations completely. Considering the limit \( L \gg \ell_p \), Vroege and Odiijk presented various arguments to suggest that [145]

\[
K_1 = \frac{k_B T}{D} \frac{1}{8 \sqrt{\pi}} \frac{L}{\ell_p} \alpha^{3/2}
\]  

(34)

\[
K_2 = \frac{k_B T \pi^{3/2}}{2 D \sqrt{\alpha}}
\]  

(35)

\[
K_3 = \alpha K_2.
\]  

(36)

where \( \alpha \) controls the amount of bond orientational fluctuations in the nematic phase (see equation (4)).

The DFT approach presented by Milchev et al [101] uses again the excluded volume interactions computed by Fynewever and Yethiraj [87] and combines them with an approach due to Lee [155], based on the rescaling of the Onsager-like direct correlation function, similar in spirit to the rescaling of the free energy [83]. This approach had been originally developed for a system of hard spherocylinders, and also
Figure 11. DFT results for the elastic constants (a) \( K_2 \) and (b) \( K_3 \) plotted vs monomer density \( \rho \), for the four chain lengths \( N = 16, 32, 64, \) and 128, as indicated, and three stiffness parameters \( \kappa = 16 \) (main panel), \( \kappa = 32 \) (insets, solid curves), and \( \kappa = 128 \) (insets, broken curves). Adapted and reprinted from reference [101], with the permission of AIP Publishing.

Figure 12. Variation of the elastic constant (a) \( K_1 \), (b) \( K_2 \), and (c) \( K_3 \) with chain length \( N \) for \( \kappa = 16 \) and \( \kappa = 64 \) at monomer density \( \rho = 0.66 \), according to MD simulations (filled symbols connected by solid lines). Predictions from Vroege and Odijk [145] (equations (34–36)), with \( \alpha \) taken from the simulations are shown with open symbols connected by dotted lines. Predictions from equations (34–36) using the theoretical result for \( \alpha \) [145], \( \alpha = (4\pi)^{1/3}(D^2\ell p\rho)^{2/3} \), are shown as dotted lines. Adapted and reprinted from reference [101], with the permission of AIP Publishing.

The MD results, however, suggest a less dramatic variation with density and chain length (see figure 12). Those results for the elastic constants are in qualitative accord with the results proposed by Vroege and Odijk [145], in particular when one takes into account that \( \alpha \) has not reached its limiting value for large \( N \) yet for the chosen parameters. Thus, the theoretical situation concerning the behavior of the elastic constants is still somewhat unsatisfactory.

Figure 13 shows experimental results for poly-\( \gamma \)-benzylglutamate (PBG) [156, 157]. The experiments imply that the twist elastic constant \( K_2 \) depends on neither the chain length nor the density (or, equivalently, the volume fraction of the polymers) [156, 157]. Indeed, the MD data (figure 12(b)) show that the chain length dependence of \( K_2 \) is much weaker than that of either \( K_1 \) or \( K_3 \) (note that the ordinate of figure 12(b) extends over a single decade, whereas \( K_1 \) and \( K_3 \) vary over two and three decades, respectively). In contrast,
the DFT results imply a strong chain length dependence of $K_2$ (cf figure 11(a)), and also the density dependence is much more pronounced. The theory by Vroege and Odijk also implies a non-negligible dependence of $K_2$ on $\rho$ [145], due to $\sqrt{\alpha} \propto \rho^{1/3}$. Unfortunately, the MD data [101] are only available over such a restricted density range that neither the linear density dependence of $K_1$ (figure 13(a)), which is supported by equation (34), nor the claim that $K_2$ is independent of density could be tested so far.

Experiments on the Frank elastic constants of liquid-crystalline polymers are extremely scarce (the methods applied in references [156, 157] require the preparation of ‘monodomain’ samples, i.e. uniform nematic order throughout the sample). Unfortunately, liquid crystalline polymers typically develop non-uniform orientational order, due to disclinations and defects, leading to polydomain structures, rendering the application of formulas such as equations (32, 33) impossible. This difficulty explains why experimental results on elastic constants of liquid crystalline polymers are so rare. This lack of experimental data is rather regrettable, since the elastic anisotropy of liquid-crystalline polymers can be much larger than for their small molecule counterparts [156], which could be an advantage with respect to applications. Very large elastic anisotropies have been also found for thermotropic liquid-crystalline polymers by a step-rotation rheo-nuclear magnetic resonance experiment [158]. These anisotropies were observed for a single molecular weight and using melt densities, finding that $K_1$ exceeds $K_2 \approx K_3$ by two orders of magnitude (while the latter are already two orders of magnitude larger than those of low molecular weight liquid crystals).

An interesting lyotropic material is filamentous actin (F-actin), with diameter $D \approx 8$ nm and persistence length $\ell_p$ in the range from 10 $\mu$m to 17 $\mu$m [160, 161]. The contour length $L$ can be tuned (in a range...
Phase separation

Already for flexible chains, one can observe phase separation between a dilute solution and a concentrated solution for temperatures below the critical temperature [106, 164–166]. This type of phase separation for isotropic systems of flexible polymers has been extensively studied before, and is not of interest here. Phase separation in solutions containing semiflexible polymers may be driven by entropy or by attractive effective interactions between the monomers (i.e. rather than good solvent conditions one deals with solutions at temperatures below the theta temperature [130, 131]). Entropically driven phase separation in systems with purely repulsive effective interactions among the monomers can be expected when we consider, e.g. binary mixtures of semiflexible polymers that differ strongly either in their chain lengths \(N_1 \gg N_2\) or in their stiffness \(\ell_{p,1} \gg \ell_{p,2}\) or both [122]. In principle, both isotropic-isotropic and nematic-nematic phase separations are possible, competing with the isotropic-nematic phase separation. While interesting phase diagrams have been predicted by theory [122], this problem has not yet been extensively studied by molecular simulations and hence will not be considered here further. We shall also not discuss (thermotropic) solutions, where the interactions between monomeric units depend on the orientations of the corresponding bond vectors.

In this review, we focus on the case of monodisperse solutions of semiflexible polymers in solvents of varying quality [106, 123, 124, 167], where the monomer-monomer interaction has an additional attractive contribution. Phase separation in these systems has been studied both for lattice models [124] and for bead-spring type models in the continuum [106, 123, 124]. Padmanabhan et al [167] used MC methods for a model where attractive interactions were of square-well type. Isotropic-isotropic (I-I) phase separation was observed for polymers with chain lengths \(N = 5\) to \(30\), while for \(10 \leq N \leq 35\) also isotropic-nematic (I-N) transitions could be located. The phase diagrams then have a ‘chimney’-type topology. While the isotropic-isotropic critical phenomena are believed to remain in the Ising model universality class (like liquid-vapor phase separation for systems of small molecules [54]), a nontrivial question concerns the stiffness dependence of the (effective) critical temperature \(T_{\text{eff}}\): while Sheng et al found that stiffness leads to a decrease of \(T_{\text{eff}}\) in comparison with the corresponding flexible chain model [123], other studies reached the opposite conclusion [106, 124]. It must be noted, however, that unlike all other studies [106, 124], Sheng et al [123] used also a torsional potential in their microscopic model of the semiflexible chains. Thus details of the chosen models are important, and hence one must be careful with conclusions about real systems, where chemical details may matter.

The most recent simulation study by Midya et al [106] presented a detailed comparison between MD and DFT results. In that work, the attraction strength between monomeric units was controlled by the (effective) inverse temperature \(T^{-1}_{\text{eff}}\) (see section 2.5). Note that \(k_B T = \varepsilon\) was kept in the MD simulations, so that the spring constant between neighboring beads along the chain described by equations (15) and (18) remained precisely the same as in the purely repulsive case. Another advantage of this model is that it allows for a gradual transition to good solvent conditions by choosing \(T_{\text{eff}} \to \infty\). In the DFT calculations, the temperature \(T\) was varied while simultaneously adjusting the stiffness parameter \(\varepsilon_b\) to achieve a constant reduced stiffness parameter \(\kappa \equiv \varepsilon_b/(k_B T)\).

In reference [106], both the variation of chain length \(8 \leq N \leq 32\) and stiffness (from flexible chains, \(\kappa = 0\), to semiflexible ones \(\kappa = 32\)) was studied. Figure 15 gives an example of results. One can see that the critical point of I-I phase separation occurs in this model at much lower monomer densities \(\rho\) compared to the I-N coexistence, for the chosen parameters. At the temperature of the triple point, the width of the I-N two-phase coexistence region is distinctly wider than at high temperatures. When \(N\) and/or \(\kappa\) increases, this
width decreases, however. Note that when \( N \rightarrow \infty \), we expect that the critical density \( \rho_{\text{cr}} \rightarrow 0 \) and that the critical temperature \( T_{\text{cr}}^{\text{eff}} \) saturates at the theta temperature \([130, 131]\). On the other hand, when \( \kappa \) increases at fixed \( N \), we expect that \( \rho_{\text{cr}}(\kappa \to \infty) = \rho_{\text{cr}}^\infty > 0 \). From the DFT results (figure 15(d)) we can expect that the data for \( \rho^\infty(\kappa = 32) \) and \( T^\infty(\kappa = 32) \) are already rather close to their limiting values for hard rods (\( \kappa = \infty \)).

The situation is rather intricate, since for increasing chain stiffness the topology of the phase diagram changes: triple point and critical temperature become identical at some specific value \( \kappa^* \) (which for \( N = 32 \) is slightly larger than \( \kappa = 64 \), according to DFT). For \( \kappa > \kappa^* \) there is a single first order transition from isotropic to nematic solution, and the phase diagram then has a ‘swan-neck’ topology (figure 16(b)). The phase separation between the vapor-like (low density) phase and the high density isotropic liquid then occurs as a metastable equilibrium within the vapor-nematic (V-N) two-phase coexistence region only (figure 16(d)). Due to its mean-field character, DFT yields well-defined metastable states, which in MD simulations (as well as in real systems) have at best a limited ‘lifetime’ and their observability is doubtful. Another consequence of this mean-field character is the prediction that the shape of the vapor-isotropic (V-I) coexistence curve is parabolic, i.e. \( \rho_I - \rho_V \propto (1 - T/T^\text{cr})^\beta \) with \( \beta = 1/2 \), while the MD results are compatible with the expected Ising-like behavior \([106]\), \( \beta \approx 0.325 \). However, the advantage of DFT is that the statistical mechanics is also accessible in ensembles that use intensive variables only, see e.g. figure 16(d), that give a particularly clear description of the possible phase transitions.

5. Semiflexible chains in confinement

While confinement effects for fully flexible polymers are predominantly entropic \([130]\), confining semiflexible chains incurs both energetic and entropic penalties, where the balance between the two contributions is primarily controlled by the stiffness of the chain and the length scale of the confinement \([168, 169]\). In a nematic system under confinement, the natural tendency of forming an ordered bulk configuration is impeded by the boundary conditions or curvature of the enclosing walls. There are numerous parameters that control the packaging of semiflexible polymers in confinement, such as the size, shape and topology of the confining geometry, the architecture and size of the enclosed polymers, etc. For example, the length scale regime where the contour length of the confined particles is much smaller than the...
and section 195 used throughout. Attractive walls were modeled using the Mie 10-4 potential. The attraction strength of $x$ where $x$ denotes the normal distance from the closest confining wall. For simplicity, $\varepsilon_w = \varepsilon$ and $\sigma_w = \sigma$ was used throughout. Attractive walls were modeled using the Mie 10-4 potential

$$U_{\text{Mie}}(x') = \varepsilon_{\text{Mie}}\left[\left(\frac{\sigma}{x'}\right)^{10} - \left(\frac{\sigma}{x'}\right)^{4}\right].$$

The attraction strength of $U_{\text{Mie}}$ was typically set to $\varepsilon_{\text{Mie}} = 3$ in references [194, 195], and the potential was cut at $x' = 5$. A potential of the type $U_{\text{Mie}}$ is appropriate as a coarse-grained description of a surface where the attractive interaction results from a two-dimensional surface layer, e.g. suitable surfactants at a silicon surface can control the wettability of a surface over the full range from complete wetting to drying [197].
In the MD simulations, typically the case of one wall being attractive and the opposite wall being repulsive was simulated. If both walls were attractive, it may happen that the number of chains that adsorb from the solution at $x = 0$ may differ from the number of chains adsorbed at the wall at $x = L_x$, although on average they should be equal. Note that one can not simply symmetrize a posteriori the simulated density profiles by mirroring the system along the origin, as some properties such as the nematic parameter depend on the local density in a non-linear fashion.

DFT calculations can be carried out rather easily in the grand-canonical ensemble, so that for large enough slit widths $L_x$, the local density in the center of the slit is identical to the density of the corresponding bulk system, i.e. $\rho(L_x/2) = \rho_b$. This is, however, not necessarily true for MD simulations in the canonical ensemble, where the total density is strictly conserved, and hence

$$\rho = \rho_b + \frac{1}{L_x}(\rho_{\text{att}} + \rho_{\text{rep}}),$$

where $\rho_{\text{att}}$ and $\rho_{\text{rep}}$ describe the excess densities at both walls:

$$\rho_{\text{att}} = \int_0^{L_x/2} [\rho(x) - \rho_b]dx, \quad \rho_{\text{rep}} = \int_{L_x/2}^{L_x} [\rho(x) - \rho_b]dx.$$

This problem of finite size effects of order $1/L_x$ must be carefully considered when one compares results from MD simulations with the corresponding results from DFT calculations (figure 17).

An important quantity for confined systems is the excess free energy due to the walls, i.e. the surface tension. In the MD framework, it can be extracted from the anisotropy of the pressure tensor. In DFT, it follows as an $1/L_x$ correction to the grand potential $\Omega$ that is computed [198]. (In the DFT framework, instead of working with a slit of width $L_x$, one can also compute surface tension by considering a semi-infinite system with a single wall and by imposing bulk boundary condition sufficiently far away from the wall.) Figure 18 shows typical results: in the purely repulsive case, the surface tension originates from a subtle balance of various entropic contributions and it is numerically small; in the attractive case, it is orders of magnitude larger and strongly negative, because the chains aligning at the wall lower the potential energy of the system.

When two repulsive walls are chosen, the difference between $\rho$ and $\rho_b$ is rather small, and hence can be ignored. Figure 19(a) shows the nematic order parameter $S$ for various choices of $L_x$, and it is evident that the walls stabilize some order already in the isotropic phase. This picture is corroborated by DFT calculations (figure 19(b)), and hence one can conclude that there is capillary nematicization, i.e. the transition to uniform nematic order in the center of the slit occurs at a smaller density $\rho_b$ than in the bulk. When the distance between the walls then gets small enough, the discontinuous isotropic–nematic transition disappears in favor of a gradual, non-singular, onset of nematic order with increasing density. This problem has already been studied with a lattice model [60–62].

Finally we note that for the strongly attractive wall potential, equation (38), the enhancement of the local density near the wall (figure 17) induces some quasi-two-dimensional order in the adsorbed surface layer, as shown in figure 20 for semiflexible chains with $N = 32$ [194, 195]. While in the case of $\kappa = 3$ one finds a standard isotropic fluid (figure 20(a)), a lot of small nematic clusters form at $\kappa_b = 5$, including a significant

![Figure 17](image_url)
fraction of hairpin-like conformations (figure 20(b)). As the stiffness is further increased to $\kappa = 15$, the (defective) nematic order extends throughout the system, as shown in figure 20(c): note, however, that nematic long-range order is ruled out in strictly two-dimensional systems. For the highest stiffness $\kappa = 128$, some local order of smectic C type clearly seems to be present (figure 20(d)). Also strictly long-range smectic order in two dimensions is not expected either, nevertheless systems such as shown in figure 20(d) could find potential applications to manufacture patterned substrates.

6. Summary

In this topical review, computer simulations and Density Functional Theory (DFT) treatments of semiflexible polymers that can form liquid crystalline structures were discussed. The considered coarse-grained models did not address the specific aspects related to the chemical composition of particular materials, but rather aimed at providing qualitative insights into the generic features of a broad class of materials. Thus, the persistence lengths of the examples mentioned in this review range from a few nm up to 17 $\mu$m (in the case of F-actin), depending on the applied mapping.
Figure 20. Snapshots of systems of semiflexible polymers of length $N = 32$, that reside predominantly in the region $x \leq 2$ (cf figure 17), projected into the $yz$-plane. The total monomer density in the box is $\rho = 0.1$. Cases shown are (a) $\kappa = 3$, (b) 5, (c) 15, and (d) 128. Box lateral linear dimensions are (a-c) 96 and (d) 192, respectively. Reproduced from reference [194] with permission from The Royal Society of Chemistry.

We have emphasized that a minimal model of semiflexible polymers in this context must be described in terms of three lengths, i.e. the persistence length $\ell_p$ that describes the local bending stiffness, the effective diameter $D$ of the ‘worm-like’ chain, and the contour length $L$. For bead-spring models, a fourth length is given by the distance $\ell_b$ between effective monomers along the chain. These subunits are typically much larger than actual ‘chemical monomers’, since often it is convenient to choose $\ell_b \approx D$. For example, in the case of ds-DNA in a solution at high salt concentration the distance between subsequent base pairs is 0.34 nm, but $D$ can be chosen as the diameter of the helix, $D = 2$ nm, so that there are 6 base pairs per subunit. For such conditions, the persistence length is roughly $\ell_p = 50$ nm so the corresponding stiffness parameter of the model presented in section 2.5 would be $\kappa = \ell_p/\ell_b = 25$.

Single semiflexible polymers (as they physically occur in very dilute solutions under good solvent conditions) are typically well described by the Kratky-Porod (KP) worm-like chain model when $\ell_p \gg D$. However, apart from extremely long chains, this model is inappropriate for ‘thick worms’ with $D$ and $\ell_p$ of the same order, which is found sometimes for bottlebrush polymers, dendronized polymers, etc. Also semiflexible polymers strongly adsorbed on attractive substrates have to be considered with care: their effective persistence length, measured from the decay of bond-orientational correlations along the contour of the chain molecule, exhibits crossovers from $\ell_p$ to $2\ell_p$ for distances $s$ along the contour less than $2\ell_p$; for large distances, the power-law decay of orientational correlations implies that the KP model fails qualitatively due to its neglect of excluded volume interactions.

The excluded volume interaction is also the central mechanism for the onset of nematic order in semidilute or concentrated lyotropic solutions of semiflexible polymers. We have discussed various
theoretical predictions for the resulting phase diagrams (in terms of the variables osmotic pressure and density of effective monomeric units), focusing both on the classical Onsager-style Khokhlov-Semenov-Odijk-Chen theory and more recent DFT treatments due to the authors of this review. There, excluded volume between interacting chains is described more realistically, and the strength of this excluded volume is appropriately renormalized. The MD work reviewed here has validated this DFT treatment, apart from deviations in the nematic phase, where DFT predicts too much order, due to the neglect of collective ‘deflection fluctuations’. However, important problems about bulk nematic phases that are still incompletely understood concern the Frank elastic constants, and how they show up in suitable experimentally observable response functions. So far, DFT includes orientational distribution functions only, without proper coupling between local density and orientational fluctuations; fully conclusive MD work would require the study of considerably larger systems and strongly enhanced statistical effort, which is still beyond reach at the present time.

We have also mentioned the extension of the description to solvents of variable quality, where unmixing in the isotropic phase competes with the isotropic-nematic transition. Finally, effects of confinement in pores with slit geometry have been discussed. As expected, slit pores favor chains parallel to the walls of the slit, and hence lead to the phenomenon of ‘capillary nematization’. Further, attractive monomer-surface interactions can give rise to interesting textures of locally ordered structures in wall-attached domains of semiflexible chains. Clearly, a very rich behavior then is possible, and only selected facets of this behavior have been studied and presented here.

Finally, we emphasize that liquid crystalline polymers offer ample opportunities for the study of defects in liquid crystalline order [146–150], but this aspect has not been covered in the present review for brevity. We have also not considered the response of polymeric liquid crystalline systems to external perturbations, such as flow [199–202], electromagnetic fields [203], etc. These phenomena are also important for applications, and constitute a promising area for future simulation studies, with the ever increasing computational power of the available computing resources.

Acknowledgment

We acknowledge financial support by the German Research Foundation (DFG) under Project Nos. NI 1487/2-1, NI 1487/4-2, and BI 314/24-2. S A E further acknowledges financial support from the Alexander von Humboldt Foundation. The authors gratefully acknowledge the computing time granted on the supercomputer Mogon at Johannes Gutenberg University Mainz (hpc.uni-mainz.de).

ORCID iD

Arash Nikoubashman @ https://orcid.org/0000-0003-0563-825X

References

[1] Ciferri A 1991 Liquid Crystallinity in Polymers: Principles and Fundamental Properties (New York: VCH Publishers)
[2] Ciferri A, Krigbaum W R and Meyer R B 1982 Polymer Liquid Crystals (New York: Academic)
[3] Donald A M, Windle A H and Hanna S 2006 Liquid Crystalline Polymers (Cambridge University Press: Cambridge)
[4] Chen R H 2011 Liquid Crystal Displays: Fundamental Physics and Technology (Weinheim: Wiley-VCH)
[5] Li Q 2012 Liquid Crystals Beyond Displays: Chemistry, Physics and Applications (New York: Wiley)
[6] de Gennes P G and Prost J 1995 The Physics of Liquid Crystals ed 2nd (Oxford: Clarendon)
[7] Brown G H and Wolen J J 1979 Liquid Crystals and Biological Structures (New York: Academic)
[8] Koster S, Weitz D A, Goldman R D, Aebi U and Herrmann H 2015 Curr. Opinion Cell Biol. 32 82
[9] Voth G A 2009 Coarse-Graining of Condensed Phase and Biomolecular Systems (Boca Raton: CRC Press)
[10] Palermo M F, Pizzirosso A, Muccioli L and Zannoni C 2013 J. Chem. Phys. 138 204901
[11] Sidky H, de Pablo J J and Whitner J K 2018 Phys. Rev. Lett. 120 107801
[12] Finkelmann H, in ref. 1, Chap. 8.
[13] Poier P, Egorov S A, Likos C N and Blaak R 2016 Soft Matter 12 7983
[14] Sato T and Teramoto A 1996 Adv. Polym. Sci. 126 85
[15] Hase M and Yoshikawa K 2006 J. Chem. Phys. 124 104903
[16] Reisner W, Pedersen J N and Austin R H 2012 Rep. Prog. Phys. 75 106601
[17] Binder K 1995 Monte Carlo and Molecular Dynamics Simulations in Polymer Science (New York: Oxford Univ. Press)
[18] Attig N, Binder K, Grahmüller H and Kremer K 2004 Computational Soft Matter: From Synthetic Polymers to Proteins (Jülich: NIC Directors, John von Neumann Institute for Computing)
[19] Fleer G J, Stuart M A C, Scheutjens J M H M, Cowie T and Vincent B 1993 Polymers at Interfaces (London: Chapman and Hall)
[20] Evans R 1979 Adv. Phys. 28 143
[21] Henderson D 1992 Fundamentals of Inhomogeneous Fluids (New York: Dekker)
Frenkel D and Eppenga R 1985 Phys. Rev. A 31 1776
Bates M A and Frenkel D 2000 J. Chem. Phys. 112 10034
Wilson M R and Allen M P 1993 Mol. Phys. 80 277
Kramarenko E Y, Winkler R G, Khalatbar P G, Kohkhlov A R and Reineker P 1996 J. Chem. Phys. 104 4806
Kamien R D and Grest G S 1997 Phys. Rev. E 55 1197
Cinacchi G and Gaetani L D 2008 Phys. Rev. E 77 051703
Naderi S and van der Schoot P 2014 J. Chem. Phys. 141 124901
Brelsford G L and Krigbaum W R, in ref. 1, p. 61.

[93] Frenkel D and Eppenga R 1985 Phys. Rev. A 31 1776
[94] Bates M A and Frenkel D 2000 J. Chem. Phys. 112 10034
[95] Wilson M R and Allen M P 1993 Mol. Phys. 80 277
[96] Kramarenko E Y, Winkler R G, Khalatbar P G, Kohkhlov A R and Reineker P 1996 J. Chem. Phys. 104 4806
[97] Kamien R D and Grest G S 1997 Phys. Rev. E 55 1197
[98] Cinacchi G and Gaetani L D 2008 Phys. Rev. E 77 051703
[99] Naderi S and van der Schoot P 2014 J. Chem. Phys. 141 124901
[100] de Braaf B, Menegon M O, Paquay S and van der Schoot P 2017 J. Chem. Phys. 147 244901
[101] Milchev A, Egorov S A, Nikoubashman A and Binder K 2018 J. Chem. Phys. 149 174909
[102] Milchev A, Nikoubashman A and Binder K 2019 Comput. Mat. Sci. 166 230
[103] Brelsford G L and Krigbaum W R, in ref. 1, p. 61.
[166] Silmore K S, Howard M P and Panagiotopoulos A Z 2017 Mol. Phys. 115 320
[167] Padmanabhan V, Kumar S K and Yethiraj A 2008 J. Chem. Phys. 128 124908
[168] Odijk T 1993 Macromolecules 26 6897
[169] Odijk T 1996 J. Chem. Phys. 105 1270
[170] Rudolph A S, Ratna R R and Kahn B 1991 Nature 352 52
[171] Fernández-Nieves A, Vitelli V, Utada A S, Link D R, Márquez M, Nelson D R and Weitz D A 2007 Phys. Rev. Lett. 99 157801
[172] Lopez-Leon T, Fernández-Nieves A, Nobili M and Blanc C 2011 Phys. Rev. Lett. 106 247802
[173] Lopez-Leon T, Koning V, Devaiah K, Vitelli V and Fernández-Nieves A 2011 Nature Phys. 7 391
[174] Gartrea J, Mulder P, Alvarado J, Dammore O, Aarts D, Lettinga M, Koenderink G and Mulder B 2016 Nature Commun. 7 12112
[175] Kornberg R D 1974 Science 184 868
[176] Bednar J, Horowitz R A, Grigoryev S A, Carruthers I M, Hansen J C, Koster A J and Woodcock C I 1998 Proc. Natl. Acad. Sci. USA 95 14173
[177] Olins D E and Olins A I 2003 Nat. Rev. Mol. Cell Biol. 4 809
[178] Earnshaw W and Harrison S 1977 Nature 268 598
[179] Cerritelli M, Cheng N, Rosenberg A, McPherson C and Steven A 1997 Cell 91 271
[180] Smith D E, Tans S J, Smith S B, Grimes S, Anderson D L and Bustamente C 2001 Nature 413 748
[181] Jiang W, Chang J, Jakana J, Weigle P, King J and Chiu W 2006 Nature 439 612
[182] Stoop N, Najafi J, Wittel F, Habibi M and Herrmann H 2011 Phys. Rev. Lett. 106 214102
[183] Marenduzzo D, Micheletti C, Orlandini E and Sumners D 2013 Proc. Natl. Acad. Sci. USA 110 20081
[184] Liang Q, Jiang Y and Chen J Z Y 2019 Phys. Rev. E 100 032502
[185] Nikoubashman A, Vega D A, Binder K and Milchev A 2017 Phys. Rev. Lett. 118 217803
[186] Milchev A, Egorov S A, Nikoubashman A and Binder K 2017 J. Chem. Phys. 146 194907
[187] Milchev A, Egorov S A, Nikoubashman A and Binder K 2018 Polymer 145 463
[188] Milchev A, Egorov S A, Vega D A, Binder K and Nikoubashman A 2018 Macromolecules 51 2002
[189] Khadikar M R and Nikoubashman A 2018 Soft Matter 14 6903
[190] Zhou X, Guo F, Li K, He L and Zhang L 2019 Polymers 11 1992
[191] Egorov S A, Milchev A, Vinrnap A and Binder K 2016 J. Chem. Phys. 144 174902
[192] Egorov S A, Milchev A and Binder K 2016 Polymers 8 296
[193] Egorov S A, Milchev A and Binder K 2017 Macromol. Theory and Simulations 26 1600036
[194] Milchev A, Egorov S A, and Binder K 2017 Soft Matter 13 1888
[195] Milchev A and Binder K 2017 Nano Lett. 17 4924
[196] Solar M, Binder K and Paul W 2017 J. Chem. Phys. 146 203308
[197] Xu X M et al 2014 ACS Nano 8 885
[198] Rowlinson J S and Widom B 1982 Molecular Theory of Capillarity (Oxford: Clarendon)
[199] Larson R G and Ottinger H C 1991 Macromolecules 24 6270
[200] Burghardt W R 1998 Macromol. Chem. Phys. 199 471
[201] Nikoubashman A and Howard M P 2017 Macromolecules 50 8279
[202] Xu X and Chen J 2017 ACS Macro Lett. 6 331
[203] Leferink op Reinink A B G M, van den Pol E, Petukhov A V, Vroege G J and Lekkerkerker H N W 2013 Eur. Phys. J. 222 3053

28