PREDICTING MOLECULAR PROPERTIES AND PHASE BEHAVIORS FOR CONJUGATED POLYMERS

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by
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Abstract

Conjugated polymers, though still outperformed by their inorganic counterparts, are promising materials for flexible electronics, including field-effect transistors and solar cells. The mechanical and electrical properties of this class of materials depend strongly on the morphological order. In order to design new materials and optimize existing polymers, establishing concrete links between fundamental molecular properties and structural order is necessary. As consequence, the ability to predict the properties of novel materials from their molecular structures is essential.

This dissertation focuses on predicting fundamental properties and phase behaviors of conjugated polymers from molecular structures. We develop tools and methods, combining molecular simulations and analytical theories, to predict material parameters, including the chain stiffness, the nematic coupling constant, and the Flory-Huggins $\chi$ parameter, for conjugated polymers. These fundamental parameters govern the mesoscale structures and phase behaviors for chains in melts and solutions, in turn affect the mechanical and electrical properties of conjugated polymers in the final semi-crystalline state.

Using molecular dynamics (MD) simulations, we also investigate the role of thermal fluctuations in the performance of crystalline conjugated polymers. We show that thermal fluctuations can lead to cumulative lattice disorder in conjugated polymers, in turn enhance the inter-chain charge transport. Because the fluctuations of crystal shape are related to the mechanical properties of conjugated polymers, we can also obtain the elastic moduli for crystalline conjugated polymers by measuring the fluctuating box sizes in MD simulations.

Altogether, this dissertation reports our progress on predicting the electrical and mechanical properties from molecular structures for conjugated polymers in both the precursor (melt and solution) and the crystalline states. Our results lay the foundation for understanding the structure-property relations of conjugated polymers in their final semicrystalline forms.
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Dedication

I dedicate this work to my parents and Xin.
Conjugated polymers are promising materials for stretchable and bendable electronic applications, including solar cells, field effect transistors and organic light-emitting diodes (OLED). The electronic properties and resulting device performance for conjugated polymers, however, are usually outperformed by their inorganic counterparts. Developing new polymers and optimizing existing materials are necessary. In this work, we apply molecular simulations and analytical theories to investigate and predict the molecular properties and phase behaviors that may affect charge transport in conjugated polymers. Being able to predict these properties from molecular structures can facilitate the development of novel materials.

1.1 Chain stiffness and conformations

Different from flexible conventional polymers, most conjugated polymers are semiflexible. The backbone stiffness, arising from electronic delocalization, bond angles, or steric interactions, can penalize the deflection of the backbone tangents, in turn leads to locally straight chain paths for conjugated polymers. Conformationally, conjugated polymers in melt and solution are worm-like chains, different from flexible polymers, which are often regarded as Gaussian coils.

The chain stiffness affects not only the chain conformations, but also many other behaviors of conjugated polymers, including the nematic phase behaviors, the interfacial alignment, and the mixing behaviors of inhomogeneous systems. The phase behaviors and molecular packing can significantly affect the structural order in the semicrystalline state and the resulting electronic properties for conjugated polymers. The ability to predict chain stiffness is therefore important for designing
novel conjugated polymers.

1.2 The nematic phase of conjugated polymers

Because of the anisotropic shapes of chain backbones, conjugated polymers may exhibit the nematic phase, in which chains tend to align uniaxially and remain translationally disordered. In concentrated solutions, semiflexible polymers behave like sequences of rigid rods that are dispersed in solvent. In melts, the stiff backbones of semiflexible polymers are dispersed by their flexible side chains, which act as “bound solvent”. At low concentrations, the backbone segments orient isotropically, maximizing the entropy of the system. At high enough concentrations, however, the isotropic phase is no longer entropically viable [1–3]. The concentrated semiflexible polymers can exhibit the nematic phase because randomly placing and orienting the rod-like segments would lead to many collisions of polymer backbones.

The nematic phase is important for a variety of applications, including displays, high strength fibers, microelectromechanical systems, and biomedical devices [4–7]. Moreover, as a precursor to crystallization, the nematic phase also enables better processing of conjugated polymers [8–11]. Crystallization from the nematic phase or other liquid crystalline phase may lead to large crystalline domains and ordered amorphous regions in the final semicrystalline state for conjugated polymers. The ordered final morphology may in turn enhance the electronic properties for these semiconducting materials. Establishing a relation between the nematic phase and molecular structure for conjugated polymers can be useful.

1.3 Interfacial alignment of semiflexible chains

Semiflexible polymers also exhibit different molecular packings at interfaces from conventional flexible polymers. Because the chain trajectories cannot bend sharply to avoid the collisions with impenetrable “walls”, semiflexible polymers tend to align parallel to impenetrable surfaces, creating an alignment layer of thickness about a persistence length [12–15].

For flexible electronics, chain alignment at polymer-polymer interfaces or polymer-substrate interfaces is essential for charge transfer and overall device performance. For example, ordered donor-acceptor interfaces may promote mobil-
ity of separated electrons and holes, resulting in enhanced efficiency for polymer photovoltaics [16,17]. Chain alignment near the gate dielectric can also enhance charge mobility because the charge carriers are strongly localized in the alignment layer as a result of the applied gate voltage in organic field effect transistors [18–23]. The charge transport may be enhanced in the aligning direction for chains in the alignment layer. As a consequence, systematic investigations of the interfacial alignment as a function of chain stiffness, nematic interactions, and molecular weight is helpful for establishing the structure-property relationship of conjugated polymers.

1.4 Mixing behaviors for inhomogenous systems

Many applications, including block copolymer solar cells and stretchable field-effect transistors, rely on blending properties of different polymers [16,24,25]. The performance of the devices depends on the mixing behaviors of different species in the active materials, which are governed by the Flory-Huggins $\chi$ parameter. Being able to accurately predict $\chi$ from molecular structure is critical for designing inhomogeneous polymers for novel applications.

Although $\chi$ can be measured experimentally, predicting $\chi$ from molecular structures has always been a challenge for the polymer community. The free energy parameter depends on many factors, including mismatch in enthalpic interactions and chain stiffness of different polymers. In principle, $\chi$ can be obtained from molecular simulations. Current methods for computing $\chi$ from simulations, however, are usually limited to system with rather large $\chi$ or associated with large errors. Developing new approach for predicting $\chi$ is desirable for not only conjugated polymers, but also other polymer classes.

1.5 Crystalline conjugated polymers

The ability to predict the properties of crystalline conjugated polymers is also important. The charge conductivity in the crystalline domains sets the upper limit of performance for electronics [26]. The mechanical properties, such as elastic modulus, governs the suitability of conjugated polymer for bendable and stretchable devices [24,25].
For the charge conductivity, local order is critical. Conformational and configurational disorder can affect charge delocalization, in turn lead to localized trap states in these materials. Although small conjugated molecules can be well-ordered, many conjugated polymers exhibit significant disorder [26]. Even in the crystalline regions, where conformational disorder may be negligible, conjugated polymers can have lattice disorder.

In fact, the lattice disorder may arise from processing and chemical defects, impurities, and even thermal fluctuations, because crystalline conjugated molecules are only weakly bonded by Van der Waals interactions.

Revealing the lattice disorder induced by thermal fluctuations and the resulting effect on charge mobility using simulations may help us understand the charge transfer events in crystalline conjugated polymers.

Extracting the mechanical properties for crystalline conjugated polymers from simulations is also helpful. Because most conjugated polymers are semicrystalline, measuring the mechanical properties only for the crystalline chains experimentally is challenging. Being able to obtain the mechanical properties of the crystalline molecules from simulations can help us understand the overall ability for conjugated polymers to withstand stretching and bending.

\section*{1.6 Objectives and outline}

In this dissertation, I report our progress on predicting molecular properties and phase behaviors for conjugated polymers. We use atomistic simulations to reveal detailed behaviors and structures for realistic conjugated polymers, such as poly(3-hexylthiophene) (P3HT) in melt and crystalline form. Coarse-grained simulations and analytical theories are employed to bridge the time and length scale between atomistic simulations and experiments.

In Chapter 2, I describe a numerical and an analytical tool we develop for predicting the chain stiffness and dimensions for semiflexible polymers from their chemical structures.

In Chapter 3, we discuss a method that combines self-consistent field theory (SCFT) with atomistic molecular dynamics (MD) simulations for extracting the nematic coupling parameter $\alpha$ of conjugated polymers from their chemical structures. Using $\alpha$, a variational free energy can be constructed to locate the isotropic-to-
nematic (IN) phase transition.

In Chapter 4, we demonstrate how chain stiffness and the nematic coupling parameter $\alpha$ can affect the interfacial alignment for conjugated polymer. A lattice version of SCFT is developed to predict the behaviors of semiflexible chains near planar interfaces. We validate our prediction by comparing the SCFT results to coarse-grained simulations of semiflexible bead-spring chains.

Chapter 5 reports the isotropic-to-nematic phase boundary for semiflexible chains in the $\phi - N_p$ plane, where $\phi$ is the volume fraction and $N_p$ is the persistence measured in numbers of monomers. The phase boundary is obtained using surface-induced nematic ordering in molecular dynamics simulations.

In Chapter 6, I discuss how nematic order can affect charge transport for conjugated polymers with the help of an analytical model.

In Chapter 7, we introduce a general method, based on a novel thermodynamic integration scheme, for accurately predicting the Flory-Huggins $\chi$ parameter for inhomogeneous polymers.

Chapter 8 includes the atomistic simulation results for crystalline poly(3-hexylthiophene) (P3HT). We show that thermal fluctuations can induce cumulative lattice disorder for P3HT. The cumulative lattice disorder can in turn enhance the inter-chain charge transport in the crystalline P3HT.

Chapter 9 reports the elastic modulus of crystalline P3HT, obtained from isothermal-isostress ($N\sigma T$) simulations of crystalline P3HT.

Chapter 10 summarizes the dissertation and discusses the possible future research directions.
Chapter 2  
Predicting chain stiffness and dimensions

We develop a numerical and an analytical approach to estimate the persistence length $l_p$ and mean-square end-to-end distance $\langle R^2 \rangle$ of complex semiflexible polymers. Numerically, $l_p$ and $\langle R^2 \rangle$ are determined by averaging a large set of single chain conformations with the correct dihedral angle distributions $p(\phi_i)$. Analytically, $l_p$ and $\langle R^2 \rangle$ are extracted from the tangent-tangent correlation function. We apply both approaches to two semiflexible conjugated polymers, poly(3-hexylthiophene) (P3HT) and poly-((9,9-dioctylfluorene)-2,7-diyl-alt-[4,7-bis(thiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl) (PFTBT). Results obtained via the two methods agree for polymers with any degree of polymerization $N$. Our methods can be applied to any semiflexible polymers with any number of distinct moieties. The results shown in this chapter has been published on *Macromolecules* [27].

2.1 Introduction

Many properties of polymer materials are governed by the stiffness of chains. For example, the flow behavior of entangled polymers depends on the backbone stiffness. In entangled polymer melts and solutions, each chain is confined into a tube-like region and its motion is restricted along the tube axis [28]. The effect of confinement can be characterized by the tube diameter, which is related to the chain stiffness [29–31]. Molecular packing of polymer blends or block copolymers at interfaces and in mesophases is also affected by chain stiffness, which governs the energy cost to make an excursion into the opposite phase [12,32,33]. Moreover,
the critical concentration at which long-chain molecules undergo an isotropic to nematic transition depends on the chain stiffness [2].

The persistence length $l_p$, which describes the stiffness of backbone segments, is the most important dimensional property of semiflexible polymers. $l_p$ is the characteristic length scale for the exponential decay of the backbone tangent-tangent correlation functions. When $l_p$ is comparable to the monomer size, the polymer behaves as a flexible coil. If $l_p$ is considerably larger than a monomer, the polymer is semiflexible. The value of $l_p$ also determines the regimes of different statistical behaviors of single chain conformations. When the chain contour length $L$ is much shorter than $l_p$, a polymer behaves like a rigid rod with a mean-square end-to-end distance $\langle R^2 \rangle$ equal to $L^2$. In the flexible regime ($L$ much larger than $l_p$), a semiflexible polymer can be regarded as a random walk of Kuhn segments of length $l_k$ ($l_k = 2l_p$), with a mean-square end-to-end distance equal to $Ll_k$. [34]. In the semiflexible regime ($L$ is comparable to $l_p$), polymers can be described by the worm-like chain (WLC) model [35].

Many functional polymers are semiflexible for chain lengths at which they are commonly used and studied. Examples include polymers with side-chain induced helical conformations such as poly(n-hexyl isocyanate) and poly($\gamma$-benzyl-L-glutamate) [36], biomolecules such as DNA and proteins, and conducting conjugated polymers such as poly(3-hexylthiophene) (P3HT) and poly-((9,9-dioctyfluorene)-2,7-diyl-alt-[4,7-bis(thiophen-5-yl)-2,1,3-benzothiadiazole]-2′,2′′-diyl) (PFTBT).

It is useful to be able to estimate the persistence length $l_p$ analytically or numerically, from which many interesting macroscopic properties of semiflexible functional polymers, such as tube diameters and morphologies, can be predicted. For example, we are interested in diblock copolymers of P3HT-b-PFTBT for organic photovoltaics. Guo et al. have demonstrated an efficiency near 3% for P3HT-b-PFTBT block copolymer solar cells, while only about 1% efficiency is achieved for devices composed of physical bends of P3HT and PFTBT homopolymers [16]. The efficiency improvement is associated with the self-assembly of the block copolymers in the OPV active layer, which depends on the chain stiffness and bulkiness of P3HT and PFTBT.

Although persistence length can be obtained via molecular dynamic (MD) simulations, atomistic simulations of equilibrated semiflexible polymer melts are computationally expensive. Furthermore, appropriate force field parameters must
be developed before simulating novel materials.

The hindered rotation (HR) model [37,38] has been used to estimate \( l_p \). The averaged chain dimensions are governed by the rotations of backbone dihedral angles \( \phi \), which are “hindered” by the dihedral potential \( U(\phi) \). The dihedral potential \( U(\phi) \) can be computed using density functional theory (DFT). Dihedral angle correlations are excluded in the HR model, and steric interactions between consecutive moieties are neglected once the dihedral potential has been determined. Thus, the HR model works better for semiflexible chains, where steric self-interactions are geometrically restricted.

The HR model can be simplified to the rotational isometric state (RIS) model by considering only discrete states for the dihedral angles, which is a valid approximation when isomeric states are narrow and well-defined [39]. To estimate \( l_p \), the mean-square end-to-end distance \( \langle R^2 \rangle \) of a long polymer is equated to the corresponding result for a freely jointed chain of step length \( l_k = 2l_p \). A recent application of the RIS model estimated the persistence length of P3HT in a dilute marginal solvent at room temperature to be 3.2 nm [40]. The trans and cis probabilities are determined from the corresponding potential energy difference, obtained from DFT studies of thiophene dimers [41,42].

Unfortunately, the HR and RIS models are limited in their ability to estimate chain dimensions of semiflexible macromolecules. The two models are easily applied only to polymers with a single type of backbone segment. Moreover, the HR model can only estimate chain dimensions in the limit of long chains, for which semiflexible chains behave as Gaussian random walks. More general approaches are needed for estimating chain dimensions of conjugated polymers or biopolymers at chain lengths for which worm-like chain behavior is expected.

Here, we present two approaches to estimate \( l_p \) and \( \langle R^2 \rangle \) of semiflexible polymers from their dihedral potentials and monomer geometries. In the first approach, we numerically average the backbone conformations of a single polymer by generating sets of dihedral angles according to the Boltzmann distribution. In the second approach, we analytically compute the backbone tangent-tangent correlation functions for a single chain using transformation matrices, which relate the average orientation of successive backbone vectors, given fixed deflection angles and Boltzmann-averaged dihedral angles. Multiple types of backbone moieties, with different deflection angles and dihedral angles are allowed in this approach.
We estimate the chain dimensions for P3HT and PFTBT as examples of polymers with a single type of backbone segment or multiple types of backbone segments, respectively. The results obtained using our numerical and analytical methods agree well with each other for chain lengths in both the semiflexible and flexible regimes.

This chapter is organized as follows. 1) We review the assumptions, approaches, and limitations of the HR model. 2) Our numerical averaging technique to determine persistence lengths and mean-square end-to-end distances is presented. 3) We introduce our analytical approach for estimating the tangent-tangent correlation function. From the tangent-tangent correlation function, $l_p$ can be extracted and $\langle R^2 \rangle$ can be computed via the WLC model. 4) We compare and discuss the two approaches, applied to regioregular P3HT and PFTBT.

### 2.2 Hindered Rotation model

In the HR model, dihedral angles $\phi$ are assumed to be independent of each other, and the dihedral probability distribution $p(\phi)$ is determined by the Boltzmann factor $e^{-\beta U(\phi)}$, with $U(\phi)$ the corresponding dihedral potential:

$$p(\phi) = \frac{e^{-\beta U(\phi)}}{2\pi \int_0^\pi e^{-\beta U(\phi')}d\phi'}$$  \hspace{1cm} (2.1)

This assumption is appropriate for stiff macromolecules, where the steric interactions between successive monomers are geometrically restricted.

A polymer backbone is represented as a sequence of backbone displacement vectors $\mathbf{r}_i$ with fixed length $l$. The deflection angles $\theta_i$ between successive backbone vectors $\mathbf{r}_i$ and $\mathbf{r}_{i-1}$ are likewise fixed at a constant value. Each backbone vector can be rotated by a dihedral angle $\phi_i$ (Figure 2.1). All dihedral angles $\phi_i$ have the same distribution (eqn 2.1).

We define a local coordinate system for each bond $\mathbf{r}_i$, in which $\hat{x}$ points along the bond, $\hat{z}$ points along $\mathbf{r}_i \times \mathbf{u}_{i-1}$, and $\hat{y} = \hat{z} \times \hat{x}$. Transfer matrix $T_i$ relates the components $\mathbf{v}^{(i+1)}$ of a given vector $\mathbf{v}$ in the $(i+1)$st coordinate system, to its components $\mathbf{v}^{(i)}$ in the $i$th coordinate system, by $\mathbf{v}^{(i+1)} = T_i \cdot \mathbf{v}^{(i)}$. The transformation

9
matrix $T_i$ is written as:

$$
T_i = \begin{pmatrix}
\cos \theta & \sin \theta & 0 \\
-\sin \theta \cos \phi & -\cos \theta \cos \phi & \sin \phi \\
-\sin \theta \sin \phi & -\cos \theta \sin \phi & -\cos \phi
\end{pmatrix}
$$

(2.2)

Here $\theta$ and $\phi$ are the deflection and dihedral angles of the (i+1)st bond.

Hence the components of the $n$th tangent vector in the coordinate system of the first tangent vector are $T_1 \cdot T_2 \cdot ... \cdot T_{n-1} \cdot \hat{x}$, and the inner product $v_1 \cdot v_n$ can be written as:

$$
v_1 \cdot v_n = \hat{x} \cdot \prod_{i=1}^{n-1} T_i \cdot \hat{x}
$$

(2.3)

Using the transformation matrix $T$, the mean-square displacement $\langle R^2 \rangle$ can be calculated:

$$
\langle R^2 \rangle = \langle (\sum_{i=1}^{n} r_i^2)^2 \rangle
$$

$$
= nl^2 + 2 \sum_{i=1}^{n} \sum_{j=1}^{i-1} \langle r_i^2 \cdot r_j^2 \rangle
$$

(2.4)

$$
= nl^2 + 2l^2 \hat{x} \cdot \sum_{i=1}^{n} \sum_{k=1}^{i-1} \langle T \rangle^k \cdot \hat{x}
$$

This expression can be further simplified and evaluated exactly for a finite chain length $n$ using eigenvectors and eigenvalues of $T$ (see Appendix A). When $n$
approaches infinity, we reach the final expression of the hindered rotation model:

$$\langle R^2 \rangle = nl^2 \frac{(1 + \cos \theta)(1 + \langle \cos \phi \rangle)}{(1 - \cos \theta)(1 - \langle \cos \phi \rangle)} \equiv C_\infty nl^2$$ \hfill (2.5)

where $C_\infty$ is the characteristic ratio.

In the large $n$ limit, the persistence length $l_p$ can be calculated by equating $\langle R^2 \rangle$ to the result $2nll_p$ for a random walk of freely-joint Kuhn segments:

$$l_p = \frac{l (1 + \cos \theta)(1 + \langle \cos \phi \rangle)}{2 (1 - \cos \theta)(1 - \langle \cos \phi \rangle)} = \frac{C_\infty l}{2}$$ \hfill (2.6)

The HR model is well suited for its original purpose of estimating end-to-end dimensions of long polyolefin polymers. For such molecules, the length $l$ and deflection angle $\theta$ of backbone units are roughly fixed, and all backbone segments can be rotated by the dihedral angle $\phi$.

The HR model can also be used to estimate chain dimensions of semiflexible polymers with a single type of aromatic backbone unit, such as P3HT. Along the polymer backbone, the dihedral angle $\phi$ between the planes of adjacent aromatic rings can be rotated around an inter-moiety bond. As a consequence, the polymer backbone can be represented as a sequence of effective segments by extending and connecting the inter-moiety bonds.

The HR model, however, cannot accurately describe chain dimensions of semiflexible polymers with multiple types of backbone units. Polymers of this sort of architecture are critical to tuning the electronic and structural properties of organic photovoltaics by "blending" the behaviors of different moieties. Eqn 2.5 and 2.6 are not applicable to polymers with multiple types of backbone segment lengths $l_i$, deflection angles $\theta_i$ and dihedral distributions $p(\phi_i)$.

To overcome this limitation of the HR model, we define a more complex transfer matrix $T_r$ to describe the orientations of repeat units in our analytical approach (see below). We use $T_r$ to compute the orientational correlation functions of backbone tangents, from which the persistence lengths can be obtained. From the analytical correlation function, we can also determine the mean-square end-to-end distance $\langle R^2 \rangle$ by comparison with the worm-like chain model assuming an effective repeat unit size and an average deflection angle.
2.3 Numerical averaging

In this section, we present an efficient numerical approach for estimating $l_p$ and $\langle R^2 \rangle$ of semiflexible polymers, by numerically averaging backbone conformations over a set of suitably generated random dihedral angles. This approach allows us to estimate the chain dimensions of any semiflexible polymer, including polymers with multiple dihedral potentials and multiple types of segments. Each backbone conformation corresponds to a set of dihedral angles $\phi_i$, randomly generated from a dihedral distribution $p(\phi)$. Our numerical averaging technique is essentially a stochastic integration ($\int p(\phi_1)p(\phi_2)\ldots p(\phi_n)d\phi_1d\phi_2\ldots d\phi_n$) rather than a numerical simulation.

To generate dihedral angles $\phi_i$ according to the Boltzmann distribution $p(\phi_i)$ (eqn 2.1), the cumulative dihedral probability $p^c(\phi_i)$ is defined as:

$$p^c(\phi) = \int_0^\phi p(\phi')d\phi'$$

(2.7)

Random values of $\phi$ with distribution $p(\phi)$ can be obtained by applying the inverse function $\phi(p^c)$ to uniformly distributed values of $p^c$ on the interval $[0, 1]$. The inverse function $\phi(p^c)$ can be constructed by interpolating a table of values $\{\phi_i, p^c(\phi_i)\}$ [43]. For each set of dihedral angles $\phi_i$, the corresponding conformation is generated by rotating the polymer backbone to the value $\phi_i$ starting from a trans conformation. During dihedral rotations, all deflection angles $\theta_i$ are fixed.

The tangent-tangent correlation function $\langle \mathbf{v}_0 \cdot \mathbf{v}_n \rangle$ of polymer backbones can be computed from single chain conformations. $\mathbf{v}_0$ and $\mathbf{v}_n$ represent the orientations of the backbone tangent vector of monomer 0 and monomer $n$, respectively. The correlation function $\langle \mathbf{v}_0 \cdot \mathbf{v}_n \rangle$ is averaged over many single chain conformations, resulting in an exponential decay for $\langle \mathbf{v}_0 \cdot \mathbf{v}_n \rangle$, from which persistence lengths $l_p$ can be determined.

We extract the persistence length as characteristic exponential decay of $\langle \mathbf{v}_0 \cdot \mathbf{v}_n \rangle$ with:

$$\langle \mathbf{v}_0 \cdot \mathbf{v}_n \rangle = e^{-n/N_p} \quad (n = 0, 1, \ldots N - 1)$$

(2.8)

where $N$ is the number of repeat units along polymer backbone and $N_p$ is the persistence length measured in repeat units. The persistence length in dimensional
units $l_p$ is estimated as $N_p \alpha$, in which $\alpha$ is the length of a repeat unit along the undeflected all-trans conformation. The mean-square end-to-end distance $\langle R^2 \rangle$ is likewise determined by averaging squared end-to-end distances of the numerically generated conformations.

While the conventional HR model can only estimate $\langle R^2 \rangle$ for long polymers with single type of repeat units as $C_{\infty}n_l^2$ (eqn 2.5), our numerical estimation of $\langle R^2 \rangle$ can handle multiple backbone segment lengths $l_i$ and deflection angles $\theta_i$, as well as arbitrary chain lengths. This is particularly useful for chains in the semiflexible regime, and architectures of current semiconducting polymers.

2.4 Analytical approach

Now, we compute analytically the tangent-tangent correlation function $\langle v_0 \cdot v_n \rangle$ for polymer backbones with various step sizes and dihedral potentials. This approach makes the same assumptions as in the HR model. Namely, deflection angles $\theta_i$ are fixed, and dihedral angles are assumed to be uncorrelated, governed only by the potential $U(\phi)$ (eqn 2.1). From the tangent-tangent correlation function $\langle v_0 \cdot v_n \rangle$, we extract the persistence length $N_p$ (and $l_p$). We also approximate an effective deflection angle $\theta_e$ from $\langle v_0 \cdot v_n \rangle$ and define an effective monomer size $\alpha_e$ (described below). The mean-square end-to-end distance $\langle R^2 \rangle$ can be determined via correspondence with the worm-like chain model.

Effective backbone vectors for each monomer are defined by extending and intersecting inter-moiety bonds for polymers with planar repeat units (see Figure 2.2). The dihedral angles between two adjacent rings can be rotated around the effective vectors. These effective backbone vectors capture the hindered rotations of dihedral angles and the lengths of successive rigid backbone units. The molecular geometries of P3HT and PFTBT are shown in Figure 2.2 as examples of how effective backbone vectors are defined. For the case of PFTBT, the bonds connecting thiophene and benzothiadiazole are almost parallel. Thus, a single vector (shown as dotted arrow in Figure 2.2b) is used to simplify later calculations.

The tangent-tangent correlation function $\langle v_0 \cdot v_n \rangle$ can be computed for polymers with a single type of repeat unit (such as P3HT) by using the transformation matrix
Figure 2.2. Backbone units and effective tangent vectors of P3HT (a) and PFTBT (b). Side chains removed for clarity. Effective tangent vector $r$ (dashed), deflection angle $\theta$, and dihedral angle $\phi$ for P3HT. $\theta_0$ is deflection angle between inter-moiety bond and ring tangent of P3HT. Three effective vectors $r_1$, $r_2$, and $r_3$, and two types of dihedral angle $\phi_A$ and $\phi_B$ for PFTBT. The choices of tangents agree in both analytical and numerical approaches. Effective tangent vectors (for analytical approach) are extensions of inter-moiety vectors (for numerical approach).

$T$ (eqn 2.2):

$$\langle v_0 \cdot v_n \rangle = \hat{x} \cdot T^n \cdot \hat{x}$$

$$= \sum_{\alpha=1}^{3} \lambda_\alpha^n (\hat{x} \cdot \hat{e}_\alpha)^2 \approx e^{n \ln \lambda_1} (\hat{x} \cdot \hat{e}_1)^2$$  \hspace{1cm} (2.9)

where $\lambda_\alpha$ and $\hat{e}_\alpha$ are the eigenvalues and eigenvectors of $T$. $\lambda_1$ and $\hat{e}_1$ in eqn 2.9 are the largest eigenvalue and the corresponding eigenvector, which dominates for large $n$. The length scale of exponential decay of $\langle v_0 \cdot v_n \rangle$ equals $N_p$ (eqn 2.8). From eqn 2.9 it is evident that for large $n$, we have an exponential decay with $N_p = (\ln(1/\lambda))^{-1}$.

The transformation matrix $T$ (eqn 2.2) and the result shown in eqn 2.9 cannot describe polymers with multiple types of backbone units, such as PFTBT (Figure 2.2b) or random copolymers. Such polymers contain multiple types of deflection angles $\theta_i$ and dihedral angles $\phi_i$. To compute the tangent-tangent correlation function $\langle v_0 \cdot v_n \rangle$ for such systems, we define the monomer transformation matrix $T_r$, which relates the orientation of the first tangent vector $v_n$ of monomer $n$ to the first tangent vector $v_{n-1}$ of the previous monomer $n - 1$. $T_r$ is given as a product
of transformations for each dihedral in the monomer:

\[ T_r = \prod_{j=1}^{n_d} T_j \]  

(2.10)

where \( T_j \) is the transfer matrix for rotating dihedral angle \( \phi_j \) and \( n_d \) is the number of dihedral angles per repeat unit. The correlation function \( \langle v_0 \cdot v_n \rangle \) can be written in terms of \( T_r \) as before (eqn 2.9). From the tangent-tangent correlation function, \( N_p \) is extracted using eqn 2.8.

Mean-square end-to-end distances \( \langle R^2 \rangle \) of polymers consisting of a single type of effective vectors are estimated using the worm-like chain model (WLC). For a polymer with single repeat unit and one type of dihedral angle such as P3HT, the mean-square end-to-end distance can be approximately calculated by assuming that the tangent-tangent correlation function is purely exponential, \( e^{-n/N_p} \). The stochastic end-to-end vector \( R \) can be written \( R = \alpha \int d n v_n \), and thus \( \langle R^2 \rangle \) computed as the usual WLC result:

\[
\langle R^2 \rangle = \alpha^2 \int_0^N dn \int_0^N \langle v_n \cdot v_n' \rangle dn' \\
= 2NN_p\alpha^2 \left[ 1 - \frac{N_p}{N} (1 - e^{-N/N_p}) \right] 
\]

(2.11)

\[ \alpha \]

\[ r_n \]

\[ r_m \]

\[ \theta_e \]

\[ \theta_e/2 \]

\[ \alpha \]

\[ r_n^e \]

\[ r_m^e \]

\[ \alpha_e \]

\[ \theta_e \]

Figure 2.3. PFTBT backbone units (a) and effective monomer vectors (b). Side chains removed for clarity. (a): effective vectors \( r_n \) (solid arrows), and monomer end-to-end vector \( r_m^n \) (dashed arrow). (b): effective monomer vectors \( r_m^e \) (dashed arrows) with length \( \alpha_e \), monomer end-to-end vector \( r_m^m \) (solid arrow connectng centers of successive \( r_m^e \)) with length \( \alpha \), and deflecting angle \( \theta_e \).
We define an effective monomer size $\alpha_e$ and deflection angle $\theta_e$ to estimate $\langle R^2 \rangle$ for complex polymers. Because the end-to-end monomer vectors $r_m$ are not the same as the backbone vectors $r_n$ used to construct the generalized HR model (see Figure 2.3a), the monomer size $\alpha$ cannot be directly used in the worm-like chain model (eqn 10). Instead, we represent the polymer as freely rotating “effective monomers”. The “effective monomers” are constructed by extending and connecting the effective backbone vectors. Because the tangent-tangent correlation decays by $e^{-1/N_p}$ over the length of one monomer, the deflection angle $\theta_e$ is defined as $\cos^{-1}(e^{-1/N_p})$. PFTBT is shown in Figure 2.3 as an example of defining an effective monomer. The size of the effective monomer $\alpha_e$ is computed as:

$$\alpha_e = \frac{\alpha}{\cos(\theta_e/2)} \quad (2.12)$$

By replacing $\alpha$ with $\alpha_e$ in eqn 2.11, $\langle R^2 \rangle$ can be estimated for semiflexible polymers with multiple types of monomer segments.

### 2.5 Results and discussion

#### 2.5.1 P3HT chain dimensions

We compute the dihedral potential $U(\phi)$ of a 3-methylthiophene (3MT) tetramer (Figure 2.4) via DFT calculations to study the chain conformations of P3HT. As demonstrated by Darling and Sternberg, the potential of the central dihedral angle in a 3-alkylthiophene (3AT) tetramer can sufficiently represent the torsional disorder of P3AT [41]. We replace the side chains of P3HT by methyl groups, both to reduce the DFT computational cost and to eliminate spurious contributions to $U(\phi)$ from colliding side chains of a single oligomer in vacuum, which we expect will be largely screened away in a melt. The dihedral potential $U(\phi)$ of 3MT tetramer is calculated using a rigid (non-optimized) scan of the dihedral angle after optimization of the molecular geometry. All our DFT calculations are done using Gaussian 09 with the B3LYP functional and 6-31G*(d,p) basis set.

The computed dihedral potential $U(\phi)$ has its global minimum at the trans state ($0^\circ$ and $360^\circ$) and a local minimum at the cis state ($180^\circ$). We define the trans state as the conformation in which the sulfur atoms on adjacent rings point in
Figure 2.4. Dihedral potential of 3MT tetramer ($\phi$) and effective dihedral potential of P3HT 20 mer from MD simulation (+). $0^\circ$ is defined as the planar conformation with S atoms on opposite sides (trans). Potentials are fitted to $U(\phi) = \sum_{i=0}^{5} c_i \cos^i(\phi)$ (dashed curve for 3MT and solid curve for P3HT).

opposite directions. The energy difference between the trans and cis states is about 4 kJ/mol, very similar to the 3 kJ/mol trans-gauche difference for polyethylene [44].

The dihedral potential $U(\phi)$ obtained from DFT calculations is not identical in principle to the effective dihedral potential $U_{eff}(\phi)$ for P3HT. As we have described, $U(\phi)$ is computed for a single chain of 3MT tetramer in the gas phase, whereas interactions between molecules including Lennard-Jones attractions and steric repulsions contribute to $U_{eff}(\phi)$. The effective dihedral potential can be determined using MD simulations of polymer chains in isotropic phases, by converting the observed dihedral distribution to $U_{eff}(\phi)$ using Boltzmann factors (inverse of eqn 2.1). However, MD simulations are relatively expensive compared to single chain DFT calculations in the gas phase.

To assess the validity of approximating $U_{eff}(\phi)$ by $U(\phi)$, we compare the dihedral potential $U(\phi)$ of P3HT obtained via DFT calculations with NPT simulation results. The force field parameters we used in simulating P3HT melts were developed by Huang and coworkers. [45,46] $U(\phi)$ and $U_{eff}(\phi)$ from our MD simulation (at 700K, in the isotropic phase) agree reasonably well for P3HT (Figure 2.4), though the local and global minimums of the effective dihedral potential $U_{eff}(\phi)$ both deviate from those in $U(\phi)$ (trans and cis states) by roughly $30^\circ$. 
To apply our numerical approach, the dihedral potential $U(\phi)$ is converted to a dihedral distribution $p(\phi)$ via eqn 2.1 (Figure 2.5a), with a temperature of 700K (we chose this rather high temperature for comparison to our MD simulations, for which P3HT melts readily to an isotropic phase). The corresponding cumulative dihedral distribution $p_c(\phi)$ is then calculated with eqn 2.7 (Figure 2.5b).

The tangent-tangent correlation functions $\langle v_0 \cdot v_n \rangle$ for a chain of 25 monomers is numerically averaged over a large number of conformations until the correlation function converges: over 10,000 backbone conformations were used (see Figure 2.6). The numerical calculation is done on a workstation using Mathematica with a computation time of 1 minute. The Mathematica notebook can be found in the Supporting Information.

To apply the analytical method, we define the effective backbone vectors of P3HT by extending the inter-thiophene bonds. The vectors connecting successive intersections are defined as the effective vectors $r$ (see Figure 2.2a). The length $l$ and deflection angle $\theta$ of the effective vectors are obtained using the inter-monomer
Figure 2.6. Tangent-tangent correlation function $\langle v_0 \cdot v_n \rangle$ of P3HT vs. repeat unit $n$, by numerical averaging (circles), and analytical calculation (solid curve).

bond length $l_1$ of P3HT, width of thiophene ring $l_2$, and the deflecting angle $\theta_0$ between the thiophene backbone tangent and the inter-monomer bond. After some geometry calculations, we find $l = l_1 + l_2 / \cos \theta_0$ and $\theta = 2 \theta_0$.

The tangent-tangent correlation function $\langle v_0 \cdot v_n \rangle$ is computed analytically via eqn 2.9, from which we estimate $N_p$ as 10.0 repeat units. The numerical and analytical results for the correlation functions are in excellent agreement (see Figure 2.6). With the length of a P3HT monomer $\alpha$ taken as 0.4 nm, the persistence length $l_p$ is estimated as 4.0 nm.

Our estimated persistence length for P3HT is somewhat larger than experimentally measured values. Heffner and Pearson inferred the persistence length of P3HT to be 2.4 nm from dilute solution light scattering [47]. More recently, McCulloch and coworkers measured the persistence length of P3HT to be 3.0 nm in dilute marginal solvent with small angle neutron scattering (SANS) [40].

Our relatively large value for $l_p$ reflects our use of the dihedral potential $U(\phi)$ of a 3MT tetramer, as an approximation of the true effective potential $U_{eff}(\phi)$. In Figure 2.4 we see that $U_{eff}(\phi)$ is somewhat softer than $U(\phi)$, presumably because of the effects of steric interactions between different chains and their side groups. Of course, $U_{eff}(\phi)$ derived from MD simulation reproduce the persistence length of the simulated chains (assuming the dihedral angles are largely uncorrelated along a chain, which we observe to be true). Indeed, the persistence length of
P3HT obtained from our simulation at 700K (where P3HT is isotropic) is 3.2 nm. Still, our value for \( l_p \) from the DFT-derived \( U(\phi) \) alone is reasonably close, and inexpensive to obtain.

The mean-square end-to-end distance \( \langle R^2 \rangle \) of P3HT can be likewise estimated numerically by averaging its value over many different conformations. The resulting \( \langle R^2 \rangle \) are shown in Figure 2.7 for P3HT with \( N \) varying from 1 to 25 (these results were generated in about 10 minutes on a workstation).

![Figure 2.7. Mean-square end-to-end distance \( \langle R^2 \rangle \) of P3HT vs. number of repeat units \( N \). From numerical averaging (circles), analytical calculation (solid curve), and large \( N \) limit of HR model (dot-dashed line for \( N > 2N_p \)).](image)

We estimated \( \langle R^2 \rangle \) analytically using the worm-like chain model (eqn 2.11) with our value of \( N_p = 10 \). \( \langle R^2 \rangle \) of P3HT are estimated with various degrees of polymerization \( N \) (shown in Figure 2.7). The results obtained via the numerical averaging approach and the analytical approach agree well with each other over a range of backbone lengths, from the rigid rod limit (small \( N \)) to the flexible regime (when \( N \) is greater than roughly two \( N_p \)). In the flexible regime, \( \langle R^2 \rangle \) obtained via our numerical and analytical methods scale with \( N \), with prefactors close to the value of \( C_\infty \alpha^2 \) (from the HR model, eqn 2.5).

### 2.5.2 PFTBT chain dimensions

Two types of dihedral angles must be considered in estimating the chain dimensions of PFTBT. Type A dihedral angle is between thiophene and benzothiadiazole moities
and the type B dihedral angle is between adjacent thiophene and fluorene groups (see Figure 2.2b). The dihedral potentials are calculated with the same procedures, functional, and basis set as we used for computing the dihedral potentials of the 3MT tetramer. Dimers are used and side chains are removed to reduce computational cost. The two dihedral potentials are shown in Figure 2.8. The corresponding dihedral distributions and cumulative dihedral distributions (computed at 700K for isotropic PFTBT) are shown in Figure 2.9.

![Figure 2.8.](image)

**Figure 2.8.** Two types of dihedral potential of PFTBT. Type A (circles) for the thiophene-benzothiadiazole dihedral angle. Type B (triangles) for the thiophene-fluorene dihedral angle (0° is trans and 180° is cis). Potentials are fitted to $U(\phi) = \sum_{i=0}^{5} c_i \cos^i (\phi)$ (dashed curve for A and solid curve for B).

Type A dihedral angle has a global minimum at the trans state (0° and 360°), where sulfur on thiophene and sulfur on benzothiadiazole are oriented in opposite directions, and a second local minimum at the cis state (180°), where sulfurs on thiophene and benzothiadiazole point in the same direction. The dihedral potential is qualitatively similar to the dihedral potential of a 3MT tetramer. The trans-cis energy difference is about 3 kJ/mol, again comparable to the trans-gauche difference for polyethylene.

Type B dihedral angle exhibits a trans minimum potential at about 30° (rather than at 0° as for P3HT) where the sulfur on thiophene and the side chains of fluorene (replaced by hydrogens) point to opposite directions. A second, lower minimum is found at around 150°, corresponding to the cis state. The trans-cis
energy difference is about 2 kJ/mol. The type B dihedral potential is similar to the previously reported dihedral potential of 3-alkylthiophene dimers, and its minima may shift towards $0^\circ$ and $180^\circ$ as the oligomer length increases [41]. As for PFTBT, both the type A and type B dihedral angles have relatively modest trans-cis energy differences.

![Figure 2.9. Dihedral distribution (a) and cumulative dihedral distribution (b) of PFTBT. Type A (dashed curve) and Type B (solid curve).](image)

Numerically, the tangent-tangent correlation function $\langle v_0 \cdot v_n \rangle$ of the inter-moiety vectors between thiophene and the successive fluorene ($r_1$ in Figure 2.2b) is averaged until the result stops changing (over 50,000 backbone conformations). The computing time is about 10 minutes with Mathematica on a workstation. The plot of $\langle v_0 \cdot v_n \rangle$ vs. repeat unit $n$ is shown in Figure 2.10.

Estimating chain dimensions of PFTBT via our analytical approach starts with defining effective backbone vectors and an effective monomer (Figure 2.2b and 2.3). Each monomer of PFTBT is represented by three effective vectors: $r_1$ and $r_2$ are the extended inter-monomer bonds connecting fluorene and thiophene; $r_3$ is the
vector connecting two thiophenes across a benzothiadiazole. The effective deflection angles and effective vector lengths are determined by following the procedures used for P3HT. The effective monomer size $\alpha_e$ is determined to be 2.2 nm from the monomer length $\alpha$ using eqn 2.12.

Analytically, $N_p$ of PFTBT is determined from the tangent-tangent correlation function of the first effective vector $r_1$ in all the monomers. The semi-log plot of the tangent-tangent correlation function $\langle v_0 \cdot v_n \rangle$ is consistent with our numerical result (Figure 2.10). $N_p$ of PFTBT is about 2.7 repeat units, from which $l_p$ of PFTBT is estimated as 5.9 nm. No experimental value for $l_p$ of PFTBT has been reported.

$\langle R^2 \rangle$ of PFTBT with $N$ monomers is also estimated by numerically averaging 10,000 different conformations. The resulting $\langle R^2 \rangle$ are shown in Figure 2.11 for PFTBT with $N$ varying from 1 to 20. The time cost for generating $\langle R^2 \rangle$ in Figure 2.11 is about 30 minutes on a workstation. The longer computation time required than what was used for P3HT is a result of the larger number of dihedral angles per monomer.

$\langle R^2 \rangle$ of PFTBT with any given degree of polymerization $N$ can be estimated analytically using eqn 2.11 with effective monomer size $\alpha_e$. Figure 2.11 shows the plots of $\langle R^2 \rangle$ vs. $N$, computed both numerically and analytically. The two approaches agree well with each other. When $N$ is larger than roughly $2N_p$, $\langle R^2 \rangle$ scales with $N$ with prefactor $C_\infty \alpha_e^2$ (HR model, eqn 2.5), indicating the PFTBT
backbone behaves as a flexible chain of Kuhn segments. The nonlinear behavior of the plots when \( N \) is comparable to \( N_p \) indicates PFTBT is in the semiflexible regime for such chain lengths.

Although the persistence length \( N_p \) for P3HT and PFTBT are different, the dihedral angles per persistence length are roughly the same for the two polymers. P3HT has 10 dihedral angles per \( l_p \), and PFTBT has \( 2.7 \times 4 = 11 \) dihedral angles per \( l_p \). Because of the comparable backbone deflection angles and dihedral potentials (thus, similar \( \langle \cos \phi \rangle \)), the tangent-tangent correlation functions decay similarly over dihedral angles for both P3HT and PFTBT.

Semiflexible chains are stiff primarily because the deflection angles \( \theta_i \) along backbones are small. The isomeric energy differences for semiflexible chains such as P3HT and PFTBT are only a few \( kT \), similar to polyethylene. P3HT and PFTBT are semiflexible because the small deflection angles weaken the effects of dihedral rotations on the chain conformation. As the deflection angles approach zero, the backbone orientation cannot be altered by dihedral rotations, and the polymer backbone behaves like a rigid rod. Examples of the extreme case are poly(phenylene vinylene) and poly(p-phenylene), which have parallel backbone segments connecting successive aromatic rings. \( l_p \) for these rod-like polymers vary from 10 nm up to 40 nm, where deflections of the backbone tangents are due to chemical defects or bending of backbone bonds. [48, 49]
2.6 Conclusions

In this chapter, we introduce numerical and analytical approaches to estimate chain dimensions of semiflexible polymers from DFT computed dihedral potentials and molecular geometries. Both approaches can be used to estimate the persistence length \( l_p \) (or \( N_p \)) and mean-square end-to-end distance \( \langle R^2 \rangle \) for semiflexible polymers with any degree of polymerization \( N \). Our numerical method is more general than our analytical approach for systems such as relatively short random copolymers. For such polymers, the assumptions of an “average” monomer conformation in our analytical approach become invalid (eqn 2.9, 2.10 and 2.12). In our numerical approach, chain conformations and monomer sequences can both be explicitly averaged.

The DFT-derived dihedral potential \( U(\phi) \) is not the same as the true effective dihedral potential \( U_{\text{eff}}(\phi) \). However, \( U_{\text{eff}}(\phi) \) is expensive to obtain from MD simulations. It is reasonable to approximate the effective potential for semiflexible chains by \( U(\phi) \) because the stiffness of semiflexible chains primarily results from small backbone deflection angles.

To validate the two approaches, we estimate the chain dimensions of two conjugated polymers, P3HT and PFTBT. The persistence length \( l_p \) of P3HT is estimated as 4.0 nm, in reasonable agreement with experiments (3.0 nm) [40]. The difference between our prediction and experimental values may come from the difference in the effective dihedral distributions of P3HT (dihedral potential of a 3MT tetramer is used for our estimates). The persistence length \( l_p \) of PFTBT is computed as 5.9 nm, for which experimental results are not available. The mean-square end-to-end distances \( \langle R^2 \rangle \) computed using the two approaches are consistent with each other for both P3HT and PFTBT. In the flexible regime, \( \langle R^2 \rangle \) scales with \( N \) with a prefactor equal to \( C_\infty \alpha^2 \) (or \( C_\infty \alpha_e^2 \)). This scaling matches the limit of Gaussian coils in the original HR model.
Chapter 3  
Predicting the nematic phase for conjugated polymers

The nematic coupling constant $\alpha$, together with the chain stiffness $\kappa$, governs chain alignment and the isotropic-to-nematic (IN) transition temperature $T_{IN}$ for semiflexible polymers. We combine self-consistent field theory (SCFT) with atomistic molecular dynamics (MD) simulations of semiflexible chains under external tension in the isotropic phase to determine the nematic coupling constant $\alpha$. Using $\alpha$, we obtain the variational free energy of a multichain system, from which the IN transition temperature $T_{IN}$ can be calculated. We apply our method to obtain $\alpha$ and $T_{IN}$ of a commonly studied semiflexible conjugated polymer, poly(3-hexylthiophene) (P3HT). We predict $T_{IN}$ to be above the crystal melting temperature $T_m$ for P3HT, and to follow $T_{IN}(S) = 535K(1 - 1.64/S)$, in which $S$ is the number of monomers. The work shown in this chapter has been published on *Macromolecules* [50].

3.1 Introduction

Semiflexible polymers can exhibit nematic phases, resulting from the anisotropic shape of backbone segments. Semiflexible chains in a concentrated solution can be represented as a sequence of nearly rigid backbone segments dispersed in solvent. In the melt, flexible side chains act like “bound solvents”, tending to disperse the stiff backbones. Rigid rods undergo an isotropic to nematic transition as a function of concentration, as demonstrated by Onsager. [1]. The transition occurs when the volume fraction of rods $\phi$ is high enough that randomly placing and orienting the rods would lead to about one collision per rod.
At high concentrations, the isotropic phase is no longer entropically viable; the rods tend to align with each other, resulting in a nematic phase. The critical volume fraction scales as the aspect ratio \( d/l \), for rods of diameter \( d \) and length \( l \). Likewise, semiflexible rods have been shown theoretically to undergo an isotropic to nematic transition as a function of concentration. For semiflexible chains, the critical volume fraction is governed by \( d/L_p \), where \( L_p \) is the persistence length of the chain. [2,3].

The nematic phase is important for many semiflexible polymers. As liquid crystalline polymers, semiflexible polymers with nematic phases can be used in numerous applications, including displays, high strength fibers, microelectromechanical systems (MEMS), and biomedical devices [4–7]. Moreover, the existence of nematic phases enables better processing of functional semiflexible polymers. For example, crystallization from the nematic phase or other liquid crystal phases may promote the formation of large crystalline domains and ordered amorphous regions, which can in turn enhance the electrical properties of semiconducting polymers [8–11].

The nematic coupling constant \( \alpha \) quantifies the orientational coupling between backbone segments. Together with the chain stiffness \( \kappa \), \( \alpha \) governs the IN transition temperature \( T_{IN} \). For chains with stiffer backbones and stronger nematic coupling, the IN transition temperatures are higher. The value of \( \alpha \) also affects molecular ordering in mesophases and at interfaces. For example, Morse and Fredrickson predict that semiflexible chains tend to align parallel to the plane of the interface in the “stiff” regime \( (\beta \kappa \chi \gg 1 \) where \( \chi \) is the Flory-Huggins parameter) [12]. Such orientational ordering at the interface would be enhanced by nematic coupling between chain backbones.

For polymers with accessible IN transitions, \( \alpha \) can be estimated from the observed transition temperature. Olsen and coworkers estimated the nematic coupling constant from the IN transition temperature \( T_{IN} \) for rod-like poly(2,5-di(2'-ethylhexyloxy)-1,4-phenylenevinylene) (DEH-PPV) [51]. Ho et al. applied the same method to estimate the nematic coupling constants of two semiflexible polymers, poly(3-(2’-ethyl)hexyl-thiophene) (P3EHT) and poly(3-dodecylthiophene) (P3DDT) [52]. For many semiflexible chains, however, the IN transition is precluded by either crystallization or thermal degradation so that its location cannot be used for estimating \( \alpha \).
In this paper, we report a method that combines self-consistent field theory (SCFT) with atomistic molecular dynamics (MD) simulations of semiflexible chains under external tension in the isotropic phase to predict $\alpha$ from molecular structure. In MD simulations, we induce weak nematic order in semiflexible chains by applying uniaxial tension. For the same semiflexible chains, we can compute the nematic order parameter analytically for a given applied tension and $\alpha$ using SCFT. The value of $\alpha$ is determined by fitting the order parameter $q(\alpha)$ calculated by SCFT to the MD simulation results. Using the predicted $\alpha$, we calculate the variational free energy for a multichain system. The mean field free energy exhibits a first order phase transition at the IN transition temperature $T_{IN}$. Our method for predicting nematic phases is more convenient than directly observing the IN transitions in simulations, for which equilibrium is challenging to achieve and the finite system size smears the transition.

We apply our method to predict the nematic coupling constant $\alpha$ of poly(3-hexylthiophene) (P3HT), a commonly studied conjugated polymer. Using the predicted $\alpha$, we obtained the mean field free energy for P3HT, from which the IN transition temperature $T_{IN}(S)$ is calculated as a function of chain length $S$. We predict that $T_{IN}(S)$ lies above the experimental crystal melting temperature $T_{m}(S)$ of P3HT as a function of chain length, indicating that the nematic phase is stable over a range of temperatures. Our predictions are consistent with experiments, in which a nematic phase has been reported for P3HT based on polarized optical microscopy (POM) [52]. Liquid crystal order has also been observed during solvent evaporation for P3HT in 1,2,4-trichlorobenzene using polarized Raman spectroscopy [53]. The value of $T_{IN}$ is not available, however, because thermal degradation may preclude the IN transition in experiments.

### 3.2 Methods

#### 3.2.1 A single semiflexible chain under tension

We determine the nematic coupling constant $\alpha$ from the tension induced chain ordering of semiflexible chains in the simulated isotropic phase. When tension is applied to a chain in a melt, it stretches along the direction of force, and its backbone segments tend to align in that direction. When tension in a given direction
is applied to all chains in a melt, an average segmental alignment results. If the segments interact with a nematic coupling \( \alpha \), the segmental alignment is amplified, beyond what would be expected for a single chain under tension. By comparing the observed segmental alignment in MD simulations of chains under modest tension in the isotropic phase to predictions using self-consistent field theory (SCFT), we can infer the nematic coupling.

We perform MD simulations of the chains under tension in the isotropic phase, because simulations at elevated temperatures in the isotropic phase equilibrate more rapidly. For atomistic MD simulations of even rather short semiflexible chains, it is challenging to carry out properly equilibrated simulations of the nematic phase directly. Instead, we observe the isotropic phase to determine \( \alpha \), extrapolate its value to lower temperatures, and predict the nematic phase behavior using SCFT.

To carry out this procedure for determining the nematic coupling constant \( \alpha \), we construct a self-consistent field theory for a semiflexible chain under external tension, immersed in a sea of neighboring chains under the same applied tension. The applied tension induces segmental alignment at second order, creating a mean aligning quadrupolar field \( Q \). For a given \( \alpha \), we can determine the mean field \( Q \) self-consistently using the single chain model. The nematic coupling constant \( \alpha \) is determined by fitting the calculated \( Q(\alpha) \) to the observed \( Q \) in our MD simulation of many stretched chains.

The aligning potential acting on a backbone tangent \( t \) of size \( a \) on a semiflexible chain with applied tension \( f \) is

\[
V(t) = -\alpha t \cdot Q \cdot t - af \cdot t
\]  

(3.1)

The mean quadrupolar field \( Q \) is a symmetric and traceless second-order tensor with the form \( Q_{ij} = \langle t_i t_j \rangle - \delta_{ij}/3 \). With tension applied along \( \hat{x} \), the mean quadrupolar field can be written as: \( Q_{xx} = q, \ Q_{yy} = -q/2, \ Q_{zz} = -q/2 \), in which \( q \) is a quadrupolar order parameter.

Using the aligning potential \( V(t) \), we write the Hamiltonian of an aligned semiflexible chain containing \( S \) monomers of length \( a \) as

\[
H_0 = \int_0^S ds \left( \frac{\kappa}{2} \left| \frac{dt_s}{ds} \right|^2 + V(t_s) \right)
\]  

(3.2)
Here \( s \) is the monomer index, and \( \mathbf{t}_s \) is the unit tangent vector of monomer \( s \). The bending modulus is denoted by \( \kappa \), given by \( \kappa = kT N_p \), where \( N_p \) is the persistence length measured in repeat units. The first term in eqn 3.2 is the bending energy of a worm-like chain.

We expand the uniaxial aligning potential \( V \) (eqn 3.1) in Legendre polynomials \( P_n(\cos \theta) \). Because nematic ordering has azimuthal symmetry, we only consider the dependence of \( V \) on \( \mu = \cos \theta \), in which \( \theta \) is the deflection angle between a backbone tangent and the nematic director (which coincides with the axis of stretching). The quadrupolar order parameter \( q \) in the tensor \( \mathbf{Q} \) can be then written with the second-order Legendre polynomial \( P_2 \):

\[
q = \int_{-1}^{1} d\mu \Pi(\mu) P_2(\mu) \tag{3.3}
\]

in which \( \Pi(\mu) \) is the probability distribution of backbone tangents. Using the order parameter \( q \), we write \( V(\mu) \) as:

\[
V(\mu) = -\alpha q P_2(\mu) - f P_1(\mu) \tag{3.4}
\]

To self-consistently compute the tangent distribution \( \Pi(\mu) \) for a given \( \alpha \), we write a propagator \( Z(\mu; S) \) to describe the statistical weight for a chain with length \( S \) start with tangent orientation \( \mu \):

\[
Z(\mu; S) = A^S \int d\mu_1 d\mu_2 ... d\mu_S e^{-\beta H_0} \delta(\mu_1 - \mu) \tag{3.5}
\]

in which \( \beta = 1/kT \). The factor \( A \) normalizes the propagator with respect to the free chain \((V = 0)\). Our \( Z(\mu; S) \) is analogous to the propagator \( Z(\mathbf{r}, \mu; S) \) used by other authors to describe semiflexible homopolymer blends or block copolymers, for which not only the tangent orientation \( \mu \) is important but also the spatial position \( \mathbf{r} \) \([12, 54, 55]\). The tangent distribution \( \Pi(\mu) \) is proportional to the product of two propagators, integrated over the whole chain length \( S \):

\[
\Pi(\mu) = \frac{\int_0^S d\mu Z(\mu; n) Z(\mu; S-n)}{Z_0} \tag{3.6}
\]
Here $Z_0$ is the single chain model partition function, written as

$$Z_0 = \int_{-1}^{1} d\mu Z(\mu; S)$$

Using the propagator, we can determine the nematic order parameter $q$ for a given nematic coupling constant $\alpha$ self-consistently. Self-consistency is satisfied when the calculated $q$ (eqn 4.3) agrees with the input $q$ in the single chain Hamiltonian $H_0$ (eqn 3.2).

The propagator $Z(\mu; s)$ satisfies a diffusion equation, in which the backbone tangent vector $t_s$ executes a biased random walk on the unit sphere:

$$\frac{\partial Z(\mu; s)}{\partial s} = D \nabla^2_\perp Z(\mu; s) - V Z(\mu; s)$$

The diffusion coefficient $D$ is given by $D = 1/(2\beta\kappa)$; tangent-tangent correlations decay more slowly for stiffer chains. Here $\nabla^2_\perp$ is the angular Laplacian, in which only the $\theta$ dependent ($\mu$ dependent) part is considered.

The propagator equation (eqn 3.8) can be solved by expanding $Z(\mu; s)$ in the eigenfunctions $\psi_\alpha$ of the right-hand side operator in eqn 3.8:

$$Z(\mu; s) = \int_{-1}^{1} d\mu' \sum_{\alpha=0}^{N} \psi_\alpha(\mu') \psi_\alpha(\mu) e^{-\epsilon_\alpha s}$$

in which $\epsilon_\alpha$ is the corresponding eigenvalues of $\psi_\alpha$. The eigenfunctions $\psi_\alpha$ are in turn expanded in Legendre polynomials, which are the eigenfunctions of the angular Laplacian $\nabla^2_\perp$ [56]. To obtain $Z(\mu; s)$, the eigenfunction expansion (eqn 3.9) and the Legendre polynomial expansion of $\psi_\alpha$ are truncated at finite order $N$. Details for solving eqn 3.8 are given in the Appendix.

The mean field model is combined with atomistic simulations to determine $\alpha$ for a given semiflexible polymer. Atomistic simulations of semiflexible oligomers of length $S$ in the isotropic phase are used to determine the bending modulus $\kappa$. We apply a tension $f$ to all oligomer backbones in the simulated isotropic phase to induce quadrupolar ordering $q$. Using our single chain model, we self-consistently compute the nematic order parameter $q(\alpha)$ of a stretched semiflexible chain with the same stiffness $\kappa$, chain length $S$, and tension $f$. The value of $\alpha(T)$ at various temperatures is determined by fitting the calculated $q(\alpha)$ to the observed $q$ in the
atomistic simulations.

3.2.2 MD simulations of chains under tension

To estimate the temperature dependent nematic coupling constant $\alpha(T)$ for P3HT, we combine our SCFT calculations with atomistic simulations of regioregular 3-hexylthiophene (3HT) 20-mers at different temperatures. The force field parameters for our atomistic simulations were developed by Huang and coworkers [45, 46]. Bonded interactions and partial charges on the atoms are determined using density functional theory (DFT) calculations. Lennard-Jones (LJ) parameters from the OPLS-AA potential are used to describe the non-Coulomb nonbonded interactions between atoms. Huang et al. verified the atomistic model of P3HT by comparing the densities of 3HT monomers and crystal 3HT oligomers at 300K with experiments [45].

We also test the atomistic model by simulating a single crystal of P3HT at 300K. In this simulation of the crystal, P3HT chains are bonded to themselves through the periodic boundary to represent chains of infinite length. The simulated crystal structure of P3HT, including the $\pi-\pi$ stacking distance (3.64Å) and the tilt angle of backbone thiophenes ($22^\circ$), agree well with X-ray and electron diffraction results [57, 58].

For our simulations of the isotropic phase, the initial configuration of 3HT 20-mers is built according to the crystal structure of P3HT measured by X-ray diffraction [57]. Sixty-four chains are constructed in all-trans conformations with a $\pi-\pi$ stacking distance of 3.83Å and a separation distance of 16.8Å parallel to the thiophene rings. Sulfur atoms on $\pi-\pi$ stacked thiophene rings point in opposite directions (Fig. 3.1).

We obtain the isotropic phase of P3HT by melting the crystal at 700K and 1 bar. The system is equilibrated when the density $\rho$ fluctuates around its equilibrium value and the order parameter $q$ decays to zero. Starting configurations of isotropic P3HT at 650K, 600K, and 500K are obtained by equilibrating at constant pressure and temperature (NPT) after quenching from 700K. These temperatures are significantly above the experimental crystal melting temperature for 20-mers, observed to be about 450K [59]. Simulations of 20-mers in the isotropic phase at these elevated temperatures can be reliably equilibrated, as discussed further below.
Using the equilibrated NPT samples as initial configurations, simulations at constant volume and temperature (NVT) are performed to determine the bending modulus $\kappa$ for P3HT at different temperatures. NVT simulations are used for consistency with our simulations of chains under tension, for which the NVT ensemble is used to prevent deformation of the simulation box.

To induce weak quadrupolar ordering, we apply an equal and opposite force in the $x$-direction to the ends of each P3HT chain, to induce a tension $f$ of 2.2 kJ/nm along the chains. This value of $f$ corresponds to about $2 kT$ per end-to-end distance of a free chain. Starting as an isotropic melt, each simulation is equilibrated over a total time longer than $20\tau$, where $\tau$ is the autocorrelation time of order parameter $q$. Equilibrium is achieved in our simulations when $q$ fluctuates around a steady value. We collect data over a time greater than $20\tau$ for each equilibrated simulation. From the simulations of stretched chains at different temperatures, we can determine the temperature dependent nematic coupling constant $\alpha(T)$, which allows us to predict the location of the IN transition $T_{IN}$ for P3HT.

### 3.2.3 Multichain free energy

Our single chain model provides a mean-field treatment of a multichain system which exhibits an isotropic-to-nematic (IN) transition. To determine the location
of the transition, we employ the variational theorem to compute an upper bound to the multichain free energy [60]:

\[ F = \langle H \rangle - TS_0 \quad (3.10) \]

in which \( \langle H \rangle \) is the Hamiltonian of the multichain system.

\( S_0 \) is the model ensemble entropy, defined by the single chain free energy \( F_0 = \langle H_0 \rangle - TS_0 \). The single chain free energy \( F_0 \) can be obtained using our single chain model partition function \( Z_0 = e^{-\beta F_0} \) (eqn 3.7). At the critical nematic coupling constant \( \alpha_c \), the variational free energy \( F(q) \) develops a second minimum \( F(q_c) \) at critical order parameter \( q_c \) \( (q_c < 1) \). Because \( F(q_c) \) equals the isotropic free energy \( F(0) \), the multichain system has a first order IN transition.

To obtain the variational free energy \( F(q) \), we first compute the model ensemble entropy \( S_0 \) as a function of quadrupolar order parameter \( q \). We consider a single semiflexible chain aligned in an external quadrupolar field \( A \). The aligning potential of the single chain now takes the form \( V(\mu) = -A P_2(\mu) \). The order parameter \( q \) is an increasing function of the external field \( A \), which can be computed numerically as a function of \( A \).

Operationally, we can compute both \( q \) and the single-chain free energy \( F_0 \) as a function of \( A \), thereby obtaining \( F_0(q) \) as a function of \( q \). The entropy \( S_0(q) \) (defined with respect to a free chain with \( A = 0 \)) is then obtained as

\[ -TS_0(q) = F_0(q) - F_0(0) + Aq \quad (3.11) \]

For a multichain system, we write the variational free energy \( F(q) \) with respect to the isotropic phase using \( S_0(q) \):

\[ F(q) = -\frac{1}{2} \alpha q^2 - TS_0(q), \quad (3.12) \]

The \( 1/2 \) in the nematic coupling term avoids double counting in the multichain model. The variational free energy can be used to determine the critical nematic coupling constant \( \alpha_c \) at which a given semiflexible polymer undergoes an IN transition. Knowing the temperature dependent nematic coupling constant \( \alpha(T) \) for a given semiflexible polymer, we can predict the IN transition temperature \( T_{IN} \).
3.3 Results

Atomistic simulations of P3HT

Our initial configurations are oriented single crystals of 64 chains of P3HT, with 20 monomers each (Fig. 3.1). Equilibrating from the initial crystal phase, we observe that P3HT is an isotropic melt above 500K. We detect nematic order in the simulations using the quadrupolar order parameter $q$ (eqn 4.3). In our equilibrated simulations without applied tension, $q$ (eqn 4.3) fluctuates about zero (Fig. 3.2a), consistent with an isotropic phase. No remnant of the initial crystal orientation survives.

From NVT simulations of the unoriented isotropic phase, we determine the persistence length of P3HT. We use the tangent-tangent correlation function $\langle t_0 \cdot t_s \rangle$ (Fig. 3.3) to estimate the characteristic length of the exponential decay $\langle t_0 \cdot t_s \rangle = e^{-s/N_p}$, the persistence length $N_p$, and so determine $\kappa$ ($\kappa = kTN_p$).

As shown in Fig. 3.3, $\langle t_0 \cdot t_s \rangle$ is essentially temperature independent, with only slight variations in $\langle t_0 \cdot t_s \rangle$ at large $s$ (which may reflect poor statistics). Thus, we conclude that $\kappa$ is temperature independent. This is not unexpected: for molten P3HT, the dihedral angles can rotate nearly freely in the isotropic phase. The chain stiffness primarily arises from the small backbone deflection angles, which are insensitive to temperature [27]. Even though P3HT is semiflexible, the conjugation along the P3HT backbone, which gives rise to delocalized electronic states observable with UV-vis spectroscopy, is not so easily disrupted. The conjugation is only efficiently broken for dihedral angles near 90 degrees, which are relatively rare given the P3HT dihedral potential.

We determine the temperature independent value $N_p = 7.1$ (hence $\kappa = 7.1 \cdot kT$) by averaging the exponential decay lengths of $\langle t_0 \cdot t_s \rangle$ for the first ten repeat units over different temperatures. The freely rotating chain model yields $N_p = 7$. Fitting the entire range of $\langle t_0 \cdot t_s \rangle$ gives a slightly different value $N_p = 8$ [27]. Our estimated $N_p$ agrees with the experimentally measured persistence length $L_p$ of $3.0 \pm 0.2$ nm (corresponding to an $N_p$ of $7.5 \pm 0.5$) for P3HT in a marginal solvent [40].

To directly observe the IN transition in simulations, isotropic P3HT needs to be slowly cooled and the nematic observed to form, or the P3HT crystal slowly heated to form a nematic which is then heated further until the isotropic phase forms.
From Fig. 3.2c, we can estimate the equilibration time for simulations at a given temperature, in terms of the correlation time $\tau$ for order parameter fluctuations. At higher temperatures, $\tau$ is conveniently short — 5 ns at 700K, up to 14 ns at 600K. But at lower temperatures, the correlation time becomes quite long (over 200ns at 500K). Thus it would be rather challenging to accurately locate the IN transition by directly observing the appearance or disappearance of nematic order. Instead of observing the IN transition directly in simulations, we predict the nematic phase
and the coupling constant $\alpha$ of P3HT from the tension-induced ordering in the isotropic phase.

By applying uniaxial tension, we can induce weak quadrupolar ordering in P3HT in the isotropic phase. Figure 3 shows the snapshots of our MD simulations at 600K for unstretched chains (a) and stretched chains (b), from which we see that P3HT backbones tend to align along the stretching axis ($x$-axis). The order parameter $q$ becomes non-zero for the stretched P3HT chains (Fig. 3.2b).
3.3.1 Determining the nematic coupling parameter $\alpha$

We analytically compute the quadrupolar order parameter $q$ for a given $\alpha$ for P3HT (Fig. 3.5a) using SCFT. To efficiently compute $q(\alpha)$, the eigenfunction and Legendre polynomial expansions are truncated at fourth order. The results obtained with this truncation are indistinguishable from $q(\alpha)$ retaining higher order terms. The SCFT results for $q(\alpha)$ are fitted to the MD simulation results to determine $\alpha$ for P3HT at different temperatures (600K, 650K and 700K).

We use the three high temperature simulations because equilibrating at lower temperatures is increasingly expensive, indicated by the increasing autocorrelation time $\tau$ for the order parameter $q$ (Fig. 3.2c). The results for $\alpha$ at the three temperatures are fit to the form $A + B/T$, used previously by Olsen and coworkers, analogous to the form of the Flory-Huggins interaction parameter $\chi$ [51]. The temperature independent term $A$ captures the entropic contributions, including the steric exclusions, where $B$ denotes the enthalpic interactions. In this way, we obtain the temperature dependent $\alpha(T)$ for P3HT as $\alpha(T) = -(1.63 \pm 0.30) + (1550 \pm 190)/T$, in which we include the standard errors of the fitting parameters.

For sufficiently long chains, SCFT calculations can be simplified using ground state dominance (GSD). In the long chain limit, only the lowest eigenfunction (ground state) contributes to propagators and partition functions (see eqns 3.7 and 3.9). By comparing the order parameter $q_{\text{GSD}}(\alpha)$ obtained using GSD to the full SCFT calculation of $q(\alpha)$ at 700K (Fig. 3.5a), we see that GSD is not a good approximation for oligomeric P3HT. The two results do not agree for small $\alpha$, indicating the 3HT 20mer is too short to be described well by GSD. For polymers with small $\alpha$, the relative error $\Delta q/q$ from using GSD is less than 10 percent only when the chain length $S$ is much greater than $N_p$ (Fig. 3.5b).

The distribution of chain tangent vectors $\Pi(\mu)$ gives a more detailed picture of chain orientation than the order parameter $q$, which is simply the average of $P_2(\mu)$ over the distribution $\Pi(\mu)$. (Here $\mu = \cos \theta$, where $\theta$ is the angle between the tangent and the axis of stretching.) We compare the SCFT predictions for $\Pi(\mu)$ to the MD simulation results to further validate our method (Fig. 3.6).

The SCFT results agree almost perfectly with the tangent distributions $\Pi(\mu)$ from our MD simulations. The asymmetry of $\Pi(\mu)$ about the origin $\mu = 0$ is a result of the applied tension, while the upwards curvature is characteristics of induced
Figure 3.5. Order parameters computed using SCFT. (a) order parameter versus nematic coupling constant $\alpha$: 600K (red), 650K (green), 700K (blue). The purple curve presents results at 700K assuming ground state dominance (GSD). (b) Relative error $\Delta q/q$ for using GSD versus $S/N_p$. $S$ is the chain length and $N_p$ is the persistence length. $q$ is obtained using fourth order eigenfunction expansions (eqn 3.9) and $\Delta q = q_{GSD} - q$.

nematic order ($\mu$ near $\pm 1$ is favored over $\mu = 0$). With no applied tension, $\Pi(\mu)$ is symmetric about $\mu = 0$, flat in the isotropic phase, and spontaneously concave up in the nematic phase.

3.3.2 Locating the IN transition

To predict the location of the IN transition, we first calculate the single chain model entropy $S_0(q)$ for chains with different stiffness $\kappa$ as a function of an applied quadrupolar aligning field $A$ (eqn 3.11). Because $\kappa$ characterizes the orientational correlations between the backbone segments along a chain, the entropic cost of anisotropic ordering is lower for chains with stiffer backbones (Fig. 3.7).

Using the model entropy $S_0(q)$, we can compute the variational free energy $F(q)$ of a semiflexible chain as a function of quadrupolar order $q$ (eqn 3.12). The
Figure 3.6. Tangent distribution functions for stretched 3HT 20-mers at 700K (blue), 650K (green), 600K (red); symbols are simulation results, curves are SCFT calculations.

Figure 3.7. Model entropy for semiflexible 20-mers with different stiffness $\kappa$.

The variational free energy $F(q)$ decreases with increasing nematic coupling $\alpha$. At a critical value $\alpha_c$, $F(q)$ develops a second minimum at finite order parameter $q_c$, corresponding to the first-order IN transition (Fig. 3.8a).

We construct the IN phase boundary using the critical nematic coupling constant $\alpha_c(\kappa)$ for polymers with various stiffness and chain lengths (Fig. 3.9a). The critical nematic coupling constant decreases with increasing chain length or the chain stiffness. By projecting the 3D phase boundary onto the $\kappa$-$\alpha$ plane, we obtain the two-dimensional IN phase boundary for different chain lengths.

The phase boundaries for different chain lengths are shown in Fig. 3.9b, in which a crossover from rod-like to semiflexible chain behavior can be seen at a chain length of about one persistence length $N_p (\beta \kappa)$. The value of $\alpha_c$ is estimated as 4.54 kT for chain length of unity, in agreement with Maier-Saupe theory [61].
Figure 3.8. Free energy vs. order parameter for 3HT 20-mers. (a) With various nematic coupling constants: red ($\alpha = 1.50kT$), green ($\alpha = 1.51kT$), and blue ($\alpha = 1.52kT$). (b) At different temperatures: 494K (red), 493.3K (green) and 493K (blue).

The 2D phase boundaries are also presented in Fig. 3.9c for chains with different values of $S/N_p$ (chain length in units of $N_p$). For chains that are many persistence lengths long ($S/N_p \gg 1$), the critical nematic coupling constant $\alpha_c$ scales as $1/\kappa$.

To understand why $\alpha_c\kappa$ is a constant for semiflexible chains much longer than the persistence length $N_p$, we make a simple argument as follows. The mean-field free energy of a multichain system can be obtained from the single chain partition function, which is the integral over chain configurations of the single-chain Hamiltonian without applied tension. By expressing the arclength in units of $N_p$ ($\beta\kappa$), the single-chain Hamiltonian is written as

$$
\beta H = \int_0^{S/N_p} dz \left( \frac{1}{2}(dt/dz)^2 - \beta^2\alpha\kappa t(z) \cdot Q \cdot t(z) \right)
$$

Hence, the free energy $F$ is only a function of $\alpha\kappa$, not $\alpha$ or $\kappa$ independently. For long semiflexible chains, $S/N_p$ approaches infinity, and the free energy $F$ develops a second minimum corresponding to the IN transition at a single critical value of
Figure 3.9. The IN phase boundary for semiflexible polymers. (a) Phase boundary for various values of chain length $S$ and stiffness $\kappa$. (b) Phase boundary in $\kappa$-$\alpha$ plane for various chain lengths $S$. (c) Phase boundary in $\kappa$-$\alpha$ plane for various values of $S/N_p$. Inset: phase boundaries for chains with $S/N_p \gg 1$.

We predict the IN transition temperature $T_{IN}$ for P3HT with various chain lengths $S$ using the temperature dependent nematic coupling constant $\alpha(T)$. From the variational free energy (eqn 3.12), we determine the critical nematic coupling constant $\alpha_c$ for P3HT of different lengths. The free energy of 3HT 20-mers is plotted in Fig. 3.8b as an example. Because $N_p$ is temperature independent (Fig. 3.3), $T_{IN}$ is determined by equating $\alpha(T)$ to $\alpha_c$.

We obtain the IN phase boundary for P3HT with length $S$ as $T_{IN}(S) =$
535K(1 − 1.64/S) by fitting the predicted $T_{IN}$ to the form $A(1 + B/S)$. The uncertainty of the IN phase boundary, as a result of the uncertainties in $\alpha(T)$, is about 15K. The experimental crystal melting temperature $T_{m}(S)$ is estimated as 533K(1 − 3.25/S) by fitting the experimentally observed $T_{m}$ for P3HT of different molecular weights [52, 59]. The phase transition temperature $T_{IN}$ is above the crystal melting temperature (Fig. 3.10), indicating the nematic phase should be accessible for P3HT at elevated temperatures.

To further compare our predictions with experiments, we predict the IN transition enthalpy $H_{IN}$ for P3HT. We expect a small $H_{IN}$ for semiflexible polymers. At the IN transition, the change in enthalpy $H_{IN}$ equals the loss in orientational entropy $T\Delta S$, which is only of order kT per Kuhn segment for semiflexible chains. Because the Kuhn segments are large objects, $H_{IN}$ per volume is small. We predict the IN transition enthalpy $H_{IN}$ using the model entropy $S_0$ and the critical order parameter $q_c$ in our mean field theory. The critical order parameter $q_c$ is about 0.12 and $H_{IN}$ is about 0.3 J/g for P3HT. The predicted $H_{IN}$ is much smaller than the enthalpy of fusion for P3HT (99 J/g), measured using differential scanning calorimetry (DSC) [62]. Hence, our predictions are consistent with DSC experiments that only observe a crystal melting peak for P3HT [52].

Figure 3.10. P3HT phase diagram, with crystal (red), nematic (green), and isotropic phase (blue). The IN phase boundary (dashed blue curve) is $T_{IN}(S) = 535K(1 − 1.64/S)$, obtained by fitting our numerical results (blue circles). The crystal melting temperature (dashed red curve) is $T_{m}(S) = 533K(1 − 3.25/S)$, obtained by fitting reported $T_{m}$ (red circles [52], red triangles [59]).
3.4 Discussion

In this paper, we report a hybrid method, combining self-consistent field theory (SCFT) with atomistic simulations of semiflexible chains under tension, to estimate the nematic coupling constant $\alpha$ for semiflexible polymers. We employ a mean field model to describe the uniaxial alignment of a semiflexible chain under tension. Using the mean field model, we self-consistently compute the quadrupolar order parameter $q(\alpha)$. The value of $\alpha$ is determined by fitting the predicted $q(\alpha)$ to the simulation results for semiflexible chains under tension in the isotropic phase.

In this way, we can obtain the nematic coupling without directly observing the IN transition in simulations, or for polymers for which the IN transition is precluded by crystallization. Direct observation of the IN transition in atomistic simulations is challenging, because equilibration times at lower temperatures become increasingly long. Thus, the isotropic phase must be cooled very slowly to identify the IN transition with any accuracy, resulting in very expensive simulations.

We have applied our method to determine the nematic coupling constant for P3HT. MD simulations of 20-mer chains under tension in the isotropic phase were carried out at 700K, 650K, and 600K. At these temperatures, simulations can be equilibrated in less than 300 ns. Values of $\alpha$ at lower temperatures are calculated by extrapolating our results, fitted to the form $A + B/T$.

With the nematic coupling in hand, we can predict the IN transition temperature for P3HT as a function of chain length, using self-consistent field theory. The predicted nematic phase behavior of P3HT agrees quantitatively with experiments. Ho et al. observed a nematic phase under polarized optical microscopy for P3HT with length $S$ between 43 and 73 [52]. For such chain lengths, the nematic temperature window is estimated to be about 18K wide (Fig. 3.10), so that the nematic phase should be readily accessible experimentally. For longer chains, the nematic phase is stable only in an increasingly narrow temperature range, and thus is more difficult to access.

Our method is robust to inaccuracies of atomistic force fields, even though the nematic coupling constant $\alpha$ is determined by fitting to atomistic simulation results. We expect the location of the IN transition to be affected primarily by the shape and stiffness of the chains. MD accurately describes local packing, but error in the potential can lead to incorrect overall densities. We have verified that our
simulations give comparable quadrupolar alignment (with $q$ decreasing by less than 5%) for chains under tension at 700K, when the simulation density is artificially reduced by 5 percent (Fig. 3.11a). Correspondingly, the value of $\alpha$ is reduced by 7% for the system with the reduced density.

Likewise, error in the atomistic detailed potential can in principle lead to incorrect values for the chain stiffness. Nevertheless, we have shown that for conjugated polymers the stiffness arises primarily from the small deflection angle, not the details of the dihedral potential [27]. To demonstrate this, we set the dihedral potentials to zero at 700K, corresponding to freely-rotating P3HT in the gas phase with $N_p = 7$. In the melt, however, the inter-chain interactions of the chains with the flat dihedral potentials favor planar conformations along the backbones, resulting in a persistence length $N_p$ of 8.3 (Fig. 3.11b).

For the artificially stiffened chains, the induced quadrupolar ordering $q$ is about 8% higher (Fig. 3.11a). The resulting nematic coupling constant $\alpha$ at 700K is about 23% higher than the value of $\alpha$ for the hindered-rotating P3HT. Because the relative error in $N_p$ of the stiffened P3HT is rather large (17%), we expect our method is robust to milder errors in the dihedral potentials.

Our method can be also extended to polymers other than the semiflexible linear homopolymers. The extension to alternating copolymers is straightforward, and low levels of long-chain branching would be only a perturbation. For alternating copolymers, an effective persistence length can be determined. Together with the size of the repeat unit, the effective persistence length can be used in our method for predicting $\alpha$. For semiflexible polymers with low levels of long-chain branching, the joints have little effect on the overall aligning behaviors so that our method is still applicable.

In summary, we compute the variational free energy $F(q)$ of a multichain system using our mean field model. We consider a single chain immersed in an external quadrupolar aligning field $A$, to compute the entropy $S_0$ as a function of the order parameter $q$ (eqn 3.11). By adding a nematic coupling term to the entropy $S_0(q)$, we obtain $F(q)$ with respect to free chains (eqn 3.12), from which the IN transition can be located.

We demonstrate our method by estimating the nematic coupling constant $\alpha(T)$ and the IN transition temperature $T_{IN}$ for P3HT. Combining the SCFT calculations with the atomistic simulations of stretched 3HT 20-mers at different temperatures,
we determine $\alpha$ as $-(1.63 \pm 0.30) + (1550 \pm 190)/T$ for P3HT. The IN phase boundary is obtained for semiflexible chains using the variational free energy. The critical nematic coupling constant $\alpha_c$ is lower for longer or stiffer chains. Because the bending stiffness $\kappa$ is temperature independent, we directly estimate $T_{IN}$ for P3HT with various lengths $S$, given by $T_{IN}(S) = 535K(1 - 1.64/S)$. Using the estimated $T_{IN}$, we predict that P3HT is nematic above the reported crystal melting temperatures.

**Figure 3.11.** Dependence of quadrupolar ordering on force fields at 700K: (a) quadrupolar order parameters $q$, (b) tangent-tangent correlations functions. Our regular simulation with density $\rho_0$ (Hindered), a less dense system with density $\rho = 0.95\rho_0$ (green), and freely-rotating chains (blue).
Chapter 4  
Surface induced chain alignment of semiflexible polymers

Semiflexible polymers tend to spontaneously align parallel to an impenetrable surface, creating a mean aligning field. The backbone segments interact with the aligning field, further enhancing the chain alignment. Using molecular dynamic (MD) simulations of bead-spring chains, we demonstrate that the thickness of the aligned layer is about a persistence length $L_p$ for semiflexible polymers in the isotropic phase. To investigate the effect of nematic coupling on the surface induced alignment, we develop a lattice version of self-consistent field theory (SCFT) for semiflexible chains. We predict that the strength and range of the alignment increase with increasing nematic coupling, quantified by the nematic coupling constant $\alpha$. The impenetrable surface acts as a perturbation on the chain alignment, and the nematic coupling $\alpha$ amplifies the perturbation. By comparing the SCFT predicted order parameter profile for chains near an impenetrable surface to MD simulations, we can estimate $\alpha$ for semiflexible polymers. The work shown in this chapter has been published on *Macromolecules* [63].

4.1 Introduction

The interfacial structures of semiflexible polymers are important for many applications, such as organic electronics. Thin films of polymer semiconductors, composed of conjugated semiflexible polymers, are increasingly used in electronic applications, including field effect transistors, photovoltaics, and light-emitting diodes. The chain alignment at polymer-polymer interfaces or polymer-substrate interfaces is critical
for electronic properties and resulting overall device performance. For example, ordered donor-acceptor interfaces may promote mobility of separated electrons and holes, resulting in enhanced efficiency for polymer solar cells [16,17]. Chain alignment near the gate dielectric can also enhance charge mobility in organic field effect transistors [18–23].

Semiflexible polymers behave differently from flexible polymers at interfaces. Backbone stiffness, arising from electronic delocalization, bond angles, or steric interactions, can constrain the packing of semiflexible polymers at an interface. Morse and Fredrickson predict that chains align parallel to the interface between incompatible semiflexible polymers [12]. Similarly, Chen and coworkers predict that a long semiflexible chain confined in a slit tends to align parallel to the impenetrable surface [13,14]. Using grand-canonical lattice Monte Carlo simulations with a bond-fluctuation model, Ivanov et al. show that impenetrable surfaces can induce nematic ordering in athermal solutions of semiflexible polymers [15].

To study the surface induced alignment in melts of semiflexible polymers, we perform molecular dynamic (MD) simulations for bead-spring chains confined between two Lennard-Jones (LJ) “frozen” liquid substrates. These impenetrable surfaces are macroscopically flat but slightly rough, with a root-mean-square surface roughness of order of the size of a monomer. We use these disordered surfaces in the simulations because perfectly smooth surfaces induce crystallization and layering near the wall. This behavior is largely artificial, as no real interface or surface is perfectly flat.

In our simulations, semiflexible chains align parallel to the impenetrable surface, creating an aligned layer of thickness about a persistence length \( L_p \). The nematic interactions between the backbone segments of semiflexible polymers in this layer further enhance the strength and range of alignment near an interface. This nematic enhancement of surface alignment occurs even for polymers that are isotropic in the bulk. The strength of the nematic interactions is characterized by the nematic coupling constant \( \alpha \). Because longer and stiffer semiflexible chains have larger \( \alpha \), the thickness of the ordered layer increases with increasing chain length and stiffness in the simulations.

To analyze the effect of nematic coupling on the induced alignment, we develop a lattice version of self-consistent field theory (SCFT) to describe incompressible melts of semiflexible chains near impenetrable surfaces. Using the SCFT lattice
model, we predict quantitatively how the surface induced alignment is enhanced by the presence of nematic coupling. The strength and the range of nematic ordering increases for chains with larger $\alpha$.

By comparing MD results for alignment of semiflexible chains near an interface to SCFT predictions, we can infer the strength of the nematic coupling. For chains with mild coupling, the estimated $\alpha$ is consistent with the value we obtained using our previously reported method for semiflexible chains in bulk, in which external tension is used to induce weak nematic ordering in the isotropic phase [50]. With sufficiently strong nematic coupling, semiflexible chains can exhibit biaxial alignment near the surface: the chains spontaneously select a preferred alignment direction parallel to the surface, which invalidates our assumption of uniaxial symmetry in the lattice model.

\section*{4.2 MD simulations}

To investigate the chain alignment induced by an impenetrable neutral surface, we simulate semiflexible chains confined between two parallel slabs of a Lennard-Jones (LJ) \textquotedblleft frozen\textquotedblright liquid. By \textquotedblleft frozen\textquotedblright liquid, we mean an equilibrated LJ fluid in which the monomers are no longer allowed to move. We use a coarse grained bead-spring model to represent the molten polymer chains, in which the non-bonded interactions are modeled using the purely repulsive Weeks-Chandler-Anderson (WCA) pair potential:

$$U_{nb}(r) = \begin{cases} 
4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - 2 \left( \frac{\sigma}{r} \right)^{6} + 0.25 \right] & \text{if } r \leq 2^{1/6}\sigma \\
0 & \text{if } r > 2^{1/6}\sigma 
\end{cases} \tag{4.1}$$

in which $\epsilon = kT$. We choose the number density of the beads to be $0.7\sigma^{-3}$ to represent the melt condition [64,65].

The bonded beads interact through a harmonic stretching potential and a harmonic bending potential:

$$U_b = \frac{1}{2} k_l \left( \frac{l}{l_{1/6}\sigma} - 1 \right)^2 + \frac{1}{2} k_\theta \theta^2 \tag{4.2}$$

where $l$ is bond length, $\theta$ is bond angle, $k_l = 400kT$ and $k_\theta = 5kT$. The harmonic
bending potential penalizes the deflection of backbone tangents, resulting in a persistence length $N_p$ of about five monomers for the worm-like chains ($N_p = \beta k_\theta$, where $\beta = 1/kT$).

To study the chain length dependence of the surface induced alignment, we use chains of length $N=5, 10, or 40$ to create a slab of melt of dimension $45 \times 45 \times 45\sigma^3$. Along the $\hat{z}$ axis (perpendicular to the impenetrable surfaces) the slab thickness is about $40a$, where $a$ is the monomer diameter ($a = 2^{1/6}\sigma$). At the center of the system, the chains orient isotropically, corresponding to an isotropic bulk phase. Because the transverse dimension of the system is about $4R_g$ for $N = 40$, self-interactions across the periodic boundaries are negligible for our chains.

The LJ frozen liquid that forms the impenetrable surface is composed of the same type of beads as the semiflexible chains, with number density again equal to $0.7\sigma^{-3}$. The root-mean-square surface roughness of the substrates is about $0.3a$. If we take the monomer size $a$ to be of order 1 nm to correspond with the dimension of real semiflexible chains, the substrates in our simulations have roughnesses comparable to the surface of fused silica or crystalline silicon [66].

In our simulations, we avoid using perfectly smooth surfaces because such surfaces induce crystallization and layering in the monomers near the surface. This behavior is evident in the 2D radial distribution function $g(r)$ for monomers within a persistence length $L_p = 5a$ of the surface (Figure 4.1a). The beads pack hexagonally near the smooth surfaces, resulting in the oscillating profiles for the density $\rho(z)$ and order parameter $q(z)$ (Figure 4.1). The quadrupolar order parameter $q(z)$ is defined as

$$q(z) = \langle P_2(\mu) \rangle_z$$ (4.3)

in which $P_2(\mu)$ is the second order Legendre polynomial and $\mu = \cos \theta$, where $\theta$ is the deflection angle between a backbone tangent and $\hat{z}$. The value of $q$ equals -0.5 for chains aligned perfectly parallel to the substrate, and zero for isotropic orientation.

The crystallization and layering induced by a smooth surface may also result in an artificial distribution of chain ends. Near a smooth surface, the end segments tend to segregate near the surface for semiflexible polymers (Figure 4.2). A similar segregation effect is observed for flexible chains next to a perfectly smooth wall [67,68]. For semiflexible polymers near a slightly rough wall, however, we detect a mild depletion of chain ends over a distance of about several monomer size
Figure 4.1. Comparison of simulations using smooth and rough surfaces for bead-spring chains with $N = 40$ beads and bending stiffness $\beta\kappa = 5$. (a) Radial distribution functions in the xy plane near the surface ($z/a < 5$). Dashed lines indicate peak locations for hexagonal close packing in 2D. Inset: density profile near the surface. (b) Order parameter profiles as a function of distance away from the surface ($z$).

In our simulations, the impenetrable boundary forces the backbone segments to align parallel to the surface (Figure 4.3). The backbone tangent-tangent correlations, characterized by the bending stiffness $\beta\kappa$, ensure this alignment survives over a distance of about a persistence length $L_p$.

Nematic coupling between backbone segments amplifies the strength and range
of surface-induced alignment. We observe that both the thickness and ordering of the alignment layer increase with increasing chain length. This happens because longer chains have fewer chain ends, which leads to stronger nematic coupling for chains of the same stiffness.

In the next section, we introduce a lattice version of self-consistent field theory (SCFT) for describing semiflexible chains near an impenetrable surface. We use our SCFT lattice model to analyze the effect of nematic coupling on the surface induced alignment. Combining our SCFT model with MD simulations, we can determine the nematic coupling strength for our semiflexible chains. Readers less concerned with the details of our SCFT model may proceed to the results session, consulting the methods section as needed.

4.3 Self-consistent field lattice model

To model an incompressible melt of semiflexible chains near an impenetrable substrate, we introduce a self-consistent field lattice model. Assuming uniaxial symmetry, we model the chains as semiflexible random walkers on a 2D lattice of \( z \) and \( \mu \), in which \( z \) is the perpendicular distance from the interface and \( \mu = \cos \theta \), where \( \theta \) is the angle between the chain and the \( \hat{z} \) axis. Our model can describe uniaxial alignment with respect to the \( \hat{z} \) axis as a function of distance from a planar
interface. Our model is equivalent to the SCFT lattice model used by other authors for describing flexible polymers or copolymers, in which the chains are Gaussian random walkers on a 1D lattice [69–72], but differ in how we treat the orientational degree of freedom.

Near the impenetrable surface, the backbone segments align parallel to the wall, creating a mean quadrupolar aligning field $Q(z)$. The aligning field $Q(z)$ varies with distance from the surface, decaying to zero in the bulk region for chains in the isotropic phase. The mean aligning field is a symmetric and traceless second-order tensor of the form $Q_{ij} = \langle t_i t_j \rangle - \delta_{ij}/3$, where $t$ is the chain tangent.

To simplify the expression for the aligning potential, we replace the tensor field with the scalar field $q(z)$ (eqn 4.3) and assume chains are isotropic in the xy plane:

$$V(\mu, z) = -\alpha q(z) P_2(\mu)$$

in which $\alpha$ is the nematic coupling parameter. For bead-spring chains, the nematic coupling results from the excluded volume interactions of Onsager type. The value of $\alpha$ is governed by the stiffness, bulkiness, and length of the semiflexible polymer chains. For real polymers, the nematic coupling can include other interactions such as dipole-dipole interactions so that $\alpha$ is analogous to the Maier-Saupe parameter for rod-like molecules. Near an impenetrable surface, the aligning potential promotes alignment of chains parallel to the wall and penalizes alignment of chains along $\hat{z}$. Far from the surface, the system is isotropic (above the isotropic-to-nematic (IN) transition), and the aligning potential vanishes.

For an incompressible system, the Hamiltonian $H_0$ of a single chain configuration $\mathbf{R}$ is given as

$$\beta H_0(\mathbf{R}) = \int_0^N ds \left( \frac{\beta \kappa}{2} \left| \frac{dt(s)}{ds} \right|^2 + \beta V(\mu, z) + \beta P(z) \right)$$

in which $N$ is the chain length, $s$ is a monomer index, $t$ is the chain tangent and $\beta$ is $1/kT$. The quantity $\beta \kappa$ is the dimensionless bending modulus of a semiflexible chain, which is equivalent to the persistence length measured in number of repeat units $N_p$. A hydrostatic pressure $P(z)$ acts to maintain a uniform density for the incompressible melt.

Using the single chain Hamiltonian, we define the propagator $\psi(\mu, z; s)$ for
the semiflexible chain. The propagator gives the conditional Boltzmann weight of a chain with length $s$, starting at $z$ with tangent orientation $\mu$ and otherwise unconstrained:

$$\psi(\mu, z; s) = \frac{1}{Z_0} \int D[R] e^{-\beta H_0(R)} \delta(z_1 - z) \delta(\mu_1 - \mu)$$  \hspace{1cm} (4.6)

Here $D[R]$ represents an integral over paths of arclength $s$. We normalize the conditional Boltzmann weight $\psi$ with respect to the partition function of a free semiflexible chain $Z_0$. Our propagator is similar to those used by other authors for describing molten semiflexible chains in blends or block copolymers [12,54,55].

We write the equation of motion for the propagator by differentiating the path integral in eqn 4.6 with respect to $s$:

$$\frac{\partial \psi(\mu, z; s)}{\partial s} = \frac{1}{2\beta \kappa} \nabla_\perp^2 \psi(\mu, z; s) - a\mu \nabla_z \psi(\mu, z; s) - (V(\mu, z) + P(z)) \psi(\mu, z; s)$$  \hspace{1cm} (4.7)

where $\nabla_\perp^2$ is the angular Laplacian operator. The first term on the right-hand side of eqn 4.7 represents the orientational relaxation of the monomers. The second term describes the advection of the monomers. The final term represents the bias in the overall motion of the monomers imposed by the nematic field $V$ and the hydrostatic pressure $P$.

To discretize eqn 4.7, we regard the chain trajectories as semiflexible random paths, which can bend at a given location $z$ from direction $\mu$ to $\mu'$, and then jump in the direction $\mu'$ to a new site $z'$. We design the lattice in $z$ and $\mu$ with intervals $\Delta z$ and $\Delta \mu$ such that a single step of length $a$ satisfies $a\Delta \mu = \Delta z$. This guarantees that a path with any sequence of allowed directions stays on the lattice. The incoming propagator $\psi(\mu, z'; s)$ is then biased by the aligning potential $V(\mu, z)$ and the hydrostatic pressure $P(z)$.

To carry out the discretization, we treat the angular diffusion, advection, and bias in turn. To discretize the angular diffusion, we first write the $\mu$ dependent part of the angular Laplacian, which describes angular diffusion with respect to $\hat{z}$:

$$\frac{\partial \psi(\mu, z; s)}{\partial s} = \frac{1}{2\beta \kappa} \frac{\partial}{\partial \mu} \left( (1 - \mu^2) \frac{\partial}{\partial \mu} \psi(\mu, z; s) \right)$$  \hspace{1cm} (4.8)

Eqn 4.8 takes the form of a conservation equation for the propagator $\psi$, which
represents the Boltzmann weight density on the $\mu$, $z$ lattice. For isotropic chains, $\psi$ is uniform. We identify the diffusive flux of $\Psi$ as $J(\mu) = -\frac{1}{2\kappa} \frac{\partial \psi}{\partial \mu}$, which flows across a cross sectional area $1 - \mu^2$.

To express the conservation equation on lattice, we discretize the angular diffusion using finite difference. We assume that the diffusive current of Boltzmann weight into a given $\mu$ can only come from the two adjacent $\mu$ lattice sites for semiflexible chains (Figure 4.4). The angular diffusion of Boltzmann weight is now written as

$$\psi(\mu_i; s + \Delta s) = \psi(\mu_i; s) + J_+ A_+ - J_- A_-$$  \hspace{1cm} (4.9)$$

in which $J_+ = \frac{\psi(\mu_{i+1}) - \psi(\mu_i)}{\Delta \mu}$ is from $\mu_{i+1}$ lattice site and $J_- = \frac{\psi(\mu_i) - \psi(\mu_{i-1})}{\Delta \mu}$ is from $\mu_{i-1}$ lattice site. The “cross sectional areas” $A_\pm$ across which the fluxes flow are given by $A_\pm = 1 - (\mu_{i\pm1} + \mu_i)^2/4$. We use the average $\mu$ for writing $A_\pm$ because the cross sectional area varies linearly across a $\mu$ site.

**Figure 4.4.** Cartoon for SCFT evolution of semiflexible chains on a 2D lattice. The absorbing boundary is on the left (red). The reflection boundary is on the right (blue). The probability of a monomer entering a green site comes from a yellow site via advective motion (red arrows) after bending (changing $\mu$) from the adjacent sites (blue arrows). A chain cannot enter the gray sites due to the absorbing boundary.

Because the discretized angular diffusion equation is linear, a transfer matrix $T_\mu$ describes the semiflexible diffusion of Boltzmann weight density $\psi$ on the $\mu$ lattice: $\psi(z; s + ds) = (T_\mu \psi)(z; s)$. The transfer matrix is a $M \times M$ tridiagonal
matrix \( (M \) is the number of \( \mu \) sites), in the form of
\[
T_{\mu} = I_M + \frac{1}{2\beta K} \begin{bmatrix}
\frac{1-\tilde{\mu}_1^2}{\Delta \mu_1^2} & \frac{1-\tilde{\mu}_2^2}{\Delta \mu_2^2} & \cdots & \frac{1-\tilde{\mu}_{M-1}^2}{\Delta \mu_{M-1}^2} \\
\frac{1-\tilde{\mu}_2^2}{\Delta \mu_2^2} & \frac{1-\tilde{\mu}_1^2}{\Delta \mu_1^2} & \cdots & \frac{1-\tilde{\mu}_{M-1}^2}{\Delta \mu_{M-1}^2} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{1-\tilde{\mu}_{M-1}^2}{\Delta \mu_{M-1}^2} & \frac{1-\tilde{\mu}_{M-2}^2}{\Delta \mu_{M-2}^2} & \cdots & \frac{1-\tilde{\mu}_1^2}{\Delta \mu_1^2}
\end{bmatrix}
\]

(4.10)

where \( I_M \) is an identity matrix of size \( M \), and \( \tilde{\mu}_i = (\mu_i + \mu_{i+1})/2 \), which covers \( \Delta \mu_i \) on the \( \mu \) lattice. The transfer matrix \( T_{\mu} \) for angular diffusion preserves the sum of Boltzmann weights; for each \( z \), the sum over \( \mu \) of \( \psi(\mu, z) \) remains constant after applying \( T_{\mu} \).

To model advection, we discretize the \( z \) dimension into equally spaced layers (with spacing \( \Delta z \)) so that \( \psi(\mu, z; s) \) can be regarded as a vector indexed by \( \mu \) and \( z \). The transfer matrix \( T_{\mu} \) relaxes \( \psi \) at each \( z \) layer, allowing us to treat the advection separately. After angular diffusion, we define another transfer matrix \( T_z \) to move Boltzmann weight from one layer \( z \) to another along a fixed direction \( \mu \):
\[
(T_z \cdot \psi)(\mu, z') = \psi(\mu, z)
\]

(4.11)
in which \( z' = z + \mu \Delta z / \Delta \mu \), where \( \Delta \mu \) is the \( \mu \) lattice spacing. \( T_z \) is likewise conservative, preserving the sum of Boltzmann weights over all sites.

In our work, we discretize the \( \mu \) interval \((-1, 1)\) into nine equally spaced lattice sites: \( \{-1, -3/4, -1/2, -1/4, 0, 1/4, 1/2, 3/4, 1\} \). We take an odd number of sites so that the \( \mu \) lattice includes \( \mu = 0 \) that represents the perpendicular direction with respect to \( \hat{z} \), as well as \( \mu = \pm 1 \) that represent perfect alignment along \( \hat{z} \). Varying the number of \( \mu \) sites results in different resolutions for both \( \mu \) and \( z \).

The interval \( \mu = (-1, 1) \) is partitioned by the lattice into subintervals, bounded by the values \( \tilde{\mu}_i \), each associated with a given lattice point \( \mu_i \). Each \( \mu \) lattice site "owns" a subinterval of width \( \Delta \mu = 1/4 \), except for the two end site \( \mu = \pm 1 \), which own intervals of width \( \Delta \mu = 1/8 \). Together with the Boltzmann weight \( \psi(\mu, z) \), the subinterval width \( \Delta \mu_i \) gives the spread of probability over \( \mu \) for layer \( z \). Correspondingly, we divide the space lattice \( z \) into sites with spacing \( \Delta z = 1/4a \), where \( a \) is the step length along the chain.
In summary, for each step, a semiflexible chain at \( z \) may bend randomly from \( \mu \) to some adjacent \( \mu' \), and then jumps (advects) to another spatial lattice site at \( z' = z + 4\mu'\Delta z \) (Figure 4.4). Finally, the semiflexible random walk arriving at each site is biased by the hydrostatic pressure and the quadrupolar aligning potential:

\[
\psi(\mu_m, z, s + 1) = (T_z \cdot T_\mu \cdot \psi)(\mu_m, z; s)e^{-V(\mu,z)}e^{-P(z)}
\]  

(4.12)

The Boltzmann weight for monomer \( s \) on a chain of length \( N \) to locate at \( z \) with orientation \( \mu \) is defined using the product of two Boltzmann weights, one for each portion of the chain (0 to \( s \) and \( s \) to \( N \)):

\[
Q(\mu_m, z; s) = \psi(\mu_m, z; s)\psi(-\mu_m, z; N + 1 - s)\Delta\mu_m e^{V(\mu,z)} e^{P(z)}
\]  

(4.13)

The two exponential factors in eqn 4.13 correct for double counting of the penalty imposed by \( V \) and \( P \) for placing the monomer \( s \) at site \( \{\mu, z\} \).

From the Boltzmann weight, we can compute all thermodynamic quantities of interest. By summing up the Boltzmann weights of all the possible configurations, we write the volume fraction at a given \( z \) lattice as:

\[
\phi(z) = \frac{\sum_{m=1}^{9} \sum_{s=1}^{N} Q(\mu_m, z; s)}{F_n}
\]  

(4.14)

The normalization factor \( F_n \) is the Boltzmann weight averaged over the \( L \) layers:

\[
F_n = \sum_{z=1}^{L} \sum_{m=1}^{9} \sum_{s=1}^{N} Q(\mu_m, z; s)/L,
\]

where \( L \) is the total number of layers along \( \hat{z} \).

Finally, we write the quadrupolar order parameter

\[
q(z) = \frac{\sum_{m=1}^{9} \sum_{s=1}^{N} Q(\mu_m, z; s)P_2'(\mu_m)}{F_n}
\]  

(4.15)

Here \( P_2'(\mu_i) \) is a set of discretized Legendre polynomials, defined to satisfy the discrete analog of the orthogonality relations for Legendre polynomials: \( \int_{-1}^{1} d\mu P_j(\mu)P_k(\mu) = 0 \), for Legendre polynomials of different order \( (j \neq k) \). For the discretized Legendre polynomials, the orthogonality relations are given using a discrete inner product. Because the discretized usual \( P_2(\mu_i) \) is not orthogonal to \( P_0(\mu_i) \), under the discrete inner product, we define \( P_2'(\mu_i) \), which satisfies \( P_2'(\mu_i) \cdot P_0(\mu_i) = 0 \), using the
Gram-Schmidt process:

\[ P'_2(\mu_i) = P_2(\mu_i) - P'_0(\mu_i) \left( \frac{P_2(\mu_i) \cdot P_0(\mu_i)}{P'_0(\mu_i) \cdot P_0(\mu_i)} \right) \]  \( (4.16) \)

We use \( P'_2(\mu_i) \) rather than the usual \( P_2(\mu_i) \) in defining \( q(z) \) to ensure the order parameter is strictly zero for an isotropic melt.

To model the impenetrable surface, we impose conditions that prevent chain paths from ever visiting lattice sites with \( z < 0 \) (Figure 4.4). For the sites inside the wall, the Boltzmann densities are always zero:

\[ \psi(\mu_m, z_1; s) = \psi(\mu_m, z_2; s) = \psi(\mu_m, z_3; s) = \psi(\mu_m, z_4; s) = 0 \]  \( (4.17) \)

in which \( z_i \) is the \( i \)th \( z \) lattice site. We use the four layers with zero Boltzmann weight to ensure chains entering the interfacial layer at \( z_5 \) do not originate from the other side of the interface.

Because we treat a melt of semiflexible polymers confined between two parallel walls, we impose a reflection boundary condition at the middle plane (Figure 4.4):

\[ \psi(\mu_m, z_l; s) = \psi(-\mu_m, z_{2L-l-1}; s) \]  \( (4.18) \)

where \( L \) is the total number of \( z \) lattice sites in half the system. We use this condition for sites \( z_l \) near the midplane, satisfying \( L + 5 \leq l \leq L + 8 \).

We obtain the self-consistent solution for the polymer melt by the evolution withs of the Boltzmann weight \( \psi(\mu, z; s) \) from the initial condition, in which monomers are placed in the lattice sites with Boltzmann weights given as:

\[ \psi(\mu_m, z; 1) = e^{-V(\mu_m, z)} e^{-P(z)} \]  \( (4.19) \)

Self-consistency is achieved when the pressure \( P(z) \) yields a uniform volume fraction \( \phi(z) = 1 \) and the input order parameter \( q(z) \) agrees with the output. Using Mathematica, we can obtain the self-consistent solution for 40-mers with 81 lattice sites in \( \hat{z} \) by iteratively adjusting \( P(z) \) and \( q(z) \) in three hours on a single CPU.

To validate our SCFT lattice model for semiflexible chains, we compare the results for a free semiflexible random walker on the 2D lattice to results obtained using a conventional SCFT calculation, in which spatial degrees of freedom are
discretized, while angular dependence is expanded in a Legendre series. In absence of external fields, the semiflexible propagator in the 2D space of $\mu$ and $z$ is governed by:

$$\frac{\partial \psi(\mu, z; s)}{\partial s} = \frac{1}{2\beta\kappa} \nabla^2_\perp \psi(\mu, z; s) - a\mu \nabla_z \psi(\mu, z; s)$$ (4.20)

To solve eqn 4.20, we discretize in $z$, and expand the propagator at each $z$ using Legendre polynomials [56]:

$$\psi(\mu, z; s) = \sum_k c_k(z; s) P_k(\mu)$$ (4.21)

The Legendre polynomials $P_k(\mu)$ are the eigenfunction of the angular Laplacian $\nabla^2_\perp$, with eigenvalue equals $-k(k+1)$. The same procedures are used by Chen et al. for solving the propagator equation of a confined semiflexible chain in solution [13].

In the discretized equation, the advective motion of the propagator must be handled with care. The derivative $\nabla_z \psi$ is represented by an “upwind” difference $(\psi_z - \psi_{z-\Delta z})/\Delta z$ for right-moving paths and a “downwind” difference $(\psi_{z+\Delta z} - \psi_z)/\Delta z$ for left-moving paths (Figure 4.5). Using the theta function $\theta(\mu)$, we write this as

$$a\mu \nabla_z \psi(\mu, z; s) \approx \frac{1}{\Delta z} (a\mu \theta(\mu)(\psi_{z-\Delta z} - \psi_z) - a\mu \theta(-\mu)(\psi_{z+\Delta z} - \psi_z))$$ (4.22)

As a consequence, a chain launched at $z$ in direction $\mu > 0$ ($\mu < 0$) will initially propagate only rightwards (leftwards), as it should. If a centered difference $(\psi_+ - \psi_-)/(2\Delta z)$ is used for $\nabla_z \psi$, unphysical behavior results.

![Figure 4.5](image.png)

**Figure 4.5.** Advective motion of propagator on the discretized $z$ grid. Left-going propagator (green). Right-going propagator (gray).

By taking inner product of $P_k(\mu)$ with eqn 4.20 and integrate the equation over
\( \mu \), we obtain a linear system of first order ordinary differential equations:

\[
\frac{\partial c_k(z)}{\partial s} = -\frac{1}{2\beta \kappa} k(k+1) c_k(z)
+ \frac{2k+1}{2\Delta z} \sum_{j=1}^9 \left[A^+_kj (c_j(z-\Delta z) - c_j(z)) - A^-kj (c_j(z+\Delta z) - c_j(z)) \right]
\]

(4.23)

in which the \( A^\pm kj \) is defined as

\[
A^\pm kj = \int_{-1}^1 d\mu \mu \theta(\pm\mu)P_i(\mu)P_j(\mu)
\]

(4.24)

We numerically solve the differential equations to obtain the expansion coefficients \( c_k(z) \), from which we construct the propagator for the semiflexible random walker.

We validate our discretization of angular diffusion by calculating the tangent-tangent correlation function for a free chain. We consider a semiflexible walker with bending stiffness \( \beta \kappa = 5 \), initially directed along \( \hat{z} \) \( (\mu = 1) \). The tangent-tangent correlation function can be computed analytically, as the correlation function of the first order Legendre polynomials \( \langle P_1(\mu_s)P_1(\mu_0) \rangle = e^{-s/\beta \kappa} \), where \( P_1(\mu_s) \) represents the first order Legendre polynomial for tangent \( t_s \), i.e., \( \hat{z} \cdot t_s \). Because the first chain tangent \( t_0 \) aligns along \( \hat{z} \) so that \( P_1(\mu_0) = 1 \), \( \langle P_1(\mu_s)P_1(\mu_0) \rangle \) is equivalent to the tangent-tangent correlation function \( \langle t_s \cdot t_0 \rangle \). The correlation function \( \langle P_1(\mu_s)P_1(\mu_0) \rangle \) obtained using our lattice model agrees well with results from truncating the Legendre polynomial expansion at \( P_8 \). The characteristic length of the exponential decay is given by the bending stiffness \( \beta \kappa \) (Figure 4.6).

To validate our discretization of advective evolution, we compute the Boltzmann weight distributions \( \psi(z) = \int_{-1}^1 d\mu \psi(z,\mu) \) for a semiflexible walker starting at \( z = 0 \) with \( \mu = 1 \). Our lattice model agrees well with the results obtained by truncating the Legendre polynomial expansion at the 8th order (Figure 4.7a).

We find that to obtain a sharply defined propagating front for the Boltzmann weight distribution \( \psi(z) \) using Legendre polynomial expansion, we must use a rather fine mesh in the \( z \) dimension, with grid size several times smaller than that used in our lattice model (Figure 4.7b). Taking more expansion terms in the Legendre series has little effect on the sharpness of the front.
**Figure 4.6.** Tangent-tangent correlation function for our lattice model (circles), by Legendre expansion (squares), and analytically (dashed line) for chains with stiffness $\beta \kappa = 5$.

**Figure 4.7.** (a) Boltzmann weight distribution for a free semiflexible walker initiated at $z = 0$ with $\mu = 1$ and $\beta \kappa = 5$. Legendre expansion is truncated at $P_8$ and the $z$ grid spacing is 0.2. The lattice model has a $z$ grid size of 0.25. (b) Boltzmann weight distribution for $t = 10$ obtained using Legendre polynomial expansion with different $z$ grid spacings. Legendre polynomial expansion results are in open symbols and lattice model results are in filled symbols.

## 4.4 Results and discussion

Even without the orientational coupling between backbone segments, the impenetrable boundary compels chain segments to align parallel to the surface. This alignment propagates in from the surface until the chains can “forget” their direction. For semiflexible chains, tangent-tangent correlations decay slowly, resulting
in an aligned layer of about a persistence length $L_p$. For rod-like chains ($N < \beta \kappa$), the thickness of the ordered layer is less than a persistence length $L_p$.

This local alignment can be predicted using SCFT. First, we predict the order parameter $q(z)$ with no nematic coupling, for chains of various length. Our results for the longest chains ($N = 40$) agree closely with the results of Morse and Fredrickson for chains of infinite length (using ground state dominance) [12] (Figure 4.8).

**Figure 4.8.** Order parameter profile for semiflexible chains with $\beta \kappa = 5$ near a rigid surface (a). A semi-log plot of normalized order parameter (b). The open symbols are theoretical predictions. The filled symbols are from MD simulations. The solid line is from Morse and Fredrickson.

Without nematic coupling, our SCFT results agree only qualitatively with the MD simulation results. We compare our predictions for chains with zero nematic coupling to the MD simulations (See Figure 4.3). For chains in the rod-like regime ($N = 5$), the predicted order parameter profile agrees well with the MD simulation (Figure 4.8). Because the nematic coupling is small for short chains, the uniaxial alignment perpendicular to $\hat{z}$ is a result of the chain stiffness and the impenetrable surface. For longer chains, the nematic coupling is more significant, resulting in an enhanced alignment (Figure 4.8b).

To explore the effect of nematic coupling on the surface induced alignment, we vary the coupling parameter $\alpha$ in our SCFT lattice model. We find that the alignment decays more slowly with increasing nematic coupling parameter $\alpha$ (Figure 4.9). Nematic coupling between chains can amplify and stabilize the alignment induced by the wall.

Nematic coupling also reduces the hydrostatic pressure near the surface for
Figure 4.9. Order parameter profile for semiflexible chains with $\beta \kappa = 5$ and $N = 40$ near a rigid surface (a). A semi-log plot of normalized order parameter (b).

molten semiflexible polymers. To maintain a uniform density, a large negative pressure is required to pull monomers in to the region near the wall, where their orientational entropy is reduced (Figure 4.10). Nematic coupling, reduces the free energy cost for finding a monomer in the aligned region near the wall. Hence, a less negative pressure is required for chains with stronger coupling constant $\alpha$, as shown in Figure 4.10.

Figure 4.10. Hydrostatic pressure for semiflexible chains of stiffness $\beta \kappa = 5$ and length $N = 40$ (a). A semi-log plot of the normalized pressure (b).

Because nematic coupling enhances the chain alignment, MD simulations of semiflexible chains near an impenetrable surface can in principle be used to determine the nematic coupling parameter $\alpha$. For a given $\alpha$, we can obtain the order
parameter profile for semiflexible chains near the surface using SCFT. Finding $\alpha$ by comparing SCFT predictions to MD results is analogous to our previously reported method, in which we find $\alpha$ by fitting SCFT to MD results for semiflexible polymers under external tension in a bulk isotropic phase [50]. To investigate this new approach to finding $\alpha$, we show that with the correct values of $\alpha$ the predicted order parameter profiles agree better with the MD simulations than the SCFT results with no nematic coupling for 10-mers and 40-mers (Figure 4.8).

We first determine the nematic coupling for the 10-mers and the 40-mers with our previous method based on tension induced alignment. We apply a weak uniaxial tension (of about $2kT$ per chain end-to-end distance) to chains in the bulk isotropic phase. The tension-induced alignment is promoted by nematic coupling. For a given $\alpha$, we compute the chain alignment $q(\alpha)$ using SCFT. By fitting the SCFT predictions to the MD simulations, we determine the nematic coupling $\alpha$ for 10-mers and 40-mers as $\alpha = 0.2kT$ and $\alpha = 0.95kT$, respectively.

We use these values of $\alpha$ in our SCFT lattice model to compute the order parameter profiles for 10-mers and 40-mers. For the 10-mers, the effect of nematic coupling on surface alignment is weak; SCFT results with $\alpha = 0$ already agree reasonably well with MD simulation results. The predicted order parameter profile of the 10-mers agrees with MD simulations, slightly better than the results with no nematic coupling (compare Figure 4.11 and Figure 4.8).

![Figure 4.11](image)

**Figure 4.11.** Order parameter profile for the semiflexible chains with $N = 40$ and $N = 10$ (a). A semi-log plot of normalized order parameter is shown in (b). The bending stiffness $\beta\kappa = 5$ for both chains.

For the 40-mers, the effect of nematic coupling is much stronger. Our SCFT
predictions with nematic coupling describe much better the overall decay of nematic order than SCFT predictions with no nematic coupling (compare Figure 4.11 and Figure 4.8).

Quantitative discrepancies, however, remain between our SCFT and MD results for $N = 40$. One possible origin for the discrepancy is that with sufficiently strong nematic coupling, semiflexible chains can exhibit biaxial alignment, breaking cylindrical symmetry near the impenetrable surface.

In our MD simulations, the 40-mers are indeed anisotropic in the xy plane near the surface, as quantified by the biaxiality parameter $\eta$ (Figure 4.12). The biaxiality is defined as $\eta = \lambda_2 - \lambda_3$, where $\lambda_2$ and $\lambda_3$ are the second and the third eigenvalue of the order tensor $Q_{ij}$, respectively [73]. The biaxiality $\eta$ equals zero for uniaxial alignment and $1/3$ for biaxial alignment. Our lattice calculations, however, assume the system exhibits uniaxial symmetry about the $\hat{z}$ axis. The 40-mers do not satisfy our assumption, which may be the origin of the quantitative discrepancy between our SCFT prediction and MD results.

![Figure 4.12](image)

**Figure 4.12.** Biaxiality $\eta$ for chains with bending stiffness $\beta \kappa = 5$ in the MD simulations.

For semiflexible polymers, the biaxial alignment at the interface is due to the nematic interactions between the backbone segments. The slightly rough surfaces can induce weak anisotropic ordering near the wall, which is amplified and stabilized by the nematic interactions. Thus, the strength and the range of biaxiality $\eta$ increase with increasing nematic coupling parameter $\alpha$ for semiflexible polymers (Figure 4.12).

Extracting a precise value of $\alpha$ by fitting the SCFT results to MD simulations
of surface induced alignment is challenging. For chains with small $\alpha$, the effect of nematic coupling is a rather weak correction to the SCFT prediction so that fitting $\alpha$ by comparison to MD results is difficult. Whereas, for chains with sufficiently strong $\alpha$, the surface alignment can break uniaxial symmetry so that the order parameter profile is no longer a function of $\mu$ and $z$ only. Still, comparing our lattice model predictions with MD simulations provides a useful estimation of the strength of nematic coupling for semiflexible polymers.

Based on the MD simulations and the SCFT results, we predict that semiflexible conjugated polymers can form a strongly ordered layer parallel to the flat surface of an impenetrable substrate or a highly incompatible phase. For example, for poly(3-hexylthiophene) (P3HT), the bending stiffness $\beta \kappa$ is about 7 ($L_p$ about 3nm) and the value of $\alpha$ is about $kT$ [40, 50]. The nematic coupling for P3HT is comparable to that of the 40-mers in our simulations. Hence, we expect that P3HT can form a well-aligned layer about $1.5L_p=4.5$nm thick near an impenetrable surface (Figure 4.11). In thin-film transistors, P3HT may align parallel to the surface of the gate dielectric, creating an aligned layer of about 4.5nm thick. For stiffer conjugated polymers such as poly((9,9-diocetylfluorene)-2,7-diyl-alt-[4,7-bis(thiophen-5-yl)-2,1,3-benzothiadiazole]-2âĂš2âĂš2âĂš2âĂš-diyl) (PFTBT) and poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT), the surface induced alignment may be even more substantial, because of the stronger nematic coupling expected for stiffer chains. After crystallization, the uniaxial and biaxial aligned layers may lead to larger crystalline domains and more ordered amorphous regions in the final semicrystalline state. Thus, charge transport that occurs near interfaces, as in thin-film transistors, is likely more efficient than in the bulk for conjugated polymers.

4.5 Conclusions

In this paper, we investigate surface-induced alignment in semiflexible polymers using molecular dynamic (MD) simulations and self-consistent field theory (SCFT). In our simulations, molten bead-spring chains are confined between two rigid substrates, composed of frozen beads with liquid-like order. The surfaces of the resulting substrates are not perfectly smooth. We use this disordered surface to induce chain alignment because monomers tend to crystallize near a perfectly smooth surface, which creates artifacts in chain density and alignment near the
substrates.
Semiflexible chains tend to align parallel to the impenetrable surface, creating an ordered layer about a persistence length $L_p$ thick. Nematic coupling between backbone segments can increase the magnitude and range of the alignment, even for chains that are isotropic in the bulk. In simulations, the ordered layer is thicker for longer chains because they have larger nematic coupling constants: fewer ends means the chains are more strongly affected by the local nematic field. The aligned layer may be critical to organic electronics based on conjugated polymers, because inter-chain ordering may significantly promote charge transport.

To analyze the effect of nematic coupling on surface-induced alignment for semiflexible polymers, we develop a self-consistent field lattice model. We show that the alignment decays more slowly with increasing coupling strength. Our lattice model is equivalent to solving the propagator equations for semiflexible polymers using truncated Legendre polynomial expansion, but our approach directly describes the position and orientation of semiflexible chain paths. The lattice model is inexpensive to solve and can be applied to other systems with planar interfaces, such as diblock copolymers in the lamellar phase.

Combining the lattice model with MD simulations of chains near an impenetrable surface, we can estimate the strength of nematic coupling for semiflexible polymers, although extracting a precise value of $\alpha$ is challenging. Mild nematic coupling has only a small effect on the SCFT prediction, so that fitting the MD results to get an accurate value of $\alpha$ is difficult. With strong nematic coupling, semiflexible chains may exhibit biaxial ordering near the impenetrable surface, which leads to even slower decay of the order parameter than we predict under the assumption of uniaxial symmetry.
Chapter 5  
Using surface-induced alignment to locate isotropic-to-nematic transition for semiflexible polymers

Semiflexible polymers undergo a weakly first order isotropic-to-nematic (IN) phase transition when the volume fraction $\phi$ is high enough that random alignment of the backbone segments is no longer viable. For semiflexible chains, the critical volume fraction $\phi_c$ is governed by the backbone stiffness $N_p$. To locate the IN phase transition, we perform molecular dynamics (MD) simulations of bead-spring chains confined between two impenetrable parallel surfaces. We use the impenetrable surfaces to induce nematic-isotropic interfaces for semiflexible chains in the isotropic phase. By progressively increasing the backbone stiffness $N_p$, we observe the propagation of surface-induced nematic order above a critical stiffness $N_p^c$ for a given $\phi$. Using the simulation results $N_p^c(\phi)$, we construct the IN phase boundary in the $\phi - N_p$ plane, from which the scaling relation between $\phi_c$ and $N_p$ is obtained. For semiflexible chains with $N_p \leq 5.78$, our results suggest $\phi_c \sim N_p^{-1}$, consistent with prediction by Khokhlov and Semenov. For chains with $N_p \geq 5.78$, we observe a new scaling regime in which $\phi_c \sim N_p^{-2/3}$. The work in this chapter has been published on Soft Matter [74].
5.1 Introduction

Nematic polymers are important because of their unique optical, rheological and structural properties. These properties arise from the combination of translational disorder and long range orientational order, allowing nematic polymers to be used in many applications, including displays, high strength fibers, microelectromechanical systems, and biomedical devices [4–7]. The existence of a nematic phase can also enable better processing for semiconducting conjugated polymers. Crystallization from the nematic phase can facilitate the formation of ordered final morphologies, which leads to the improved electronic properties for conjugated polymers [8–11,75].

For rod-like nematic polymers, the isotropic-to-nematic (IN) phase transition is a function of concentration, as demonstrated by Onsager [1]. Rod-like molecule in solution can be represented as a suspension of rigid cylinders of length $L$ and diameter $d$. In the melt, the molecular backbones can be treated as rigid rods dispersed by “bound solvent” of flexible side chains. The rod-like objects interact via excluded volume interactions, which are governed by $L$ and $d$. At high enough concentration, the isotropic phase is no longer viable. The rigid rods tend to align uniaxially with each other to avoid overlapping, resulting in a nematic phase. The critical volume fraction $\phi_c$ for rod-like molecules scales as the aspect ratio $d/L$.

Likewise, the isotropic-to-nematic transition is a function of concentration for semiflexible polymers, for which backbone stiffness is characterized by the persistence length $L_p$. By dividing semiflexible chains into segments of length $L_p$ (persistence length) and assuming such segments interact via excluded volume of Onsager type, Khokhlov and Semenov (KS) predict the critical volume fraction $\phi_c$ scales as $d/L_p$, where $d$ is the chain diameter [2, 3, 76, 77]. For semiflexible chains in rod-like regime ($L/L_p < 1$), KS theory agrees qualitatively with Monte Carlo simulations [78–80]. By improving the treatment of segmental interactions, the theoretical predictions agree better with experiments and simulations [81, 82]. Because the scaling $\phi_c d/L_p$ results from the entropic cost for aligning Kuhn segments, the improved segmental interactions may not alter the KS scaling relation. The KS scaling relation for semiflexible polymers, however, has not been thoroughly tested for $L/L_p > 1$.

To investigate the relation between the isotropic-to-nematic transition and the chain stiffness for liquid crystal polymers in the semiflexible regime ($L/L_p > 1$),
we perform molecular dynamic (MD) simulations of bead-spring chains confined between two impenetrable surfaces, formed by “frozen” Lennard-Jones (LJ) liquid substrates. In the isotropic phase, semiflexible chains tend to align parallel to an impenetrable surface, creating an isotropic-nematic interface of width about a persistence length $L_p$.

Instead of performing many simulations at constant stiffness, we can conveniently obtain the critical stiffness $N_p^c$ for semiflexible chains at a given volume fraction $\phi$ by observing how nematic order propagates from the surfaces. Conventionally, the critical volume fraction for the phase transition $\phi^c(N_p)$ can be obtained by simulating given chains at various $\phi$. This method, however, is computationally expensive. For example, Egorov et al. obtain the IN phase boundaries for short semiflexible chains by performing many GPU accelerated NVT simulations [83,84]. The error for $\phi^c(N_p)$ determined using the conventional method is as large as the resolution of volume fraction between different simulations. A large amount of simulations with high $\phi$ resolution is required for acquiring accurate results.

To probe the IN phase transition, we initiate the propagation of the surface-induced nematic order by progressively stiffening the chains during an MD simulation. Below a critical stiffness, the nematic-isotropic interface induced by the surface is stationary. Above the critical stiffness, nematic order propagates from the surface toward the center of the sample, which becomes nematically aligned throughout. Correspondingly, the system energy drops linearly with time as the stiffness steadily increases below the critical value, decays quadratically with time as the nematic order propagates, and once again decreases linearly with time after the system has nematically aligned. By measuring how the system energy evolves as chain stiffness steadily increases, we can detect the nematic phase for semiflexible chains.

With the help of surface-induced nematic order, our method is robust to the hysteresis in locating the IN transition. Surface alignment allows for propagation of the nematic phase without the need for nucleation. Without the surface induced nematic alignment, undercooling past the critical temperature (or stiffness) is required for bulk semiflexible chains to undergo the first order transition.

Our approach is similar to the method developed in our group for obtaining the equilibrium crystal melting temperature for polypropylene from MD simulations [85]. Using $N_p^c(\phi)$, we construct the IN phase boundary in the $\phi - N_p$ plane, from which
we determine the scaling relation between the critical volume fraction and the chain stiffness for semiflexible polymers.

5.2 MD simulation details

To locate the isotropic-to-nematic transition, we simulate semiflexible chains confined between two parallel substrates of LJ “frozen” liquid, in which monomers are no longer allowed to move. We use these disordered but macroscopically flat surfaces instead of perfectly smooth repulsive walls to induce isotropic-nematic (IN) interfaces for semiflexible polymers, because perfectly smooth walls lead to artificial crystallization of the chains [63]. We also use “wavy” walls to induce surface alignment for the bead-spring chains. The “wavy” surfaces are LJ glass surfaces with stripes of valley along \( \hat{x} \), for which the surface roughness is approximated by a square wave along \( \hat{y} \), with amplitude of \( a \) and wavelength of \( 4a \). Because chains tend to align along the surface stripes, the surface-induced nematic order is more uniaxial than the alignment induced by the flat walls.

The non-bonded interactions for the beads on the polymer chains and the beads in the substrates are modeled using the purely repulsive Weeks-Chandler-Anderson (WCA) pair potential:

\[
U_{nb}(r) = \begin{cases} 
4\epsilon \left( \left( \frac{r}{\sigma} \right)^{-12} - \left( \frac{r}{\sigma} \right)^{-6} + \frac{1}{4} \right) & \text{if } r \leq 2^{1/6}\sigma \\
0 & \text{if } r > 2^{1/6}\sigma 
\end{cases} \quad (5.1)
\]

To give our bead-spring chains reasonable length and energy scales, we arbitrarily select the interaction strength \( \epsilon = 2.5 \) kJ/mol and \( \sigma = 0.2 \) nm. We define the diameter of beads \( a = 2^{1/6}\sigma \). We choose the molar mass of the beads as 12 g/mol, so that the LJ characteristic time is \( \tau = 0.00044 \) ns in our simulations.

The intra-chain interactions are represented by a harmonic stretching potential and a harmonic bending potential:

\[
U_b = \frac{1}{2} k_l \left( \frac{l}{2^{1/6}\sigma} - 1 \right)^2 + \frac{1}{2} k_\theta \theta^2 \quad (5.2)
\]

where \( l \) is bond length, \( \theta \) is bond deflection angle, and \( k_l \) is the spring constant for bond stretching, about \( 400kT \) in our simulations. The harmonic bending spring
constant \( k_\theta \) penalizes the deflection of backbone tangents, resulting in a chain stiffness \( N_p = \beta k_\theta \), where \( \beta = 1/kT \). We can convert the chain stiffness \( N_p \) to the persistence length by \( L_p = N_p a \). Because the chain diameter \( d \) is the same as the monomer size \( a \), \( N_p \) equals \( L_p/d \) in our simulations.

To probe the IN transition, we stiffen the bead-spring chains from \( N_p = 4 \) to \( N_p = 8.5 \) by linearly decreasing the simulation temperature \( T \) from 375K with a rate 0.000088 \( K/\tau \). We choose 300K as the reference temperature at which the LJ repulsion \( \beta \epsilon = kT \). The phase transition occurs at a critical stiffness \( N_p^c \), where the surface induced nematic order starts to propagate from the surface. We use chain length \( N = 40 \) in our simulations so that even the stiffest chains (\( N_p = 8.5 \)) are in the semiflexible regime (\( N/N_p \gg 1 \)).

To determine the critical stiffness \( N_p^c(\phi) \) for semiflexible chains, we steadily increase with time the backbone stiffness \( N_p \), in simulations performed at various volume fractions \( \phi \). The volume faction is varied by adjusting the simulation box size in the \( \hat{z} \) direction (perpendicular to the walls) from 45\( a \) to 60\( a \), while fixing the transverse dimension as 40\( a \). The highest volume fraction we use is 0.7, which we regard as defining the melt [64,65], and the lowest volume fraction is 0.53, representing a concentrated solution. Because the transverse dimension is about 4\( R_g \) for \( N_p = 8.5 \), where \( R_g \) is the radius of gyration of the bead-spring chains, spurious self-interactions across the periodic boundaries are negligible in the simulations.

### 5.3 Propagation of surface-induced nematic order

In the simulations, we quantify the nematic order with a symmetric traceless second-rank tensor \( Q \) of the form \( Q_{ij} = \langle t_i t_j \rangle - \delta_{ij}/3 \), where \( t \) is a backbone tangent, and the indices \( i, j = (x, y, z) \). A scalar order parameter \( S \) can be defined as the primary eigenvalue of the order tensor \( Q \). The sign of \( S \) distinguishes uniaxial alignment from biaxial order. The order parameter \( S \) is positive for uniaxial alignment, where polymer backbone segments tend to align parallel along a preferred direction. A negative \( S \) indicates biaxial order, for which chain backbones tend to be perpendicular to a preferred direction. The value of \( S \) equals 2/3, 0 and \(-1/3\) for perfect uniaxial, isotropic and perfect biaxial alignment, respectively.

In the isotropic phase, semiflexible chains tend to align parallel to the flat
substrates (perpendicular to the longitudinal direction \( \hat{z} \)), creating a nematically
ordered layer with thickness about a persistence length \( L_p \) (Figure 5.1). We regard this alignment layer as a nematic-isotropic (IN) interface, in which the nematic order decays to zero from the wall. The negative order parameter \( S \) indicates the chain alignment within the IN interface is biaxial. Indeed, for semiflexible chains near impenetrable surfaces, a first-order orientational wetting transition may occur before the bulk IN transition so that the induced alignment breaks cylindrical symmetry and becomes anisotropic in the transverse (xy) plane [14,86]. Our previous work, however, shows that the alignment near the walls is anisotropic in the xy plane, spontaneously selecting an orientation direction, even for chains with weak nematic interactions in the isotropic phase [63]. As such, the first-order transition probed by our method corresponds to the bulk IN transition.

**Figure 5.1.** Initial order parameter profile for the chains in the isotropic phase with \( N_p = 4 \) and \( \phi = 0.7 \) between two flat surfaces and between two wavy surfaces.

Because the interfacial width is about \( L_p \), the IN interfaces broaden slightly with increasing chain stiffness \( N_p \), when \( N_p \) is below the critical value. To visualize the evolution of IN interfaces, we compute the order parameter profile \( S(z) \) from snapshots along different portions of a simulation trajectory, during which chains are progressively stiffened (Figure 5.2a). The nematic interactions between backbone segments increase with increasing \( N_p \), amplifying the anisotropy in the transverse plane. Near the phase transition (\( N_p^c \)), the average nematic director in the interfacial region rotates from the longitudinal direction to the transverse direction. The alignment becomes uniaxial for backbone segments beyond the monolayer next to
the wall, indicated by the positive order parameter $S$ (Figure 5.2a).

![Figure 5.2. Order parameter profile for the chains during stiffening with $\phi = 0.7$ between two flat surfaces (a) and between two wavy surfaces (b). The critical stiffness for IN transition $N_p^c$ is 5.2. Each profiles is obtained from a piece of simulation trajectory, in which chains are progressively stiffened.](image)

For chains in the isotropic phase, the system energy decreases linearly near the phase transition as $N_p$ increases (Figure 5.3). Assuming constant “heat capacity” $C_p = \partial E/\partial N_p$ in the isotropic phase, this linear behavior is expected from the contribution of the bulk of the system, because the expansion of IN interfaces is negligible. Over a wider range of stiffness, $E$ is not a strictly linear function of $N_p$, because the contribution from the broadening interfaces is no longer negligible.

At the critical stiffness, the interfaces begin to move toward the center of the sample, corresponding to the propagation of nematic order from the wall (Figure 5.2a). The system energy $E$ decreases markedly with increasing stiffness, compared to the previous linear trend below the critical stiffness (Figure 5.3). The deflection indicates the isotropic-to-nematic transition. A quadratic behavior of $E$ versus stiffness is expected, because the propagation speed of the nematic front should be proportional to $N_p - N_p^c$ (Figure 5.3).
When propagation is complete, the two nematic regions merge into a single nematic slab, in which the alignment is uniform across the system (Figure 5.2a). The system energy resumes a linear decrease, with a slope reflecting the constant “heat capacity” for the nematic phase (Figure 5.3).

The impenetrable surfaces are necessary for accurately locating the isotropic-to-nematic phase transition. The stiffening simulations can be also performed for chains in bulk to probe the nematic phase. Without the surface induced nematic ordering, however, due to the slow kinetics of the nematic nuclei formation, an undercooling effect is observed for semiflexible chains in bulk to undergo the phase transition (Figure 5.3).

Figure 5.3. Potential energy vs. stiffness for molten semiflexible chains (\(\phi = 0.7\)) in bulk and near flat and wavy surfaces. \(N_p^c = 5.2\) for chains between impenetrable surfaces. \(N_p^c = 5.7\) for chains in bulk.

We expect that the flat surfaces are sufficient for accurately probing the IN phase transition for semiflexible polymers. Near the flat surface, the alignment layer can spontaneously break symmetry as chain stiffness increases, resulting in uniaxial nematic order that propagates when the chain stiffness above \(N_p^c\). Indeed, a “wavy” surface can induce symmetry breaking in the surface layer at a lower stiffness (Figure 5.1). Near the phase transition, the alignment induced by the “wavy” surface is more uniaxial than the order induced by a flat surface (Figure 5.2). The potential energy \(E(N_p)\) for chains near the “wavy” surfaces, however, is indistinguishable from the results obtained using the flat surfaces. Hence, we confirm that the nematic
order induced by flat surfaces is sufficient for locating the IN phase transition for semiflexible chains.

5.4 Results

We have argued that the expected behavior of the system energy as the chains stiffen is a linear decrease above the isotropic-to-nematic transition, followed by quadratic decrease as nematic order propagates, and finally a return to linear decrease when ordering is complete.

Therefore to locate the phase transition, we fit the system energy to a piecewise function of $N_p$ (Figure 5.4):

$$E(N_p) = \begin{cases} 
  aN_p + b & \text{if } N_p < N_p^c \\
  c(N_p - N_p^c)^2 + d & \text{if } N_p^c \leq N_p \leq N_p^e \\
  eN_p + f & \text{if } N_p > N_p^e 
\end{cases}$$

(5.3)

in which the lowercase letters are fitting coefficients, $N_p^c$ is the critical stiffness for the IN transition and $N_p^e$ is the stiffness at which the phase transition is complete.

**Figure 5.4.** Potential energy vs. stiffness for $\phi = 0.7$. Simulations (symbols), fitting (solid curves), critical stiffness $N_p^c$ (black dashed lines), phase transition enthalpy $\Delta H$ (arrow). Green dashed line extrapolates nematic energy to $N_p^c$. Inset: order parameter profiles for stiffness highlighted by dashed circles: $N_p = 4.8 \pm 0.1$ (red), $N_p = 5.6 \pm 0.1$ (blue), $N_p = 6.4 \pm 0.1$ (green).
To investigate the relation between the IN transition and volume fraction, we stiffen semiflexible chains at various volume fractions. We fit the system energy $E(\phi)$ to eqn 3, from which the critical stiffness for the phase transition $N_p^c(\phi)$ is obtained. We observe that the critical stiffness to undergo the IN transition $N_p^c$ is higher for chains in a more dilute environment (Figure 5.5).

Using the simulation results, we construct the isotropic-to-nematic phase boundary in the $\phi - N_p$ plane for semiflexible polymers (Figure 5.6). The fitting errors of $N_p^c(\phi)$ are represented with the error bars on the phase boundary, which are smaller than the width of the symbols. We fit the phase boundary to determine the scaling relation between the critical volume fraction $\phi_c$ and the stiffness $N_p$ for semiflexible chains. For chains with mild stiffness $N_p \leq 5.78$, our results are consistent with the KS theory, which predicts that $\phi_c$ scales as $N_p^{-1}$ [2, 3]. For chains with $N_p \geq 5.78$, however, the critical volume fraction $\phi_c$ scales roughly as $N_p^{-2/3}$. The physical origin for this scaling is currently unclear.

We expect the deviation of our results from the KS theory is not a result of changing chain diameter during the stiffening simulations. Indeed, decreasing simulation temperature can alter the repulsion strength $\beta \epsilon$ between beads. During the propagation of nematic order, however, $\beta \epsilon$ only varies between 1 and 1.5 in our simulations for chains near the IN transition (from $\beta \kappa = 5$ to 7.5. Thus, changing temperature has a negligible effect on the chain diameter and the relation
Figure 5.6. Isotropic-to-nematic phase boundary in the $\phi - N_p$ plane for semiflexible polymers.

$N_p = L_p/d$ is still valid.

As a check on our determination of the IN phase boundary, we perform simulations at constant stiffness for $\phi = 0.60$, the point where the phase boundary starts to deviate from the KS theory. The initial configurations for the equilibrium simulations are snapshots of the stiffening simulation, in which the chain stiffness equals the critical value $N_p^c = 6.3$. By observing the potential energy as a function of simulation time for chains with stiffness slightly away from $N_p^c$, we can test the stability of the isotropic phase. For chains with $N_p < N_p^c$, the isotropic phase is stable and the IN interfaces are stationary, resulting in a constant potential energy over time. For chains with stiffness above $N_p^c$, the IN interfaces propagate at a constant velocity, resulting in a linear decay of the potential energy. The potential energy plot suggests that the IN phase transition occurs at $N_p$ between 6.3 and 6.4 for chains with $\phi = 0.6$ (Figure 5.7a), consistent with our prediction of $N_p^c = 6.3$ from Figure 5.5.

By observing the decay rate of potential energy $-\partial E/\partial t$, we can confirm our assumption that the constant propagation speed of the IN interface $v(N_p)$ is proportional to $N_p - N_p^c$. During the propagation, the potential energy decreases as the system transitions from the isotropic phase to the nematic phase. The amount of materials per unit time that undergo the IN transition is proportional to $v(N_p)$. Thus, $-\partial E/\partial t$ should also scale as $v(N_p)$. Because the decay rate of potential energy satisfies $-\partial E/\partial t \propto N_p - N_p^c$, the propagation speed of the IN interface...
Figure 5.7. (a) Potential energy vs. simulation time for chains with various stiffness at volume fraction $\phi = 0.60$. Simulation results (symbols), linear fit (solid lines). (b) Decay rate of potential energy vs. stiffness deviation from the critical value. Curve is a linear fit of the data.

$v(N_p)$ is proportional to $N_p - N_p^c$ (Figure 5.7b).

From the total time it takes nematic order to propagate across the system, we can estimate the propagation speed of the IN interfaces:

$$v(N_p) = v_0 \frac{N_p - N_p^c}{N_p^c}$$  \hspace{1cm} (5.4)

Here $v_0$ is the characteristic speed of the moving nematic front, to be determined below by comparison to simulation results. The propagation of nematic order starts at $N_p^c$, and completes at $N_p^c$ when the system is fully nematic. We obtain $N_p^c$ directly from fits of the system energy $E$ to eqn 3. During propagation, the interfaces travel at velocity $v(N_p)$ over an average distance of $h/2$, where $h$ is the distance between the two substrates. The kinematic equation of the IN interfaces satisfies $\dot{x} = v(N_p)$, with boundary conditions $x(N_p^c) = 0$ and $x(N_p^c) = h/2$. Using
the constant cooling rate $\delta_T$ and the critical temperature $T_c$, we can write the chain stiffness as a function of time (valid for small temperature changes) as:

$$N_p(t) = N_p^c \frac{T_c}{T_c - \delta_T t}$$

(5.5)

Combining eqn 5.4 and 5.5, after some algebra we obtain

$$v_0 \approx \frac{\delta_T h N_p^c^2}{T_c (N_p^e - N_p^c)^2}$$

(5.6)

Because $N_p^c$, $N_p^e$ and $T_c$ are determined from fits, and $\delta_T$ and $h$ are known a priori, we can obtain $v_0$.

We normalize the characteristic speed $v_0$ by the root-mean-square thermal speed at the critical stiffness $v_{rms} = \sqrt{3kT_c/m}$, where $m$ is the monomer mass (Figure 5.8). We find the reasonable result that the propagation speed is only a tiny fraction of the “speed of sound” (thermal speed).

**Figure 5.8.** Characteristic speed $v_0$ for the propagating nematic front. $v_0$ normalized by the root-mean-square thermal speed $v_{rms}$ at critical stiffness $N_p^c$. Simulation results (disks), curve to guide the eye (dashed).

Using the potential energy $E(N_p)$ for progressively stiffened chains, we also obtain the enthalpy change at the IN transition. By extrapolation, we determine the potential energy in the nematic phase at the critical stiffness, $E_N(N_p^c)$. The phase transition enthalpy $\Delta H$ is estimated as $E_I(N_p^c) - E_N(N_p^c)$, where $E_I(N_p^c)$ is the energy in the isotropic phase at $N_p^c$ (see Figure 5.4). At the phase transition, the enthalpy change equals the loss in orientational entropy for semiflexible polymers,
of order $kT$ per persistence length (Figure 5.9). The rather small enthalpy change indicates that the IN transition is the entropically driven for our semiflexible chains.

![Graph](image.png)

**Figure 5.9.** Enthalpy change per persistence length at the IN transition. Simulation results (disks), curve to guide the eye (dashed).

### 5.5 Conclusions

We probe the isotropic-to-nematic phase transition in semiflexible polymers by observing the propagation of the nematic order induced by two impenetrable surfaces. In MD simulations, we progressively stiffen the chains, so that propagation of nematic order occurs when the chain stiffness exceeds the critical value $N_p^c$. By fitting the system energy to a piecewise function of $N_p$, we can conveniently and accurately locate the IN transition for semiflexible polymers at various concentrations.

Using our method, we construct the IN phase boundary in the $\phi - N_p$ plane, from which the scaling relation between the critical volume fraction $\phi_c$ and chain stiffness $N_p$ is obtained for semiflexible polymers. For moderately stiff chains with stiffness $N_p \leq 5.78$, the scaling relation is consistent with predictions of Khokhlov and Semenov: $\phi_c \sim N_p^{-1}$. For chain stiffness $N_p$ exceeding 5.78, the simulation results deviate from the KS theory, suggesting instead $\phi_c \sim N_p^{-2/3}$. Future work is warranted to uncover the physical interpretation of this scaling relationship for very stiff chains.
The IN phase boundary, however, does not include the coexistence densities at the isotropic-to-nematic transitions. Directly observing the IN coexistence in MD simulations is challenging, as a result of finite size effect [83]. Here we propose a method for estimating the IN coexistence boundaries from MD simulations. First, by performing equilibrium NVT simulations along the phase boundary in Figure 5.6, we can estimate the pressure \( P_c(N_p, \phi) \) at the IN transition. We can then simulate chains in NPT ensemble at \( P_c \) with stiffness slightly above and below the critical value, namely \( N_p^+ \) and \( N_p^- \). Chains with stiffness \( N_p^+ \) and \( N_p^- \) will exhibit the nematic phase and the isotropic phase at \( P_c \), respectively. By measuring the equilibrium densities for chains with \( N_p^+ \) and \( N_p^- \) at the centers of the simulation boxes, the IN coexistence boundaries can be approximated. Because equilibrating a system near the critical point is computationally expensive, constructing the IN coexistence window is beyond the scope of this manuscript and will be included in our future work.

By extrapolating the potential energy in the nematic phase back to the critical stiffness \( N_p^c \), we estimate the enthalpy change \( \Delta H \) of the weakly first order IN transition. The value of \( \Delta H \) is of order \( kT \) per persistence length \( N_p^c \) for semiflexible polymer, as expected for this entropically driven phase transition.
Chapter 6  
Effect of nematic alignment on charge transport for conjugated polymers

Chain alignment in amorphous regions can significantly affect the electronic properties of conjugated polymers. Instead of being isotropic, amorphous conjugated polymers may exhibit nematic order in bulk or at interfaces. The uniaxial alignment of chain backbones may in turn enhance the charge transport in amorphous conjugated polymers. Because many high performance materials are semicrystalline or nearly amorphous, the role of nematic order can be important in the overall charge mobilities. In this chapter, we investigate the effects of nematic order on charge mobility for conjugated polymers using an analytical model. We show that increasing the uniaxial order in the system can enhance the charge mobility for conjugated polymers. Our model also suggests that the molecular weight dependence of charge mobility is more significant for the nematic chains than for the isotropic polymers. By analyzing the probability of forming hairpin defects, we demonstrate the effect of persistence length on charge transport for nematic conjugated polymers.

6.1 Introduction

Charge transport in amorphous regions plays an important role in the overall electronic properties of conjugated polymers. For semicrystalline conjugated polymers, although charges can transfer quickly on the crystalline chains, the long-time scale...
charge mobility may depend on the inter-crystallite charge transport through the amorphous chains. When the distances between neighboring crystallites are short, of order a persistence length, the tie-chains that connect the ordered regions can be rather straight and co-planar, resulting in sufficient inter-crystalline charge transfer. As a consequence, the charge mobility of conjugated polymers depends only on the electronic properties of the crystalline chains [26]. Otherwise, the inter-crystallite charge transfer in the amorphous regions may govern the overall charge mobility of semicrystalline conjugated polymers. Recently, amorphous conjugated polymers with charge mobilities exceed 1 cm² V⁻¹ s⁻¹ have also been reported [87,88]. For these materials, the electronic properties are evidently governed by the charge transport on amorphous chains.

For isotropic amorphous conjugated polymers, the conformational order can significantly affect the electronic properties of the sample. Using density functional theory (DFT) calculations, previous authors demonstrate that the distortion of backbone dihedral angles can localize the charge carriers, in turn hinder the intra-chain charge transfer for amorphous chains [89,90]. By assuming the amorphous chains are in the isotropic phase, previous authors investigate the effect of chain conformation on charge mobility. Pearson et al. predict that the charge mobility scales linearly with molecular weight for short isotropic chains and reaches a plateau at high molecular weight [91]. Using Marcus theory and Kinetic Monte Carlo simulations, Spakowitz and coworkers show how the conformations of the amorphous chains affect the field-dependent charge mobility for semicrystalline polymers [92–94].

Conjugated polymers, however, can spontaneously exhibit nematic order in bulk and at interfaces. In bulk, the semiflexible backbones of conjugated polymers may be regarded as sequences of rod-like segments with length about a Kuhn length $l_k$ (twice of the persistence length $l_p$) and radius $r_\rho$ (given by the density and the contour length of the chain). When the concentration of the polymer is high enough, randomly placing the rod-like segments with random orientation in the system is no longer entropically viable [1–3]. The system then undergoes a first order transition from the isotropic phase to the nematic phase, in which the chain segments align uniaxially.

Near impenetrable surfaces, such as the gate dielectric substrates in field-effect transistors, conjugated polymers in the isotropic phase can also exhibit nematic
order. Instead of bending the chain trajectories sharply to avoid collisions with the walls, semiflexible polymers tend to align parallel to impenetrable interfaces, creating alignment layers of thickness of about a persistence length $l_p$ [12–14,63,74]. The nematic interactions between backbone segments can further enhance the surface-induced alignment. For chains that are near the isotropic-to-nematic phase boundary, the surface-induced alignment is uniaxial, with the nematic director parallel to the interface [63,74].

Investigating the effect of uniaxial nematic alignment on charge mobility for amorphous conjugated polymers is important for understanding the overall charge transport in electronic devices. For example, regardless of being in the nematic phase or not, conjugated polymers that can conduct charges in field-effect transistors (FET) may be uniaxially ordered. In bottom-gated FET, the charge carriers are vertically localized within a layer about 5 nm near the dielectric substrates [19]. Because the persistence length $l_p$ of high performance conjugated polymers usually exceeds 3 nm, we expect the amorphous chains align uniaxially in the conductive regions. In order to model the charge mobilities in FET, we need to consider the effect of nematic alignment on the charge transfer.

### 6.2 Analytical model for charge transport on amorphous chains

In this work, we use an analytical model to study the charge transport for uniaxially aligned conjugated polymers. The phenomenological model for charge transfer is originally proposed by Pearson and coworkers for isotropic chains [91]. The intra-chain charge transport is regarded as one-dimensional diffusion of charge carriers with the reflecting boundary condition – the intra-chain charge motions can be reflected by the chain ends. The probability density for a charge carrier that is injected at time 0 into monomer $s$ to locate at monomer $s'$ at time $t$ is

$$ p(s, s', t) = \frac{1}{N} \left( 1 + 2 \sum_{j=1}^{\infty} \cos\left(\frac{j\pi s}{N}\right) \cos\left(\frac{j\pi s'}{N}\right) \exp\left(-\frac{j^2 t}{\tau_i}\right) \right) $$

(in which $N$ is the chain length and $\tau_i$ is the characteristic time for intra chain charge transfer, defined as $\tau_i = N^2\pi^{-1}k_i^{-1}$. The parameter $k_i$ is the “mean” intra-chain
charge transfer rate. The effect of the distortion of backbone dihedral angles is not explicitly included in the model. We consider the disorder in dihedral angles only leads to a smaller $k_i$.

On average, the relative distance (measured in number of monomers) between the location of a charge carrier at $t$ and its initial position is

$$\langle \Delta N(t) \rangle = \frac{1}{N} \int_0^N ds' \int_0^N ds |s - s'| p(s, s', t)$$

$$= \frac{N}{3} \left( 1 + \frac{6}{\pi^2} \sum_{j=1}^{\infty} \frac{1}{j^2} \exp \left( -\frac{j^2 t}{\tau_i} \right) \right) \tag{6.2}$$

After diffusing on the same chain for a while, the charge carrier can hop to another chain. We assume that the time cost for inter-chain hopping follows an exponential distribution:

$$h(t) = \frac{1}{\tau_h} \exp \left( -\frac{t}{\tau_h} \right) \tag{6.3}$$

so that the mean lifetime for intra-chain charge transfer is $\tau_h = \int_0^\infty dt \, th(t)$. The value of $\tau_h$ is inversely proportional to the inter-chain charge transfer rate $k_h$.

Between two inter-chain hopping events, the trajectory of charge motion is governed by the conformation of the semiflexible chain with length equals $\langle \Delta N(\tau_h) \rangle$:

$$\langle \Delta N(\tau_h) \rangle = \int_0^\infty dth(t) \langle \Delta N(t) \rangle = \frac{N}{\gamma} (\coth \gamma - \frac{1}{\gamma}) \tag{6.4}$$

where $\gamma = \pi (\tau_i/\tau_h)^{1/2} = N(k_h/k_i)^{1/2}$. The value of $\gamma^2$ represent the ratio of characteristic time for intra- and inter-chain random charge hopping.

Using eqn 6.4, we can obtain the mean square displacement per hopping time $\tau_h$ for the charge carriers in the conducting direction as the chain dimension $\langle R_{\parallel}^2(\tau_h) \rangle$. By regarding the long-timescale charge transfer as one dimensional random walk of step length $\langle R_{\parallel}^2(\tau_h) \rangle^{1/2}$, we obtain the charge mobility from the diffusion coefficient using the Einstein relation:

$$\mu_{\parallel} = \frac{eD}{kT} = \frac{e\langle R_{\parallel}^2(\tau_h) \rangle}{2kT\tau_h} \tag{6.5}$$

For chains in the isotropic phase, Pearson et al. obtain the charge mobility by
treating the conjugated polymers as random walks of Kuhn segments [91]:

\[ \mu_i^\parallel = \frac{e\left\langle \Delta N(\tau_h) \right\rangle a l_p}{6kT \tau_h} \]  

(6.6)

in which \( a \) is the length of a monomer and \( l_p \) is the persistence length. The charge mobility scales linearly with persistence length for isotropic chains.

When the inter-chain charge hopping is slow or the molecular weight is low \((\tau_i \ll \tau_h)\), the charge carrier can explore the whole chain between two hopping events so that \( \left\langle \Delta N(\tau_h) \right\rangle \sim N \). In this case, the charge mobility scales linearly with the molecular weight. When the inter-chain charge transfer is fast or the molecular weight is high \((\tau_i \gg \tau_h)\), a charge carrier will hop to another chain before it realizes how long the polymer is. For this case, the overall charge mobility is independent of molecular weight.

As a consequence, the charge mobility for isotropic chains increases linearly with molecular weight and reach a plateau at high molecular weight. By normalizing the charge mobility with respect to the plateau value, one can obtain the molecular weight dependence of charge mobility:

\[ \frac{\mu_i^\parallel(N)}{\mu_i^\parallel(\infty)} = \coth(Nk_i^{-1/2}k_h^{1/2}) - \frac{1}{Nk_i^{-1/2}k_h^{1/2}} \]  

(6.7)

Depending on the ratio of intra- and inter-chain charge transfer rates \( k_i/k_h \), the molecular weight dependence may be significant for isotropic polymers.

### 6.3 Effect of uniaxial alignment on charge mobility

Now we consider the charge transport in semiflexible chains with uniaxial alignment. Assuming the intra-chain charge diffusion rate \( k_i \) is not affected by the uniaxial alignment, we can combine the chain dimension in the alignment direction with eqn 6.4 to predict the anisotropic charge mobility for conjugated polymers.

For conjugated polymers with nematic order, the chain backbones align along the nematic director \( \mathbf{a} \). The overall degree of alignment can be described using a quadrupolar order parameter \( q \):

\[ q = \frac{3}{2} \left\langle (\cos \theta)^2 \right\rangle - \frac{1}{2} \]  

(6.8)
where $\theta$ is the deflection angle between a backbone tangent and the nematic director.

Thermal fluctuations can lead to deviations of chain paths from the aligning direction $x$. The nematic field, however, can constrain the transverse fluctuations of chain paths $\Delta r^2_\perp$. We can define a deflection length $\lambda$ below which the transverse fluctuations of nematic chains are governed by the bending stiffness of worm-like chain and unaffected by the nematic field. The average transverse fluctuation of the ends of the deflection segments (of length $\lambda$) is

$$\Delta r^2_\perp \approx \frac{2\lambda^3}{l_p}$$

(6.9)

Effectively, the uniaxial alignment field acts as a cylindrical confinement of radius $\Delta r_\perp$ and axis in the $x$ direction [83, 84, 95, 96].

When the persistence length $l_p$ is greater than $\lambda$, the deflection segments are rather straight. And the nematic order in the system can be approximated as:

$$q = \frac{3}{2}\langle(\cos \theta_\lambda)^2\rangle - \frac{1}{2} \approx 1 - \frac{3}{2}\left(\frac{\Delta r_\perp}{\lambda}\right)^2$$

(6.10)

where $\theta_\lambda$ is the angle between the deflection segment and the nematic director $x$.

Combining eqn 6.9 and 6.10, one can also write the deflection length $\lambda$ as a function of the nematic order $q$ and the chain persistence length $l_p$:

$$\lambda = \frac{1}{3}(1 - q)l_p$$

(6.11)

In the uniaxial alignment direction, the charge carriers travels along some rod-like paths with sub sequences of length $\lambda\langle\cos \theta_\lambda\rangle$. As a consequence, the intra-chain charge trajectory between two inter-chain hopping events follows the statistics of rod-like chain:

$$\langle R^2_\parallel(\tau_h)\rangle_n = \langle\Delta N(\tau_h)\rangle^2a^2\langle\cos \theta_\lambda\rangle^2 \approx \frac{\langle\Delta N(\tau_h)\rangle^2a^2(2 + q)^2}{9}$$

(6.12)

By treating the long-time charge transfer as one-dimensional random walk in the alignment direction, we predict the charge mobility in the aligning direction for
uniaxially ordered chains:

\[
\mu_n^\parallel = \frac{e\langle R_\parallel^2(\tau_h) \rangle_n}{2\tau_h kT} = \frac{e\langle \Delta N(\tau_h) \rangle^2 a^2(2 + q)^2}{18\tau_h kT} \tag{6.13}
\]

Increasing the degree of alignment can enhance charge mobility for conjugated polymers (Figure 6.1).

![Graph showing charge mobility vs. uniaxial order q.](image)

**Figure 6.1.** Charge mobility vs. uniaxial order \(q\).

We also obtain the molecular weight dependence of charge mobility for uniaxially aligned chains. When \(\tau_i \ll \tau_h\), the charge mobility in the alignment direction scales with \(N^2\). This molecular weight dependence is the same as the prediction by Pearson and coworkers for charge transport on nematic rod-like chains. When the inter-chain charge transfer is very fast or the molecular weight is high (\(\tau_i \gg \tau_h\)), the charge mobility of the aligned polymers is independent of molecular weight. We write the normalized charge mobility in the alignment direction as

\[
\frac{\mu_n^\parallel(N)}{\mu_n^\parallel(\infty)} = \left( \coth(Nk_i^{-1/2}k_h^{1/2}) - \frac{1}{Nk_i^{-1/2}k_h^{1/2}} \right)^2 \tag{6.14}
\]

The molecular weight dependence is more significant for the uniaxially aligned polymers than for the isotropic chains (Figure 6.2).
6.4 Role of hairpin defects in charge transport for nematic chains

In the above analysis, we assume that every piece of the aligned chains uniaxially points in the alignment direction. The assumption is true when the overall chain contour length $l$ is comparable to the persistence length $l_p$. For short semiflexible chains, forming a hairpin defect involves sharply bending the stiff polymer backbone against the external field. As a consequence, the energy penalty for forming short hairpin is large and the probability for finding those defects is negligible. When chains are long enough, however, semiflexible polymers can form hairpin defects by bending the chain trajectory more smoothly over a length greater than $l_p$. In this way, the elastic energy penalty for bending a chain is smaller and the probability for forming hairpins is higher.

The existence of these “U-turns” can affect the statistics of the charge trajectories. If the intra-chain charge transport occurs on a length scale shorter than the mean distance between two hairpin defects $N_a$ (Figure 6.3), the charge trajectory is rod-like (eqn 6.12). When the contour length of the intra-chain charge trajectory is much longer than $N_a$, the intra-chain charge motions are essentially one dimensional random walks with step length equals $N_a$.

To reveal the effect of hairpin defects on charge transport for polymer nematics, we construct a simple model to estimate the bending energy cost of a hairpin $E_h$. 

Figure 6.2. Charge mobility vs. chain length $N$ for isotropic (red) and uniaxially aligned chains (blue).
and the mean “arm” distance $N_a$ between two defects. In the model, we align semiflexible chains using an external aligning field $A$ and write the single chain Hamiltonian as

$$
\beta H[u(s)] = \int_0^N ds \left( \frac{N_p}{2} \left| \frac{\partial u(s)}{\partial s} \right|^2 + U(u_s) \right)
$$

(6.15)

in which $N_p$ is the persistence length measured in number of monomers ($N_p = l_p/a$), and $u(s)$ is the normalized chain path, in which each segment is a unit vector. The interaction of a chain segment $u_s$ with the external aligning field is

$$
U(u_s) = -AP_2(\cos \theta_s)
$$

(6.16)

where $\theta_s$ is the angle between the sth chain segment and the aligning axis, and $P_2$ is the second order Legendre polynomial.

For nematic polymers, we expect the energy cost for forming a hairpin defect is expensive, of at least several $kT$. As a consequence, the conformation of the hairpin must be dominated by a classical chain path, which possesses the lowest free energy. Assuming the fluctuations around the most favorable chain path are negligible, we obtain the hairpin conformation by minimizing the free energy:

$$
0 = \frac{\delta F[u(s)]}{\delta u(s)} = \frac{\delta}{\delta u(s)} \int_0^N ds \left( \frac{N_p}{2} \left| \frac{\partial u(s)}{\partial s} \right|^2 + U(u_s) \right)
= -N_p \frac{\partial^2 u(s)}{\partial s^2} + \frac{\partial U}{\partial u(s)}
$$

(6.17)
Because the alignment is uniaxial, we only interest in the deflection angle $\theta$ of the chain path from the alignment axis:

$$\frac{\partial^2 \theta(s)}{\partial s^2} - \frac{3}{2} \omega \sin 2\theta(s) = 0$$

(6.18)

in which $\omega = \frac{A}{N_p}$. Using eqn 6.18, we can solve the most favorable conformation of a hairpin by constraining the orientation of the chain ends so that $\theta(0) = 0$ and $\theta(N) = \pi$.

In absence of the aligning field $A$ ($\omega = 0$), the solution of the above equation is evidently $\theta(s) = \pi s/N$. The hairpin is a hemicircle so that the deflection angle $\theta$ varies linearly over the chain length (Figure 6.4). The stiff polymer backbone bends uniformly to reduce the elastic energy cost.

For systems with uniaxial alignment (so that $A$ and $\omega$ are greater than zero), we analytically solve eqn 6.18 by realizing the differential equation is essentially the equation of motion for a particle subjected to a force given by $-\omega \sin 2\theta(s)$:

$$\theta(s) = 2 \arccot \left( \exp \left[ (3\omega)^{1/2} \left( \frac{N}{2} - s \right) \right] \right)$$

(6.19)

When the strength of the uniaxial aligning field increases ($\omega$ also increases), the radius of the hairpin decreases. Although the bending energy is higher for smaller hairpin, the cost of alignment against the field $A$ is lower.

**Figure 6.4.** Chain path for a semiflexible hairpin with length $N = 20$. $\omega = 0$ (red), $\omega = 0.1$ (blue), $\omega = 0.3$ (green), $\omega = 0.5$ (purple).
Using the favorable chain path $\theta(s)$, we can obtain the characteristic size of the hairpin $N_b$ (shown in Figure 6.3):

$$N_b = (3\omega)^{-1/2} = (3N_p/A)^{1/2} \quad (6.20)$$

We can also obtain the bending energy cost per hairpin defect for long nematic chains:

$$\beta E_h = \lim_{N \to \infty} \int_0^N ds \frac{N_p}{2} \left( \frac{\partial \theta(s)}{\partial s} \right)^2 = (3AN_p)^{1/2} \quad (6.21)$$

The value of $E_h$ arises from the optimal size of the hairpin elbow ($N_b$) and increases with both the aligning field $A$ and the chain stiffness $N_p$.

Because the bending energy of a hairpin is as large as several $kT$, the probability for finding these defects is low. We may consider the hairpin defects as “idea gases”, distributed randomly on the uniaxially aligned chains. The “volume fraction” of the hairpin defects can be approximated as:

$$\phi = \frac{N_b}{N_a} \quad (6.22)$$

And we can write the free energy for the “hairpin gas molecules” as:

$$F = \frac{N}{N_a} \ln \phi + \frac{N}{N_a} E_h \quad (6.23)$$

By minimizing the free energy with respect to $N_a$, we obtain the mean chain length between two defects:

$$N_a = 3^{1/2} e^{1+(3AN_p)^{1/2}} \left( \frac{N_p}{A} \right)^{1/2} \quad (6.24)$$

To demonstrate the typical value of $N_a$ for uniaxially aligned conjugated polymers, we approximate the aligning field strength $A$ for long semiflexible chains in the nematic phase. We regard the aligning field that a chain segment experiences is the product of the average order in the system $q$ and the nematic coupling parameter $\alpha$. For nematic chains near the isotropic-to-nematic phase boundary, we expect $A = \alpha_c q_c$, where $\alpha_c$ is the critical nematic coupling constant and $q_c$ is the critical order parameter for the system to undergo a first order transition from the isotropic phase to the nematic phase. In our pervious work, we estimate the values of $\alpha_c$ and $q_c$ for chains with different stiffness $N_p$ [50]. For long chains ($N \gg N_p$), the critical coupling parameter $\alpha_c \sim N_p^{-1}$ and $q_c$ is rather constant for
chains with different stiffness. As a consequence, we estimate the aligning field strength \( A \approx N_p^{-1} \) (a coefficient of about unity is dropped here). The mean arm length of the hairpin defects now only depends on the chain stiffness:

\[
N_a \approx 27N_p
\]  

(6.25)

The linearly relation between \( N_a \) and \( N_p \) agrees with the previous prediction by Vroege and Odijk, which is obtained by applying a Gaussian trial function to approximate the narrow distribution of chain tangent orientation near \( \theta = 0 \) and \( \pi \) [97]. For mildly stiff chains, we expect \( N_a \) to be as large as \( 10^2 \) (Figure 6.5).

**Figure 6.5.** The mean distance between two hairpin defects \( N_a \) vs. persistence length \( N_p \) for chains in the nematic phase.

When the chain length is much longer than the typical distance between two defects \( (N \gg N_a) \), the intra-chain charge trajectory is no longer rod like. We expect the charge motion is now an one-dimensional random walk with step length equals \( N_a a(2 + q)/3 \):

\[
\langle R^2_{\parallel}(\tau_h) \rangle_{\text{hairpin}} = \langle \Delta N(\tau_h) \rangle N_a \lambda^2 \langle \cos \theta \rangle^2 \approx 3\langle \Delta N(\tau_h) \rangle l_p a(2 + q)^2
\]  

(6.26)

The resulting charge mobility depends linearly on the persistence length \( l_p \), as same as the charge mobility for isotropic chains. For nematic chains without hairpin defects, however, the charge mobility is independent of persistence length (eqn 6.13).

We write the molecular weight dependence of charge mobility using a piecewise
function:

\[
\frac{\mu_{\text{hairpin}}(N)}{\mu_{\text{hairpin}}(\infty)} = \begin{cases} 
\frac{\alpha}{N^2} \left( \coth(Nk_i^{-1/2}k_h^{1/2}) - \frac{1}{Nk_i^{-1/2}k_h^{1/2}} \right)^2 & \text{if } N \leq N_c \\
\coth(Nk_i^{-1/2}k_h^{1/2}) - \frac{1}{Nk_i^{-1/2}k_h^{1/2}} & \text{if } N > N_c
\end{cases}
\]  

(6.27)
in which the crossover point \( N_c \) can be solved by equating the two portions of eqn 6.27. The value of \( N_c \) depends on the arm length of hairpin defects \( N_a \) and the relative charge transfer rate \( k_i/k_h \).

To observe the transition of charge trajectory from the rod-like scaling regime (\( \mu \sim N^{-2} \)) to the random coil regime (\( \mu \sim N^{-1} \)), the relative charge transfer rate \( k_i/k_h \) needs to be large enough so that

\[
\frac{k_i}{k_h} > N_a^2
\]

(6.28)

If \( k_i/k_h \) is too small, a charge carrier can hop to another chain before it realizes the existence of the hairpin defects.

**Figure 6.6.** Normalized charge mobility for isotropic chains, nematic chains, and nematic chains with hairpin defects. Relative charge transfer rate \( k_i/k_h = 10^5 \). \( N_p = 5 \) (green) and 10 (purple).

Because the density of defects is low, the existence of hairpins does not significantly alter the overall molecular weight dependence for charge mobility. For uniaxially aligned chains with hairpin defects, we expect the charge mobility increases with \( N^2 \) when the molecular weight is low (Figure 6.6). When the chain length exceeds \( N_c \), which is much greater than the hairpin arm length \( N_a \), the
molecular weight dependence of charge mobility follows the prediction for isotropic coils. Because \( N_c \) is rather large, the charge mobility for \( N > N_c \) can be close to the plateau value and the coil-like behaviors of the charge trajectories may not be obvious (Figure 6.6).

### 6.5 Comparison with experiments

Because the ratio of intra and inter-chain charge transfer rates \( k_i/k_h \) can be very large, the enhancement in charge mobility can be many orders of magnitude as the molecular weight increases for nematic chains (Figure 6.6). For example, by fitting the experimental mobility data, Spakowitz et al. suggest that the the ratio \( k_i/k_h \) can be as large as \( 10^5 \) for amorphous poly(spirobifluorene) and \( 10^4 \) for poly (3-hexylthiophene) (P3HT) in amorphous regions \([92,94]\). Using microwave conductivity measurements, previous authors also demonstrate that the intra-chain charge transfer can be \( 10^3 \)-\( 10^4 \) times faster than the overall charge motions for fluorene-thiophene copolymers \([98]\). We expect the ratio \( k_i/k_h \) to be smaller but still much greater than unity even for high performance materials.

![Figure 6.7](image.png)

**Figure 6.7.** Charge mobility vs. molecular weight for P3HT. Experimental results \([26]\) (blue dots). Charge transfer model for nematic chains (solid curves). The average mobility of the four high molecular weight samples used as plateau mobility \( \mu_n(\infty) \).

The analytical charge transfer model for nematic chains may explain the strong molecular weight dependence that is observed in experiments for P3HT \([26]\) (Figure 6.7). Although the experimentally measured charge mobility are obtained
by different groups using various processing conditions for semicrystalline P3HT, our model can qualitatively capture the molecular weight dependence of charge mobility for P3HT by assuming a relative transfer rate $k_i/k_h$ of about $10^3$-$10^4$. The different degrees of crystallinity of the P3HT samples and the uncertainties in molecular weight measurements can lead to the rather scattered experimental charge mobilities. As the rate limiting step, charge transfer in amorphous regions may significantly affects the overall charge mobility for semicrystalline P3HT. The nematic order of the amorphous chains may give rise to the significant molecular weight dependence.

6.6 Conclusions

In this work, we apply an analytical model to investigate the effect of uniaxial alignment on charge transport for conjugated polymers. We show that the charge mobilities of uniaxially aligned chains depend more significantly on molecular weight than the charge mobilities of isotropic chains. When the molecular weight is low, we predict that the charge mobility in the alignment direction $\mu_\parallel$ for nematic chains scales quadratically with the chain length ($\sim N^2$). For isotropic chains, $\mu_\parallel$, however, only scales linearly with $N$. This is because the intra-chain charge trajectories are rod-like for nematic chains in the alignment direction and coil-like for isotropic chains. For both nematic and isotropic chains, their charge mobilities reach plateau values when the time cost for a charge carrier exploring the whole chain is comparable to the slower inter-chain hopping time.

We also predict that the charge mobility $\mu_\parallel$ for nematic chains without any defects is independent of the persistence length $l_p$, although $\mu_\parallel$ of isotropic chains depends linearly on $l_p$. For isotropic chains, the straightness of local charge trajectory is governed by the bending stiffness of polymer backbone so that the charge mobility depends on $l_p$. For nematic chains, however, the rod-like intra-chain charge trajectories are controlled by the nematic order $q$ instead of the persistence length $l_p$. As a consequence, $\mu_\parallel$ scales with $(2 + q)^2$ and is independent of $l_p$ for nematic chains.

Together with the alignment field, the persistence length, however, govern the probability for forming hairpin defects in polymer nematics, in turn affect the overall charge mobility. For chains with longer persistence length $l_p$, the bending
energy penalty for forming a hairpin is larger and the concentration of these defects is lower. As a consequence, the distance between two intra-chain hairpin defects $N_a$ increases with increasing persistence length $N_p$. When the chain length $N$ is smaller than $N_a$, the charge trajectory is not affected by the existence of hairpin defects and still rod-like. When $N$ is greater than $N_a$, the nematic polymer backbones become one dimensional (1D) random walks of rod-like pieces of length about $N_a$. With large enough relative charge transfer rate $k_i/k_h > N_a^2$, we expect the intra-chain charge trajectories also behave like 1D random walks. Because $N_a$ scales linearly with $N_p$ in the nematic phase, the charge mobility for nematic polymers in the high molecular weight limit also scales linearly with the persistence length.

For many conjugated polymers, the hairpin defects may not affect the charge mobility, because their relative charge transfer rates $k_i/k_h$ are not large enough, only about $10^3-10^4$, smaller than the typical value of $N_a^2$. A charge carrier can hop to another chain before realizing the existence of hairpin “U-turns”.

Using the nematic charge transfer model, we qualitatively demonstrate that the nematic order and the rather large relative transfer rate $k_i/k_h$ may give rise to the significant molecular weight dependence of the charge mobility for semicrystalline P3HT. Indeed, the charge transport in the crystalline domains may also affect the overall charge mobility. In the future, we will perform mobility measurements for highly amorphous samples, such as regiorandom P3HT, to validate the analytical model.
Chapter 7

Predicting Flory-Huggins $\chi$ for polymers using simulations

We introduce a method, based on a novel thermodynamic integration scheme, to extract the Flory-Huggins $\chi$ parameter as small as $10^{-3}$ $kT$ for polymer blends from molecular dynamics (MD) simulations. We obtain $\chi$ for the archetypical coarse-grained model of nonpolar polymer blends: flexible bead-spring chains with different Lennard-Jones interactions between A and B monomers. Using these $\chi$ values and a lattice version of self-consistent field theory (SCFT), we predict the shape of planar interfaces for phase-separated binary blends. Our SCFT results agree with MD simulations, validating both the predicted $\chi$ values and our thermodynamic integration method. Combined with atomistic simulations, our method can be applied to predict $\chi$ for new polymers from their chemical structures.

7.1 Introduction

The Flory-Huggins $\chi$ parameter is undoubtedly important for inhomogeneous polymers. The value of $\chi$ quantifies the free energy to mix different species, and governs phase behavior and mesoscale structures of polymer blends and block copolymers, which are critical in many applications, including lithography and photovoltaics [16,99]. Predicting $\chi$ from molecular structures would accelerate development of new materials.

Although $\chi$ can be measured experimentally, for example by using X-ray or neutron scattering and the random phase approximation (RPA) [100], predicting $\chi$ is very challenging. The free energy of mixing depends on many factors, including
mismatch in enthalpic interactions and local packing of different monomers. Accurate prediction of $\chi$ can only be obtained from the proper liquidlike structures of polymers. As a consequence, the effect of the chemical structure on $\chi$ is difficult to parameterize.

In principle, $\chi$ can be predicted using molecular simulations, by imitating an experiment from which $\chi$ can be determined. For example, miscible binary blends can be simulated, the structure factor $S(q)$ measured, and RPA applied to fit $\chi$ [101]. However, this approach is limited to polymers with relatively large $\chi$ values. To observe enough variation in $S(q)$ to fit $\chi$, the blend must be not too far from phase separation, which for small $\chi$ implies long chains, hence large simulation systems and long equilibration times.

Values of $\chi$ have also been obtained from vapor-liquid equilibria densities for oligomer blends using Gibbs ensemble Monte Carlo (GEMC) [102]. However, $\chi$ obtained this way are reported with rather large uncertainties, as a result of the uncertainties in the phase equilibria densities. For blends of olefin oligomers, the uncertainty in $\chi$ is as big as the experimental value.

Finally, $\chi$ has been obtained from analyzing the coexistence volume fractions or interfacial concentration profiles between demixed chains in simulations [103,104]. However, this approach is again limited to systems with large $\chi$, because of the large systems and long times required to equilibrate a demixed configuration with long chains.

### 7.2 Extracting $\chi$ from simulation by morphing different polymers

In this work, we introduce a general method to accurately extract $\chi$ from molecular dynamics (MD) simulations. Using a novel thermodynamic integration, we compute the excess Helmholtz free energy of mixing $\Delta F_{ex}$ per monomer, from which $\chi$ can be extracted:

$$\beta \Delta F_{ex} = \beta F_{\text{blend}} - \phi_A \beta F_{\text{pure}}^A - \phi_B \beta F_{\text{pure}}^B = \chi \phi_A \phi_B$$  \hspace{1cm} (7.1)

Here $\beta = 1/kT$, $\phi_A$ and $\phi_B$ are the volume fractions of polymer A and B, and $F_{\text{blend}}$, $F_{\text{pure}}^A$, and $F_{\text{pure}}^B$ are the free energy of the binary blend, homopolymer A and
homopolymer B, respectively.

We perform a thermodynamic integration on a path along which polymer A continuously transforms (“morphs”) into polymer B. The path variable $\lambda$ represents the degree of similarity between two kinds of polymers. We obtain the free energy $F_{\text{blend}}$ and $F_{\text{pure}}^B$, with respect to the free energy of homopolymer A, as the thermodynamic work of morphing either some of the chains (for the blend) or all the chains (for pure B). The homopolymer A melt serves as the reference state. In this way, we avoid awkward reference states of polymer gases, which appear in conventional thermodynamic integration with respect to temperature. We also avoid trying to extract the mixing free energy as a small difference between large free energies (i.e., by comparing the free energy required to “boil” a blend versus pure components).

The $\chi$ parameter we obtain in eqn 7.1 is the “apparent” $\chi$, that one can extract by fitting the structure factor $S(q)$ of a miscible blend in the long wavelength limit, or the peak intensity of $S(q)$ for a disorder diblock copolymer melt to the renormalized one-loop (ROL) theory [105, 106]. This value of $\chi$ depends weakly on chain length, and can be regarded as the sum of an “effective” $\chi_e$ for chains of infinite length, plus a one-loop renormalized correction term of order $O(N^{-1/2})$. Note that $\chi$ may also depend on chain concentration $\phi$, in whatever way is necessary to reconcile the actual dependence of the mixing free energy on $\phi$ with the assumed form of eqn 7.1.

To obtain $\Delta F_{\text{ex}}$, we define two coupling functions $f(\lambda)$ and $g(\lambda)$. As $\lambda$ varies from zero to unity, $f(\lambda)$ and $g(\lambda)$ morph polymer A ($\lambda_0$) into polymer B ($\lambda_1$). The function $f(\lambda)$ transforms the intra-chain bonded and non-bonded interactions of polymer A to those of polymer B. Likewise, $g(\lambda)$ morphs the non-bonded intra-species interactions of polymer A ($E_{\text{intra}}^{\text{nb}}$) into the cross-interactions between A and B ($E_{\text{AB}}^{\text{nb}}$).

Our method relies on the fact that the partial derivative of the excess Helmholtz free energy of mixing with respect to $\lambda$ is an energy-like quantity, measurable in
simulations:

\[
\frac{\partial \Delta F_{\text{ex}}(\lambda)}{\partial \lambda} = \frac{\partial \Delta F_{\text{blend}}(\lambda)}{\partial \lambda} - \phi \frac{\partial \Delta F^B_{\text{pure}}(\lambda)}{\partial \lambda} \\
= \langle \frac{\partial f(\lambda)}{\partial \lambda} \sum_{i=1}^{N_A} \sum_{j=1}^{N_A} E_{AA} \rangle^{\text{blend}} + \frac{\partial g(\lambda)}{\partial \lambda} \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} E_{AB}^{\text{blend}} \rangle_{\text{pure}} - \phi \langle \frac{\partial f(\lambda)}{\partial \lambda} \sum_{i=1}^{N_A} \sum_{j=1}^{N_A} E_{AA} \rangle_{\text{pure}}
\]

(7.2)

Here \(\langle \_ \rangle\) denotes the ensemble average, and \(N_A\) and \(N_B\) are the total numbers of monomer A and B. (Because the volume change upon mixing and the resulting PV work are negligible, we approximate the Gibbs free energy of mixing \(\Delta G_{\text{ex}}\) from which the Flory-Huggins \(\chi(\lambda)\) is more properly obtained as equal to the excess Helmholtz free energy of mixing \(\Delta F_{\text{ex}}\).)

At each \(\lambda_i\), we perform two simulations: one for a randomly mixed binary blend, where a volume fraction \(\phi\) of the chains are morphed; and one for a homopolymer melt, where all chains are morphed. The free energy integrand can be then obtained by measuring the inter-species and intra-species potential energy of the morphing molecules from the simulations. By measuring the excess free energy integrand (eqn 7.2) at discrete points \(\{\lambda_i\}\) from simulations, we can compute the excess free energy by numerical integration, \(\Delta F_{\text{ex}} = \int_{\lambda_0}^{\lambda_1} d\lambda \frac{\partial \Delta F_{\text{ex}}(\lambda)}{\partial \lambda}\). In our method, the excess free energy of mixing is not only averaged over simulation trajectories, but also over many morphing chains, which leads to statistically robust results even for systems with small \(\chi\).

In previous work, we have obtained \(\chi\) for the special and simple case of bead-spring chains that differ only in backbone stiffness, but otherwise have identical interactions between monomers [107]. It was predicted long ago using polymer field theory that even this simple difference between chains would give rise to “entropic” repulsive interactions, arising only from non-ideal local packing [108]. Our results are in excellent agreement with those predictions, and consistent with experimental data [109]. This work, however, cannot incorporate enthalpic interactions between monomers.

In real polymers, mismatches in enthalpic interactions between monomers can arise from differences in molecular polarizability, presence of dipolar groups of different magnitude, or differences in hydrogen bonding propensity. The simplest model with different enthalpic interactions between monomers, which is a coarse-grained idealization of real nonpolar polymers with different molecular polarizability,
is the ubiquitous example of a structurally symmetric polymer blend of flexible bead-spring chains with different interactions between A and B monomers. In this work, we develop and apply a new morphing strategy (eq 2) to obtain $\chi$ from simulations of this important and widely studied system. We then confirm our results by using our $\chi$ values together with lattice self-consistent field theory (SCFT) to predict the density profiles of planar interfaces for phase separated binary mixtures, which we can compare to simulation results for immiscible blends.

### 7.3 $\chi$ for bead-spring chains with mismatch in enthalpic interactions

In our MD simulations, we describe pairwise interactions of polymer A using a Lennard-Jones (LJ) potential:

$$U_{AA}(r) = \begin{cases} 
4\epsilon \left[ \left( \frac{r}{\sigma} \right)^{-12} - \left( \frac{r}{\sigma} \right)^{-6} \right] & \text{if } r \leq 2\sigma \\
0 & \text{if } r > 2\sigma 
\end{cases}$$

(7.3)

in which $\epsilon = kT$. We morph polymer A into polymer B along a simple path: the intra-species interactions of polymer B vary linearly away from $U_{AA}(r)$, so $f(\lambda) = \lambda$ and $U_{BB}(\lambda, r) = \lambda U_{AA}(r)$. A-B interactions are controlled by $g(\lambda) = \lambda^{1/2}$, so that $U_{AB}(\lambda, r) = \lambda^{1/2}U_{AA}(r)$. This choice for $g(\lambda)$ satisfies the Berthelot mixing rule for dispersive interactions, so any value of $\lambda$ corresponds to a coarse-grained model of a nonpolar blend with A and B monomers of different polarizability. Tuning $\lambda$ away from unity creates mismatch in enthalpic interactions between different polymers. For this structurally symmetric blend, bonded interactions remain the same during morphing, described by a harmonic potential $U_b(l) = \frac{1}{2}k_b(l/\sigma - 1)^2$, with bond length $l$ and $k_b = 400 \, kT$.

We perform MD simulations using the GROMACS simulation platform [110]. For each $\lambda$, we perform $NPT$ simulations at $T = 1$ and $P = 0.1 \, kT/\sigma^3$ for a melt of homopolymer B and a symmetric binary blend ($\phi = 0.5$). Each simulation box contains 2196 chains of bead-spring 40-mers (N=40). The randomly mixed initial configurations for the blend simulations are generated by randomly labeling chains in an equilibrated homopolymer melt. To ensure sufficient sampling, our simulations last about $10\tau$, where $\tau$ is the time for chains to diffuse by their radius.
Figure 7.1. (a) Excess free energy integrand $\partial \beta F_{ex}/\partial \lambda$ (blue, left axis) and free energy $\beta F_{ex}$ (green, right axis) vs. morphing parameter $\lambda$. Points are simulation results, error bars smaller than symbols; dashed curves are linear and quadratic fits. (b) Simulation snapshots of binary blends for various $\lambda$. The critical point $\chi N = 2$ is at about $\lambda = 0.88$.

It turns out the free energy integrand varies quite linearly with respect to $\lambda$, resulting in a parabolic function for the excess free energy of mixing (Figure 7.1a). The free energy cost is positive, indicating the mismatch in enthalpic interactions results in a penalty for mixing.

When the free energy cost of mixing is large enough, the binary blends demix. Our morphing method for obtaining the excess free energy assumes a one-phase system. To stay away from demixing, we only compute $\partial \Delta F_{ex}(\lambda)/\partial \lambda$ for $\lambda \geq 0.875$. For systems with $\lambda < 0.875$, our chains tend to form large clusters (Figure 7.1b), indicating these systems may demix. For $\lambda < 0.875$, we observe weakly inhomogeneous, miscible blends. We will show later that we can accurately infer $\chi$ for demixed chains by extrapolating to smaller $\lambda$.

The value of $\chi$ is positive, increasing quadratically when $\lambda$ decreases from unity (Figure 7.2). The location of the critical point ($\chi N = 2$ for $\phi = 0.5$) is estimated at about $\lambda = 0.88$. Recall that we see indications of phase separation at $\lambda = 0.875$ (Figure 7.1b), although not fully resolved to two demixed phases because of slow equilibration, consistent with a critical point at $\lambda = 0.88$. 

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7.4 Validating the morphing method

To test our predicted $\chi$, we compare the planar interfaces of phase separated binary blends obtained using a lattice version of SCFT, to the interfaces we observe in MD simulations. Lattice SCFT has been successfully applied to describe many interfacial phenomena, including chain adsorption on a surface and gradient copolymer self-assembly [69–71,111].

In the lattice SCFT model, we treat flexible chains of type A and B as random walks on a discretized pseudo one-dimensional lattice $\{r_i\}$, biased by a chemical potential field $W_{A/B}(r_i)$ and a hydrostatic pressure field $V(r_i)$. The chemical potential field governs the cost for monomer exchanging by $W_{A/B}(r_i) = \chi(1 - 2\phi_{A/B}(r_i))/2$, where $\phi_A$ and $\phi_B$ are the local volume fractions of polymer A and B, respectively. The hydrostatic pressure $V(r_i)$ ensures the incompressibility of the melt so that $\phi_A(r_i) + \phi_B(r_i) = 1$.

The lattice spacing of the pseudo one-dimensional lattice equals the statistical segment length $b (1.23\sigma)$ of our bead-spring chains, so that random walks on the lattice have the proper mean-square end-to-end distance. Each lattice site represents a layer of polymer melt with thickness of $b$. The lattice model works well for describing phase-separated binary mixtures when the planar interface is wider than the statistical segment length $b$.

To complete the lattice SCFT model for a phase separated binary blend, we write the Boltzmann factor to place the first monomer A or B as $p_{A/B}(r_i, 1) = \ldots$
\( e^{-W_{A/B}(r_i)} - V(r_i) \). The propagation of this Boltzmann factor \( p_{A/B}(r_i, n) \) is governed by a recursion relation, which is a discretized version of the SCFT propagator equation [71,111]. We impose reflecting boundary layers to the two ends of the discretized lattice \( \{r_i\} \), and take the total number of lattice layers \( L \) to be well in excess of the ultimate planar interface width.

For a given \( \chi \) and chain length \( N \), we can compute the interface of the binary blend by solving self-consistently for the density field \( \phi(r_i) \) and the hydrostatic pressure \( V(r_i) \). For a system with \( L \) layers, computing the binary interface requires solving \( 2L \) equations for \( 2L \) variables.

Using the lattice SCFT, we predict the interfacial density profiles of symmetric blends for two different \( \lambda \) values, one with \( \chi(0.85) \) and the other with \( \chi(0.8) \). The two \( \chi \) values are obtained by extrapolation along the quadratic fitting function (Figure 7.2). These \( \chi \) values are convenient because for they result in planar interfaces for bead-spring 40mers that are neither too wide to simulate nor too narrow compared with the statistical segment length \( b \). We avoid systems too near the critical point (\( \lambda = 0.88 \) and 0.875), where the interfaces may be too wide to fit in a manageable simulation box, and the equilibration time is too long.

SCFT calculations give planar interfaces for immiscible blends of bead-spring 40-mers well described by a hyperbolic tangent function (Figure 7.3a):

\[
\phi(x) = \frac{1}{2} + \left( \frac{1}{2} - \phi_{\text{coex}} \right) \tanh \left( \frac{x}{\xi} \right)
\]  

(7.4)

Here \( x \) is the perpendicular distance from the center of the interface, \( \xi \) is the characteristic width of the interface, and \( \phi_{\text{coex}} \) is the coexistence volume fraction in the bulk region. As expected, the width \( \xi \) decreases with increasing \( \chi \). A \( \tanh \) shape for the planar interface is consistent with previous analytical SCFT results [112–114].

To compare with our SCFT interfacial profiles, we perform MD simulations of symmetric binary blends with \( \lambda = 0.85 \) and \( \lambda = 0.8 \). The initial configurations are constructed with sharp planar interfaces, built by gluing two slabs of bead-spring chains together. To help reach an equilibrated configuration more quickly, we also randomly swap chains between slab A and slab B so that the initial concentrations in the demixed slabs are as predicted by the SCFT coexistence volume fractions \( \phi_{\text{coex}} \) far from the interface.
The planar interfaces are sharp initially, broaden during our simulations, and become stable when the systems reach equilibrium. The SCFT results agree nicely with our MD simulations, providing evidence that our predicted $\chi$ values are accurate, and our thermodynamic integration method is valid (Figure 7.3).

The consistency between our SCFT calculations and MD simulations also suggests that $\chi$ depends at most weakly on blend composition $\phi$ for our bead-spring chains. We have only extracted $\chi$ for $\phi = 0.5$, but $\phi$ varies significantly through the interface. If $\chi$ depended strongly on $\phi$, the shape of the interface predicted by SCFT would be affected (e.g., if $\chi$ were smaller away from $\phi = 0.5$, the tails of the interface would be wider). In future work, we will investigate directly the dependence of $\chi$ on $\phi$, by applying our method to systems off the symmetric composition.
7.5 Remarks and conclusions

The total computational cost for predicting $\chi$ using our method is significant but manageable. Using parallel CPU computing (with typically about 1000 beads per CPU), we generate data for Figure 1 and 2 using about 120,000 CPU hours. Considering how small the errors are, one can decrease the simulation size and duration, and still obtain $\chi$ accurately.

One way of describing our method is that it effectively combines the strength of MD simulations in performing proper thermodynamic averages of many interacting flexible molecules of irregular shape, with a well-defined analytical path to morph a one-component reference system into a two-component blend. As such, it resembles the insertion free energy method, in which the thermodynamic work is computed as a single molecule in solution is transformed from invisible to visible; this method has been successfully used to compute solvation energies of dissolved species, including biomolecules [115,116].

Alternative analytical approaches to estimate $\chi$ have a hard time with averaging over the liquidlike structure, or do not perform a proper thermodynamic integral. Simple time-honored estimates for $\chi$ inevitably make uncontrolled assumptions regarding the relative positions of interacting species. For example, we may approximate a melt of bead-spring chains as a mixture of LJ monomers on a cubic lattice with a spacing of $2^{1/6}\sigma$, from which we can we can approximate $\chi_H(\lambda)$ analytically. The resulting values of $\chi_H(\lambda)$ scale correctly, but differ by more than a factor of two from our results, and provide no systematic way to introduce chain structure. More sophisticated calculations have been performed, using the self-consistent polymer reference interaction site model (PRISM) to introduce structural correlations [101]. However, formulating such calculations is not easy, especially for systems with complicated interactions, and the results are of unknown accuracy.

Although we have developed our morphing method for the mixing free energy of bead-spring polymer blends, it can be applied more generally to any liquid mixtures, as long as a suitable morphing path can be found. In particular, we can construct continuous paths along which one molecular structure can be continuously transformed into another, and derive energy-like quantities that can be measured in simulation, providing a route to mixing free energies for real molecules.
Chapter 8  
Role of thermal fluctuations in 
the performance of crystalline 
conjugated polymers

The electronic properties of conjugated molecules depend on local order. Although 
small molecules can be strongly ordered, all conjugated polymers examined to 
date exhibit significant cumulative lattice disorder. As a consequence, charge 
delocalization is affected even within crystalline planes. Using atomistic molecular 
dynamics (MD) simulations, we obtain the detailed structures for single crystals of 
a commonly studied conjugated polymer, poly(3-hexylthiophene-2,5-diyl) (P3HT). 
We show that thermal fluctuations of thiophene rings lead to cumulative disorder of the lattice with an effective paracrystallinity $g$ of about 0.05 in the $\pi-\pi$ stacking direction. The thermal fluctuation induced lattice disorder can in turn limit the apparent coherence length that can be observed in experiments. Combining the MD simulation results with a site-to-site charge hopping model, we also demonstrate that the thermal fluctuation induced lattice disorder can enhance inter-chain charge transport in crystalline P3HT.

8.1 Introduction

Local order is critical to the performance of organic semiconducting molecules. 
Conformational and configurational disorder can affect charge delocalization, in 
turn lead to localized trap states in these materials. [26, 90, 117, 118] Although
small conjugated molecules can be well-ordered, many conjugated polymers exhibit significant disorder. Even in the crystalline regions, where conformational disorder may be negligible, conjugated polymers can have lattice disorder.

In fact, all conjugated polymers examined to date exhibit cumulative lattice disorder. The cumulative lattice disorder results from random fluctuations of lattice spacing, leading to a long-range distortion of ideal crystalline lattice. Together with the sizes of crystallites, the cumulative lattice disorder governs the broadness of X-ray or electron diffraction peaks.

By performing careful peak width analysis, the degree of cumulative disorder can be extracted as paracrystallinity $g$ from diffraction experiments. [26,119] The paracrystallinity $g$ reflects the local disorder, defined as the standard deviation of lattice spacing normalized by the average lattice spacing. [119–121] For many conjugated polymers, $g$ is about 0.1 in the $\pi-\pi$ stacking direction. [26]

The cumulative lattice disorder may arise from processing and chemical defects, impurities, and even thermal fluctuations, because crystalline conjugated molecules are only weakly bonded by Van der Waals interactions. The similar degrees of disorder $g$ for various types of polymers, regardless of the processing conditions, suggest that thermal fluctuations may contribute significantly to cumulative lattice disorder.

In this work, we use atomicistic molecular dynamics (MD) simulations to demonstrate that thermal fluctuations alone can lead to significant cumulative lattice disorder in conjugated polymers. We perform simulations for poly(3-hexylthiophene-2,5-diyl) (P3HT), a commonly studied conjugated polymer for which the crystal structure has been characterized by various experiments [57,58,122,123]. From the simulations, we obtain the detailed crystal structures and the degree of local lattice disorder $g$ in the $\pi-\pi$ stacking direction for a single crystal of P3HT. Both the crystal structure and the paracrystallinity $g$ are consistent with experiments.

We also show that the thermal fluctuation induced lattice disorder is cumulative. The cumulative lattice disorder can limit the apparent coherence length, which is obtained from direct application of the Scherrer equation. As a consequence, the apparent coherence length may not reflect the true sizes of crystallites for conjugated polymers. Based on our simulation results, we predict the upper bound of the apparent coherence length is about 22 nm for P3HT (assuming a shape factor of 0.8 in the Scherrer equation), consistent with experiments [124,125].
Combining the MD results with a site-to-site charge hopping model, we demonstrate the effect of thermal fluctuations on inter-chain charge mobility for crystalline P3HT. We treat the charge transport in crystalline P3HT as two-dimensional hopping processes in both the backbone and \( \pi-\pi \) stacking direction on the disordered crystalline lattice. The intra and inter-chain charge hopping rates are described using Marcus theory, for which the parameters, such as charge transfer integral and reorganization energy of charge carrier, are obtained from density functional theory (DFT) calculations. Analytically, we obtain the inter-chain charge mobility from the diffusion constant of charge carriers in the \( \pi-\pi \) stacking direction.

We also perform kinetic Monte Carlo (KMC) simulations of charge carriers on the crystal lattice that we obtained from MD simulations. From the charge trajectories, we also compute the charge mobility for crystalline P3HT. Our KMC simulations capture the contribution of intra-chain charge transfer that is neglected in the analytical approach. Overall, our results suggest that the static disorder in \( \pi-\pi \) lattice spacing can enhance inter-chain charge transport in crystalline conjugated polymers.

### 8.2 Methods

#### 8.2.1 MD simulations

To quantify the lattice disorder in a perfect single crystal of P3HT, we perform atomistic molecular dynamics (MD) simulations using GROMACS package. The force field model for our simulations is developed by Huang and co-workers, in which the bonded interactions and the partial charges are obtained using density functional theory (DFT) calculations [45,46]. The Lennard-Jones (LJ) parameters are borrowed from the OPLS-AA potential [126]. Huang et al. showed that the atomistic model can yield densities that agree with experiments for 3-hexylthiophene (3HT) monomers and crystalline 3HT oligomers. We also demonstrated that this P3HT model results in chain dimensions and nematic phase behaviors that are consistent with experiments [27, 40, 50, 52].

Our simulation system contains \( 3 \times 40 \) chains of P3HT, forming three P3HT crystalline lamellae in the simulation box. Along the backbone direction, each P3HT chain is composed of 16 monomers, connected head-to-tail across the periodic
boundaries. In this way, our simulations represent perfect single crystals for P3HT of infinite molecular weight.

The initial configurations for our simulations are built in the way that the side chains on the two π-π stacked rings point in opposite directions (Figure 8.1a). In this way, the net dipole moment is zero in the backbone direction for the P3HT crystal. Following the X-ray diffraction results [57], we set the π-π spacing and the inter-lamellae spacing of the initial configuration to be 0.38 nm and 1.68 nm, respectively.

![Figure 8.1](image)

**Figure 8.1.** (a) Initial configuration of two π-π stacked chains. Red and blue arrows indicate ring dipole directions of chain A and B, respectively. Only two carbons on each side chain shown for clarity. (b-c) Snapshots of the P3HT crystal in the π−π stacking direction and the backbone direction. Red dashed lines indicates the relative shift in backbone direction for π-π stacked chains.

In order to study the effect of temperature on structural disorder, we perform NPT simulations for a single crystal of regioregular P3HT at one bar and six temperatures over the range from 300K to 425K, spaced 25K apart. At each temperature, we collect data over 30 ns after equilibrating the systems over 40 ns. From the MD simulations, we can obtain the detailed crystal structure and the disordered crystalline lattice for P3HT. Together with a site-to-site charge hopping
model, the disordered crystalline lattice can help us reveal the effect of thermal fluctuations on charge transport in crystalline P3HT.

### 8.2.2 Charge hopping model for crystalline P3HT

To investigate the effect of disordered crystalline structure on the charge transport for P3HT, we consider a site-to-site charge hopping model. In this model, we allow positive charge carriers (holes) to move freely (without any applied electric field) within the P3HT lamellae. Each lattice site $S_{i,j}$ can transfer charge to its intra-chain neighbors $S_{i,j+1}$ and $S_{i,j-1}$ with rates $k_{i,j+1}$ and $k_{i,j-1}$, respectively. The charge carrier can also hop to the $\pi-\pi$ stacked inter-chain neighbors with rates $k_{i+1,j}$ and $k_{i-1,j}$. In this way, the hopping model represents the two dimensional (2D) charge transfer in crystalline conjugated polymers.

The hopping rates in our treatment of charge transport are described using Marcus theory [127,128]. Similar approach has been applied by the Spakowitz group to investigate the effect of chain conformation on the field-dependent charge mobility for amorphous and semicrystalline conjugated polymers [92,93]. The intra-chain charge transfer rate $k_{\text{intra}}$ depends only on temperature:

$$k_{\text{intra}} = \frac{2\pi t_{\text{intra}}^2}{h \sqrt{4\pi \lambda_0 kT}} \exp \left[ -\frac{\lambda_0}{4kT} \right]$$  \hspace{1cm} (8.1)

in which $t_{\text{intra}}$ is the intra-chain charge transfer integral and $\lambda_0$ is the reorganization energy. We regard the intra-chain charge transfer integral as a constant to simplify the model. Indeed, the value of $t_{\text{intra}}$ and the resulting intra-chain charge hopping rate are functions of backbone dihedral angle $\phi$ for P3HT. Twisted backbones can localize charge carriers and in turn hinder the intra-chain charge transfer. Because the backbone dihedral angles of crystalline P3HT distribute narrowly about the trans state ($\phi = 0^\circ$), we treat the intra-chain transfer integral for holes as a constant $t_{\text{intra}}(0^\circ)$, which is reported by Bombile and coworkers previously [90].

The reorganization energy $\lambda_0$ is 0.26 eV, obtained by analyzing the coupling strength of ring vibrational modes to the charge carriers in a polythiophene chain. The value of $\lambda_0$ characterizes the binding strength of a charge carrier to a single thiophene ring. The details of this calculation are beyond the scope of this dissertation and included in an unpublished manuscript (by Bombile, Dr. Janik, and Dr. Milner). Indeed, a charge carrier may spread over more one ring as a
result of the kinetic energy. Still, we rely on the simplified site-to-site hopping model to demonstrate the effect of lattice disorder on charge transfer for crystalline conjugated polymers.

In fact, our assumption of site-to-site inter-chain hopping may be reasonable for crystalline P3HT. As shown by Figure 8.2, we observed that the correlation function of $\pi$-$\pi$ stacking distance decays to zero within two rings in the backbone direction in our simulations. The intra-chain fluctuations of $\pi$-$\pi$ spacing are rather independent. When distance between two inter-chain neighbors is short, the $\pi$-$\pi$ spacings of the surrounding sites are not necessarily suitable for charge hopping. As a consequence, a charge carrier may squeeze itself into a single ring before hopping to another chain. In this case, the reorganization energy $\lambda$ corresponds to the binding energy of a charge carrier to a single site.

Figure 8.2. Correlation function of $\pi$-$\pi$ stacking distance $d_z$ in the backbone ($x$) and $\pi$-$\pi$ stacking direction ($z$). $\Delta n$ is the difference in monomer index.

We can also write the inter-chain charge hopping rate $k_{\text{inter}}$ using Marcus theory:

$$k_{\text{inter}}(d_z) = \frac{2\pi}{\hbar} \frac{t_{\text{inter}}(d_z)^2}{\sqrt{4\pi\lambda_0 kT}} \exp \left[-\frac{\lambda_0}{4kT}\right]$$

(8.2)

where the inter-chain charge transfer integral $t_{\text{inter}}$ depends on the $\pi$-$\pi$ stacking distance $d_z$. In this way, we can capture the effect of local lattice disorder (fluctuations of $d_z$) on charge transport.

To obtain the inter-chain charge transfer integrals, we compute the electronic band structures using density functional theory (DFT) calculations for 2-dimensional...
P3HT crystals with various $d_z$ using the Vienna \textit{ab initio} Simulation Package (VASP) (by Bombile, Dr. Janik, and Dr. Milner). The DFT calculations are performed using a generalized gradient approximation (GGA) functional, PerdewWang 1991 (PW91), with a basis set cutoff energy of 450 eV, the projector augmented wave approach for the ionic core interactions, and k-point sampling of $7 \times 1 \times 7$. For each calculation, we construct an unit cell containing two $\pi$-$\pi$ stacked chains, each contains two thiophene rings. The two chains are longitudinally shifted with respect to each other by 1.25 Å, in correspondence with the crystalline structure we obtained in MD simulations. The $\pi$-$\pi$ stacking distance $d_z$ is varied over the range between 3.0 Å to 4.5 Å in our calculations in order the obtain $t_{\text{inter}}(d_z)$.

The charge transfer integral $t_{\text{inter}}$ is obtained by analyzing the electronic band structures of the P3HT crystals. Because the unit cell contains repeating rings along the backbone (X) and the $\pi$-$\pi$ stacking (Z) directions, the valence and conduction bands have two folds in the both directions (Figure 8.3a). The energy span of the top and bottom shaded grey areas corresponds to the valence and conduction bandwidths for the $\pi$-$\pi$ stacking direction. The inter-chain charge transfer integrals are computed as the 1/4 unfolded valence bandwidths for different interchain spacings (Figure 8.3b). By fitting the DFT calculations to an exponentially decaying function, we obtain $t_{\text{inter}}(d_z)$ for inter-chain hole transfer. The values of $t_{\text{inter}}(d_z)$ is lower than the previously reported values [129], because the $\pi$-$\pi$ stacking is not perfect for our P3HT crystals – the relative shift in the backbone direction is 1.25 Å.

With the inter and intra-chain charge transfer rates, we can estimate the charge mobility for disordered crystal analytically. By treating the inter-chain hopping as one-dimensional random walks with step size $d_z$, we can analytically compute the diffusion constant and the resulting mobility for charge carriers. The analytical estimation, however, neglects the varying $\pi$-$\pi$ spacing $d_z$ along the polymer backbones and the possible contribution from intra-chain charge transfer on the charge mobility.

To include the contribution from intra-chain charge transfer, we perform kinetic Monte Carlo (KMC) simulations. In KMC simulations, a charge carrier, instead of waiting for inter-chain transfer on a “bad” hopping site (with large $d_z$), can quickly travel along the polymer backbone and find a better hopping site (smaller $d_z$). In this way, the intra-chain charge transfer may enhance the inter-chain charge
mobility. By directly measuring the 2D charge trajectories on disordered crystalline lattice in KMC simulations, we compute the charge mobility for crystalline P3HT.

8.3 Results

8.3.1 Lattice disorder in crystalline P3HT

Using atomistic simulations, we reveal the detailed structure for crystalline P3HT. In the backbone direction, the \( \pi-\pi \) stacked thiophene rings are shifted back and forth by a small displacement \( d_x \) of about 1.25 Å at 300K (Figure 8.4a). The
misalignment $d_x$ can weaken the electronic coupling between two $\pi-\pi$ neighbors, in turn hinder the inter-chain charge transfer in crystalline P3HT. The average inter-lamellar spacing $d_y$ is 16.8 Å and the average $\pi-\pi$ spacing $d_z$ is 3.73Å, consistent with experiments [57, 58, 122, 123, 130] (Figure 8.4b and c). The broadnesses of the distribution functions suggests that thermal fluctuations can lead to static lattice disorder for a perfect single crystal of P3HT.

Figure 8.4. Crystal structure for bulk P3HT at 300K: (a) distribution of backbone shift for $\pi-\pi$ stacked rings $\Delta x$ (inset: a snapshot of $\pi-\pi$ stacked thiophenes); (b) distribution of inter-lamellae spacing $\Delta y$; (c) distribution of $\pi-\pi$ stacking distance $\Delta z$; (d) distribution of the closest distance between two inter-ring hydrogen $d_{HH}$, dashed line from experiment [123].

The $\pi-\pi$ stacking distance of P3HT depends only weakly on temperature. The value of $\Delta z$ changes less than 2% over the temperature range of 125K in our simulations (Figure 8.5a). The attractive interactions between ring dipoles may prevent the expansion of lattice spacing within P3HT lamellae.

The inter-lamellar spacing, however, can expand more significantly when temperature increases (Figure 8.5b). Below 350K, the spatial distributions of the side
Figure 8.5. (a) $\pi-\pi$ spacing $\Delta z$ vs. temperature. Linear fitting $d_z(T) = aT + b$ (dashed). (b) Inter-lamellae spacing $\Delta y$ vs. temperature. (c) Carbon maps at different temperatures for visualization of side chain melting.

chains are localized near the thiophene rings. Above 350K, the non-interdigitated hexyl side chains melt, forming homogeneous layers of “grease” between the P3HT lamellae (Figure 8.5c). The melting transition temperature is consistent with previous experiments and simulations. [131,132]

To further validate the crystal structure in our simulations, we compute the inter-ring hydrogen distance for P3HT at 300K. Combining X-ray diffraction (XRD) and solid-state NMR measurements, Dudenko and coworkers suggest that the closest distance of inter-ring hydrogen $d_{HH}$ should be shorter than 4 Å. [123] Our simulation result agrees well with the experiment (Figure 8.4d).

At equilibrium, our simulations also suggest that the thiophene rings are not tilted, consistent with the crystal structure for bulk P3HT. [123] Kayunkid and coworkers, however, proposed a different crystal structure for epitaxial P3HT films, in which thiophene rings are tilted by about $26^\circ$. [58] In epitaxial films, P3HT may exhibit a different crystal structure.

Using the distribution function of $\pi-\pi$ spacing, we extract the paracrystallinity $g$ for a perfect single crystal of P3HT. By normalizing the standard deviation $\sigma_z$ with respect to the average $\pi-\pi$ spacing $\Delta z$, we obtain $g$ of about 4.6% for a
perfect crystal of P3HT at 300K. Because $\Delta z$ remains rather constant, the thermal fluctuations lead to larger paracrystallinity $g$ for P3HT at higher temperatures (Figure 8.6a).

![Figure 8.6](image)

**Figure 8.6.** (a) Paracrystallinity in $\pi-\pi$ stacking direction $g_z$ vs. temperature. Linear fitting $g_z(T) = aT + b$ (dashed). (b) Comparison to experimental results (points) [26]. MD results for chains with infinite length at 300K (line).

We compare the effective paracrystallinity parameter $g_z$, obtained from the simulations, to the experiments (Figure 8.6b). Neriega et al. estimate the paracrystallinity $g_z$ in the $\pi-\pi$ stacking direction for P3HT from the width of a single X-ray scattering peak. [26] These authors assume that the lattice disorder dominates the peak shape and the contribution from the finite crystal size is negligible. The experimental data shows that the lattice disorder $g_z$ increases with increasing chain length for P3HT, and plateaus out at about 0.08. Of course, because the crystals in our simulations do not suffer from defects and finite sizes of crystallites, our predicted $g_z$ is smaller than the experimental paracrystallinity for P3HT.

For other conjugated polymers, especially for alkyl-functionalized thiophene-based polymers, similar degrees of lattice disorder are expected. Because the interactions between ring dipoles and the steric interactions between side chains are similar, the resulting local disorder in these semiconducting materials may be comparable to the disorder in P3HT. In fact, the reported values of $g_z$ are all about 0.08 for P3HT, poly[5,5’-bis(3-alkyl-2-thienyl)-2,2’-bithiophene] (PQT) and poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTBT). [26]

To analyze the cumulativeness of the lattice disorder, we compute the distribution functions of displacement in the $\pi-\pi$ stacking direction for rings within
the same crystalline lamella (Figure 8.7a). The disorder in the \( \pi-\pi \) spacing grows with \( \Delta n \), where \( \Delta n \) is the number of conjugation planes between two thiophene rings. The broader distribution functions at larger \( \Delta n \) indicate that the lattice disorder is cumulative. The fluctuations of rings in our simulations, however, do not exhibit the ideal behavior of cumulative disorder (Figure 8.7b). For ideally cumulative lattice disorder, where the \( \pi-\pi \) spacing fluctuate randomly, the variance follows \( \sigma_{\Delta n}^2 = \Delta n \sigma_1^2 \). In our MD simulation, we observe the correlation of inter-ring spacing in the \( \pi-\pi \) stacking direction can survive over a short distance (Figure 8.2).

**Figure 8.7.** (a) Distribution of \( \pi-\pi \) stacking distance for rings within the same lamella. (b) Lattice disorder vs. the lattice spacing \( \Delta n \). Dashed line represents ideal cumulative lattice disorder. (c) Correlation function of intra-lamellae fluctuation \( S_z(q_z) \). Magenta line for box dimension in \( z \). Green line for spacing between \( \pi-\pi \) neighbors.
The non-ideality of cumulative lattice disorder may arise from the finite system size, which can constrain the propagation of the in-plane fluctuations, in turn lead to a suppression of cumulativeness in lattice disorder. To demonstrate the finite size effect, we plot the correlation function of in-plane fluctuations, defined as \( S_z(q_z) = \langle \sum_{i=1}^{40} z_i e^{-i q_z z_i} \rangle \) (Figure 8.7c). Only the fluctuations with wavelength smaller than the box size are observed in our simulations. By increasing the system size, the lattice disorder in P3HT may become more cumulative.

Assuming the thermal fluctuations of \( \pi-\pi \) spacing are random and the cumulative lattice disorder is ideal, we predict the upper limit of the apparent coherence length in the \( \pi-\pi \) stacking direction for P3HT. Consider a crystal of infinite size and with no stacking or chemical defects, the coherence length \( \xi \) is governed by disorder \( g_z \):

\[
\xi = \frac{d_z K}{2\pi g_z^2}
\]

where \( K \) is a shape factor, typically in the range from 0.8 to 1. Assuming a shape factor of 0.8, we predict the upper bound for coherence length in the \( \pi-\pi \) stacking direction \( \xi \) to be about 22 nm at 300K for P3HT (Figure 8.8), consistent with experiments. [124,125]

![Figure 8.8](image)

**Figure 8.8.** Thermal fluctuation limited coherence length for P3HT in the \( \pi-\pi \) stacking direction.

### 8.3.2 Effect of lattice disorder on charge transport

The inter-chain charge mobilities of crystalline conjugated polymers depend strongly on local structure. To demonstrate the effect of crystal structure on charge mobility, we approximate the inter-chain charge transfer in crystalline P3HT as
one-dimensional (1D) random walks of charge carriers. Using the hopping rate \( k_{\text{inter}} \) (eqn 8.2), we write the inter-chain charge mobility using the Einstein relation as:

\[
\mu_{\text{inter}} = \frac{d_z^2 k_{\text{inter}}(d_z, T) e}{kT}
\]

(8.4)

In a perfect crystal with fixed lattice spacing \( d_z \), the charge mobility increases with temperature (Figure 8.9).

**Figure 8.9.** (a) Analytical hole mobility \( \mu \) vs. temperature for P3HT. Perfect lattice with \( d_z = 3.73 \) Å (red). Perfect lattice with \( d_z(T) \) changing with temperature (green). Disordered crystalline lattice with \( d_z(T) \) and \( g_z(T) \) (blue). (b) Charge mobility \( \mu \) vs. \( g_z \) for P3HT at 300K with fixed \( d_z = 3.73 \) Å.

Because the charge transfer integral \( t_{\text{inter}} \) decays exponentially over \( \pi-\pi \) stacking distance (Figure 8.3b), the inter-chain charge hopping rate and the resulting charge mobility can be affected by the thermal expansion of the lattice spacing. In absence of lattice disorder \( g_z \), the average \( \pi-\pi \) stacking distance \( d_z(T) \) increases with temperature, in turn hinders charge transfer in crystalline P3HT. Assuming the expansion of \( \pi-\pi \) lattice spacing is linear, we observe a drop in charge mobility.
at high temperature (Figure 8.9).

The local lattice disorder, arises from thermal fluctuations, can enhance the inter-chain charge transport in crystalline conjugated polymers. The degree of lattice disorder $g_z$ increases with temperature, lead to a larger charge transfer integral $\langle t_{inter} \rangle$ on average. We can estimate the mobility for disordered crystalline P3HT as:

$$
\mu_{inter}^{dis}(T) = \int_{-\infty}^{\infty} dx \frac{1}{2\pi d_z(T)^2 g_z(T)^2} \exp\left(-\frac{(x - d_z(T))^2}{2d_z(T)^2 g_z(T)^2}\right) \frac{x^2 k_{inter}(x) e}{kT} \tag{8.5}
$$

For a crystal with a fixed lattice spacing of $d_z$, the charge mobility increases with $g_z$ (Figure 8.9b). Using the above equation, we also demonstrate that the fluctuations of crystal lattice can compensate the penalty of thermal expansion on inter-chain charge transport for crystalline P3HT (8.9a).

Indeed, the P3HT backbone may be glassy below room temperature so that the thermal expansion of $d_z$ and the lattice disorder $g_z(T)$ may differ from the linear fittings (Figure 8.5 and 8.6). Still, the analytical expression of charge mobility qualitatively captures the effects of the fluctuations of crystal structure on charge mobility for crystalline P3HT.

Using KMC, we also demonstrate that the intra-chain charge transfer, which is neglected in the above analytical expression of charge mobility, can enhance the inter-chain charge hopping in disordered crystalline lattice. For crystalline P3HT, the distribution of the average $\pi-\pi$ stacking distance for two neighboring chains is much narrower than the distribution of the ring-to-ring stacking distance, suggesting both “traps” ($d_z$ is large) and “hot spots” ($d_z$ is small) can exist on the same chain for inter-chain charge transfer. This is because displacing a whole chain from the equilibrium position is expensive. Because the intra-chain charge transfer is much faster than the inter-chain hopping, the charge carriers, instead of being trapped, can travel along the polymer backbones and sample some “hot spots” to hop. In this way, the inter-chain charge mobility for crystalline conjugated P3HT is higher in KMC simulations than the analytical prediction (Figure 8.10).

The effective activation energy $E_A$ for charge transport, reflected in the temperature dependence of charge mobility $\mu$, however, depends only weakly on the structural order for P3HT. Regardless of the differences in the final structures, which may arise from different processing conditions, the experimentally measured
Figure 8.10. KMC hole mobility $\mu$ vs. temperature for P3HT. Perfect lattice with $d_z(T)$ changing with temperature (blue). Disordered crystalline lattice with $d_z(T)$ and $g(T)$ (red). Analytical results (solid curve).

$E_A$ are the roughly the same for P3HT, about 46 meV [133], close to the Marcus activation energy in our hopping model ($\lambda/4$). As a consequence, the temperature dependence of charge mobility we obtained is comparable to the experimental results. (Figure 8.11).

Figure 8.11. Hole mobility $\mu$ vs. temperature for P3HT. Mobilities for P3HT processed using Chlorobenzene (red) and Trichlorobenzene (blue). KMC simulations on MD crystal lattice (green). Analytical approximation using $d_z(T)$ and $g_z(T)$ (purple). Arrhenius fitting with $E_A = 46$ meV (Dashed line). Values of $\mu$ shifted vertically for comparison.
8.4 Conclusions

In this chapter, we investigate the effect of structural order on charge mobility for crystalline P3HT using MD and KMC simulations. Using MD simulations, we obtain the detailed crystal structure for P3HT, which is consistent with experiments. By analyzing the crystal structure, we also obtain the local lattice disorder, characterized by paracrystallinity parameter \( g_z \), for P3HT. The lattice disorder, arises from the thermal fluctuations of thiophene rings, is cumulative. The cumulative lattice disorder can lead to a long-range distortion of ideal crystalline lattice, in turn limit the apparent coherence length that one can observe in diffraction experiments. Using our simulation results, we predict the upper limit of apparent coherence length \( \xi \) is about 22 nm at 300K for P3HT, in agreement with experiments.

Thermal fluctuations and the resulting lattice disorder \( g_z \) can also lead to higher charge mobilities in crystalline conjugated polymers. Using an one dimensional charge hopping model with rates described by Marcus theory, we demonstrate that the charge mobility increases with the paracrystallinity parameter \( g_z \). Because the strength of inter-chain electronic coupling depends exponentially on the \( \pi-\pi \) stacking distance, increasing \( g_z \) results in a higher value of the charge transfer integral \( t_{\text{inter}} \) on average, in turn enhances the inter-chain charge transport.

The fast intra-chain charge transfer is also important for inter-chain mobility. We perform KMC simulations of charge carriers on the disorder crystalline lattice, obtained from our MD simulations. The resulting charge mobility is higher than our analytical prediction. In KMC, the charge transport is two dimensional – a charge carrier can travel fast along the polymer backbone and find some sites with small lattice spacing \( d_z \) for fast inter-chain hopping. In the analytical model, however, the charge carrier may be trapped on a site with large \( d_z \) for a long time.

Although the value of charge mobility \( \mu \) depends on the crystal structures, the temperature dependence of \( \mu \) is affected only slightly by the structural order. The effective activation energy for charge hopping is dominated by the reorganization energy \( \lambda \) of charge carriers. As a consequence, the temperature dependence of \( \mu \) is roughly the same for P3HT that are processed using different types of solvent. The agreement between the effective activation energy obtained from our model and experiments suggests that the reorganization energy of a charge carrier can be as large as 0.26 eV.
Chapter 9  
Predicting elastic constants for crystalline conjugated polymers

Together with electrical properties, mechanical behaviors of conjugated polymers govern the overall performance of flexible electronics. Although much effort has been made on investigating the relation between molecular structure and charge conductivity, the mechanical properties of conjugated polymers receive less attention. Experimentally measuring the mechanical properties for many different polymers, however, is impractical. Computer simulations can provide us an alternative route for studying the effects of chemical structures on the mechanical properties for conjugated polymers. In this chapter, we combine theory of linear elasticity and atomistic molecular dynamics simulations to predict the elastic moduli for crystalline poly(3-hexylthiophene) (P3HT). Predicting elastic moduli for crystalline chains is the first step for understanding the effect of molecular structures on the mechanical properties for semicrystalline conjugated polymers.

9.1 Introduction

The mechanical properties of conjugated polymers are important for many applications, including flexible transistors, solar cells and artificial skins [25,134,135]. In order to be used in these bendable and stretchable electronic devices, conjugated polymers need to be soft enough so that they can withstand large strain and remain conductive at deformed state.

Many high-performance conjugated polymers, such as poly(2,5-bis(3-alkylthiophene-2-yl)thieno[3,2-b]thiophenes) (PBT TT), however, are rather rigid [136].
The high charge conductivity is associated with the ordered morphology in the sample. In these materials, the crystallinity is high and the crystalline domains are large. The enhanced structural order, however, can also result in high brittleness of the materials. A balance between electrical and mechanical properties must be achieved in flexible electronic applications. Understanding the effects of molecular structures on both the charge transport and the mechanical behaviors is essential to design novel soft semiconductors.

By performing mechanical tests, including tensile and buckling experiments, previous authors demonstrate the effects of side chains on the elastic modulus of semicrystalline conjugated polymers [136, 137]. The packing and interactions between alkyl side chains can control the long-range order, in turn affect the mechanical and electrical properties of semicrystalline conjugated polymers. Nonetheless, effects of many other structural properties, such as regioregularity and compositions of comonomers, on the mechanical properties have not been thoroughly studied for conjugated polymers. Experimentally testing conjugated polymers with many different molecular structures is challenging.

In this work, we demonstrate that we can combine theory of linear elasticity with atomistic MD simulations to predict the elastic constants for crystalline conjugated polymers. We perform isothermal-isostress \((N\sigma T)\) atomistic molecular dynamics simulations for a single crystal of P3HT, from which the elastic moduli of the materials are obtained. The same approach has been applied to obtain elastic constants for generalized model systems using Monte Carlo (MC) simulations, including FCC crystals that are composed of Lennard-Jones (LJ) particles and polymer glasses composed of bead-spring chains [138–140].

Although many conjugated polymers are semicrystalline, being able to predict the elastic constants for chains in the crystalline region is the first step for establishing the relation between the molecular structures and the overall mechanical properties for conjugated polymers.
9.2 Methods

9.2.1 Estimating elastic modulus using $N\sigma T$ simulations

Elastic constants $\lambda_{iklm}$ are important material constants which govern the free energy cost for infinitesimal deformation of a solid sample. Measuring elastic constants experimentally for crystalline conjugated polymer is difficult because most conjugated polymers are semicrystalline. Using simulations with accurate force field parameters, we can predict $\lambda_{iklm}$ from strain fluctuations.

For crystalline polymers with orthorhombic lattice, such as P3HT, we consider nine independent elastic moduli $\lambda_{iklm}$ in the elastic free energy [141]:

$$F = \frac{1}{2} \lambda_{xxxx} \epsilon_{xx}^2 + \frac{1}{2} \lambda_{yyyy} \epsilon_{yy}^2 + \frac{1}{2} \lambda_{zzzz} \epsilon_{zz}^2 + \lambda_{xxyy} \epsilon_{xx} \epsilon_{yy} + \lambda_{xxzz} \epsilon_{xx} \epsilon_{zz} + \lambda_{yyzz} \epsilon_{yy} \epsilon_{zz} + 2 \lambda_{xxyy} \epsilon_{xx}^2 + 2 \lambda_{xzxz} \epsilon_{xz}^2 + 2 \lambda_{yyzz} \epsilon_{yz}^2$$

(9.1)

where $\epsilon$ are the elements in the strain tensor. For different crystal systems, the number of independent elastic moduli varies.

We reduce the dimensions of the strain tensor and elastic moduli using Voigt notation:

$$\epsilon = \{\epsilon_{xx}, \epsilon_{yy}, \epsilon_{zz}, 2\epsilon_{yz}, 2\epsilon_{xz}, 2\epsilon_{xy}\}$$

$$= \{\epsilon_1, \epsilon_2, \epsilon_3, \epsilon_4, \epsilon_5, \epsilon_6\}$$

(9.2)

in which a factor of two is used for the off-diagonal strain elements to match the free energy equation (eqn 9.1). The elastic moduli tensor is now a $6 \times 6$ matrix $\lambda_{ij}$ (index $i, j \in [1, 6]$). As a consequence, the elastic free energy can be rewritten as $F = \frac{1}{2} \epsilon^T \cdot \lambda \cdot \epsilon$.

In absence of external stress, the thermal energy in the system lead to strain fluctuations. As a consequence, we can determine the nine isothermal elastic moduli of P3HT using $N\sigma T$ simulations:

$$\lambda_{ij} = \frac{kT}{\langle V \rangle} \langle \Delta \epsilon_i \Delta \epsilon_j \rangle^{-1}$$

(9.3)

where $\langle \Delta \epsilon_i \Delta \epsilon_j \rangle$ is the covariance matrix of strain elements. In $N\sigma T$ simulations,
the covariance of strain can be determined from the fluctuating size and shape of the simulation box.

To realize eqn 9.3, we first write the Hamiltonian for the crystal as:

$$ H = \frac{1}{2} \epsilon^T \cdot \lambda \cdot \epsilon - \sigma^T \cdot \epsilon $$  \hspace{1cm} (9.4)

in which $\sigma$ is the external stress. Using the Hamiltonian, we write the partition function as:

$$ Z = \int_{-\infty}^{\infty} d\epsilon e^{-\beta H} \\
= \int_{-\infty}^{\infty} d\epsilon e^{-\beta(\frac{1}{2} \epsilon^T \cdot \lambda \cdot \epsilon - \sigma^T \cdot \epsilon)} \\
= \int_{-\infty}^{\infty} d\epsilon e^{-\frac{\beta}{2}((\epsilon^T s - \sigma s^{-1})^2 - \sigma^T \lambda^{-1} \cdot \sigma)} \\
= \sqrt{\frac{2\pi}{\beta}} e^{\frac{\beta}{2} s^T \lambda^{-1} \cdot \sigma} $$  \hspace{1cm} (9.5)

where $s$ is the square root of matrix $\lambda$.

If we take the partial derivative of the elastic free energy with respect to $\sigma$, we have the ensemble averaged strain matrix $\langle \epsilon \rangle$:

$$ \langle \epsilon \rangle = \frac{\partial \ln Z}{\beta \partial \sigma} $$  \hspace{1cm} (9.6)

And the covariance matrix becomes:

$$ \langle \Delta \epsilon_i \Delta \epsilon_j \rangle = \langle \epsilon_i \epsilon_j \rangle - \langle \epsilon_i \rangle \langle \epsilon_j \rangle \\
= \frac{\partial^2 \ln Z}{\beta^2 \partial \sigma_i \partial \sigma_j} \\
= \frac{\lambda_{ij}^{-1}}{\beta} $$  \hspace{1cm} (9.7)

As such, by measuring the strain of the crystal in absence of the external stress ($\sigma = 0$), we can obtain the linear elastic moduli.

The strain matrix $\epsilon$ is obtained from the fluctuating box shapes in $N\sigma T$ simulations. To do so, we follow the approach proposed by Parrinello and Rahman [142]. We first obtain the scaling matrix for the simulation box $h = \{a, b, c\}$, where $a$, $b$, and $c$ are the box vectors. The scaling matrix describes the shape and size of
our simulation box: the determinant of scaling matrix $h$ gives the volume of the simulation box; the averaged scaling matrix $\langle h \rangle$ maps the equilibrium locations of space points $r$ in the system to a dimensionless vector $\xi$ by $r = \langle h \rangle \xi$.

Under homogeneous deformation, particles in the sample move from $r$ to $r'$, where $r' = h\xi = h\langle h \rangle^{-1}r$. The displacement $u$ of the particles from the equilibrium positions can be written as:

$$u = (h\langle h \rangle^{-1} - I)r$$  \hspace{1cm} (9.8)

in which $I$ is the identity matrix. The strain tensor is defined as:

$$\epsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial r_j} + \frac{\partial u_j}{\partial r_i} + \sum_{k=1}^{3} \frac{\partial u_k}{\partial r_i} \frac{\partial u_k}{\partial r_j} \right)$$  \hspace{1cm} (9.9)

By taking derivative $\partial/\partial r$ on the displacement vector $u$, we have:

$$\frac{\partial u}{\partial r} = H - I$$  \hspace{1cm} (9.10)

where $H = h\langle h \rangle^{-1}$. Now the strain tensor (eqn 9.9) can be written as:

$$\epsilon = \frac{1}{2}(H^T H - I) = \frac{1}{2}[h^T (h^T)^{-1}G^{-1}G^{-1} - I]$$  \hspace{1cm} (9.11)

where the metric tensor $G = h^T h$. In this way, we can measure the covariance matrix of the strain and the elastic moduli of the sample using the dimensions of the simulation box.

### 9.2.2 MD Simulation details

To obtain the elastic moduli of crystalline P3HT, we perform atomistic molecular dynamics (MD) simulations using GROMACS package. The force field model for our simulations is developed by Huang and co-workers [45, 46], same as the one we use for the work in Chapter 8. The initial configuration is our equilibrated crystalline P3HT sample in NPT ensemble, which contains $3 \times 40$ chains of P3HT, forming three P3HT crystalline lamellae in the simulation box. In the backbone direction, each P3HT chain is 16 monomers long, connected head-to-tail across the periodic boundaries.
In isothermal-isostress ($N\sigma T$) simulations, we apply anisotropic pressure coupling to the system in all the directions. In this way, the simulation box can change size and shape as a result of thermal fluctuations. At 300K and 1 bar, the simulation box fluctuate around its equilibrium shape. In Figure 9.1, I show locations of a box corner over time for crystalline P3HT at 300K. The ellipsoidal shape of the distribution reflects the anisotropy in the elastic moduli of crystalline P3HT.

![Figure 9.1. Distribution of a box corner for crystalline P3HT at 300K.](image)

We do not obtain the elastic moduli for P3HT at higher temperatures because the alkyl side chains melt near 350K. For system with melted side chains, the crystal can deform by shearing the adjacent crystalline lamellae. In this case, the deformation is not elastic and the above analysis is no longer viable.

### 9.3 Results

We compute the strain matrix elements as a function of time (Figure 9.2) for crystalline P3HT using eqn 9.11. The strain elements fluctuate around some steady values, reflecting the small elastic deformation of the system as a result of thermal fluctuations.

From the covariance matrix of the strain, we obtain the nice elastic moduli for crystalline P3HT at 300K (Table 9.1): The first three moduli are Young’s moduli in three different directions for crystalline P3HT – $x$, $y$ and $z$ are the backbone, side chain stacking and $\pi-\pi$ stacking directions, respectively. The values of $\lambda_{ijj}$
Figure 9.2. Strain fluctuations for crystalline P3HT at 300K

<p>| | | | |</p>
<table>
<thead>
<tr>
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<tr>
<td>$\lambda_{xxx}$</td>
<td>74.94</td>
<td>$\lambda_{yyy}$</td>
<td>1.55</td>
</tr>
<tr>
<td>$\lambda_{zzz}$</td>
<td>4.34</td>
<td>$\lambda_{xyy}$</td>
<td>3.22</td>
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<tr>
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<td>4.02</td>
<td>$\lambda_{yyzz}$</td>
<td>1.05</td>
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<tr>
<td>$\lambda_{yyzz}$</td>
<td>0.22</td>
<td>$\lambda_{xzz}$</td>
<td>0.54</td>
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<tr>
<td>$\lambda_{xzx}$</td>
<td>0.54</td>
<td>$\lambda_{xyxy}$</td>
<td>0.13</td>
</tr>
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</table>

Table 9.1. Linear elastic modulus of P3HT at 300K in GPa.

correspond to the bulk moduli of the crystal. And the last three elastic constants are the shear moduli, of which the relative magnitudes can be qualitatively seen in
the scattered plot of box corners (Figure 9.1, wider the spread, smaller the shear modulus).

The large Young’s modulus in the backbone direction is a result of the periodic connection of the chains. Deforming the rigid crystalline polymer chains of infinite length in the backbone direction is hard. For system with finite molecular weight, we expect $\lambda_{xxxx}$ to be smaller. Nonetheless, the elastic moduli we predicted is reasonable. Experimentally measured elastic modulus for semicrystalline P3HT is about 0.25 GPa [136] – the existence of amorphous chains can lead to a lower overall elastic modulus.

### 9.4 Conclusions

In this chapter, we demonstrate that the elastic moduli of crystalline conjugated polymers can be obtained from atomistic simulations. In isothermal-isostress ($N\sigma T$), we allow the simulation box to deform elastically by thermal fluctuations. From the fluctuating size and shape of the simulation box, we obtain the covariance matrix of the strain, from which the elastic moduli are computed. Using this method, we predict the elastic moduli of crystalline P3HT, in qualitative agreement with experimental measurements.

Although we only predict the elastic moduli for crystalline P3HT, the same approach can be applied to predict the elastic constants for many other polymers in different states. For example, one can tune the molecular structure of conjugated polymers, such as increasing side chain branching and introducing regioregularity defects, to quantitatively investigate the effect of chemical structure on the mechanical properties for chains in the crystalline form. We may also predict the isotropic elastic modulus for glassy polymers in simulations. Overall, the ability to predict elastic modulus for conjugated polymers from simulations can be useful for designing novel soft semiconductors.
Chapter 10  
Conclusions and perspective on future work

In this chapter, I summarize all the topics and results that are discussed in this dissertation. Based on the results we have obtained and the methods we have developed, I also include my perspective of possible research topics that may worth trying in the future.

10.1 Nematic phase behaviors of semiflexible polymers

Semiflexible conjugated polymers can exhibit the nematic phase when the concentrations of their backbone segments are high enough. In the nematic phase, semiflexible chains align uniaxially and remain translationally disordered. The existence of the nematic alignment can enhance the charge transport in amorphous conjugated polymers and lead to more ordered final morphologies for chains in the semicrystalline state. The ability to predict the nematic order and phase transition is important for designing novel conjugated polymeric materials.

The value of persistence length $N_p$ characterizes the local straightness of semiflexible chain path. Together with the nematic coupling constant $\alpha$, the persistence length governs the location of the isotropic-to-nematic (IN) phase transition for conjugated polymers. To predict the nematic order and phase behaviors, we have developed a method that can predict the persistence length $N_p$ from molecular structure for conjugated polymers.
Combining self-consistent field theory (SCFT) and molecular dynamics (MD) simulations, we have also developed a method to predict the nematic coupling constant $\alpha$ for semiflexible polymers, which quantifies the interaction strength of a backbone segment with the quadrupolar nematic field $q$ of the system. By constructing a variational mean-field free energy using $\alpha$ and $N_p$, we can predict the IN transition temperatures for semiflexible polymers.

Using a lattice version of SCFT model and MD simulations, we have also investigated the effect of $\alpha$ and $N_p$ on the surface-induced nematic alignment for conjugated polymers. Near impenetrable surfaces, semiflexible polymers align parallel to the interface, creating an alignment layer of thickness about a persistence length $l_p$ ($l_p = N_p a$, where $a$ is the monomer size). The interactions between chain segments and the local nematic field (which are governed by $\alpha$) can further enhance the induced nematic order.

With the help of surface-induced alignment, we have also obtained the IN phase boundary for semiflexible polymers in the $N_p - \phi$ plane. For mildly stiff chains ($N_p < 5.78$), we show that the critical volume fraction for IN transition $\phi_c$ scales with $N_p^{-1}$, in agreement with previous theoretical predictions. For stiffer chains ($N_p \geq 5.78$), however, our results suggest $\phi_c$ scales with $N_p^{-2/3}$.

The new scaling of the critical IN transition volume fraction $\phi_c$ ($\sim N_p^{-2/3}$) may worth exploring in the future. As illustrated by previous authors [2, 3], the scaling behavior for mildly stiff chains is straightforward to understand. The semiflexible backbones can be regarded as sequences of rigid units of length equals the Kuhn length $l_k$ ($l_k = 2l_p$). When concentration is high enough, randomly placing a Kuhn segment in random orientation will lead to a collision (or a “near miss”) with another Kuhn segment. In this case, the volume per “near miss” is about $l_k^2 d$, where $d$ is the diameter of the chain. As a consequence, the critical volume fraction for the IN transition is $\phi_c \sim l_k d^2/(l_k^2 d) \sim d(aN_p)^{-1}$.

The new scaling behavior we observe ($\phi_c \sim N_p^{-2/3}$) suggests that for stiff chains the Kuhn length may not be the suitable length scale for the chain backbones to have “near misses”. Finding the correct length scale for “near misses” will be essential for understanding the physics of the isotropic-to-nematic phase transition for stiff semiflexible polymers.
10.2 Charge transport in amorphous conjugated polymers

Although many conjugated polymers are semicrystalline, some high-performance conjugated polymers are rather amorphous. Quantifying the relation between material properties, such as molecular weight and persistence length, and the electronic properties for amorphous systems is useful.

In our current work, we have predicted that amorphous conjugated polymers can exhibit uniaxial nematic order in bulk or at interfaces. We expect that the charge transport in nearly all conjugated polymers may be affected by the uniaxial alignment of their conducting backbones. Using an analytical model, we predict the effects of molecular weight and chain stiffness on charge mobility for nematic polymers. For low molecular weight materials, the charge mobility increases quadratically with molecular weight. The increasing charge mobility reaches a plateau value at high molecular weight, which scales linearly with the persistence length. Comparing the theoretical prediction with experiments would be useful in the future.

The reported data on charge mobilities as functions of molecular weight and persistence length for amorphous conjugated polymers, however, is limited. As a consequence, synthesizing amorphous conjugated polymers with tailored molecular weight and persistence length will be the first step for validating and improving the our current model. Regioregularity defects and side chain branching may be used to suppress the ability of crystallization for conjugated polymers. Substitution of backbone moieties may be used to controlled the persistence length. By fitting our model to the charge mobilities of amorphous chains with different length and stiffness, we may be able to validate our analytical predictions.

10.3 Predicting $\chi$ for polymers from simulations

In this dissertation, we have reported a novel method for extracting the Flory-Huggins $\chi$ parameter for inhomogeneous polymers from molecular dynamics simulations. The $\chi$ parameter is an important material parameter, which quantifies the net repulsion between two distinct polymers and governs the phase behaviors and
mesoscale structures of polymer blends and block copolymers. Being able to predict \( \chi \) from molecular structure is essential for designing novel polymeric materials.

In our method, we “morph” one polymer into another in simulations and measure the free energy cost during the process using a novel thermodynamic integration method. In this way, we can obtain the excess free energy of mixing for inhomogeneous polymers, from which the Flory-Huggins \( \chi \) parameter is obtained.

To demonstrate and validate our method, we have extracted \( \chi \) for flexible linear bead-spring chains with mismatch in enthalpic interactions. For the conformationally symmetric system, we find that \( \chi \) is rather independent of the blend composition, consistent with the previous theoretical prediction by Wang [143]. For conformationally asymmetric system, however, Wang predicts that the composition dependence of \( \chi \) is quadratic.

In the future, it may worth exploring the composition dependence of \( \chi \) using our method and simulations of bead-spring chains. The conformational symmetry of the bead-spring chains can be controlled by adjusting the chain stiffness. By measuring \( \chi \) for chains with both mismatches in stiffness and enthalpic interactions at different volume fractions, we can test the quadratic dependence of \( \chi \) on composition.

Together with atomistic simulations, the morphing method can be also applied to obtain \( \chi \) for realistic polymers. In the future, we may want to use the morphing method to predict \( \chi \) for novel polymers from molecular structures in order to design better applications, such as block copolymer solar cells and stretchable electronics. To do so, we must take care of some issues that may emerge in the morphing real polymers.

First, we must design suitable morphing paths. For polymers with similar molecular structures, we can morph the atoms directly in atomistic simulations in order to obtain the excess free energy of mixing. For example, transforming poly(styrene) (PS) into poly(2-vinylpyridine) (P2VP) can be achieved by morphing the CH group at the ortho position into a nitrogen atom. For polymers with distinct molecular structures, such as P3HT and PFTBT, direct morphing in atomistic simulations is no longer viable. In this case, we may have to coarse grain the atomistic model into “bead-spring” chains using techniques such as force matching [144,145]. The value of \( \chi \) is then obtained by performing morphing in coarse grain simulations.

Second, we may need to correct electrostatic interactions for blends that are com-
posed of polar and non-polar polymers. For neat polar polymers, the electrostatic interactions may be well described in atomistic simulations because the dielectric constants are dominated by contribution from the fluctuating permanent dipoles. For non-polar polymers, the partial charges and the resulting permanent dipoles in the atomistic models are small. Fluctuations of these small dipoles only lead to a dielectric constant of about unity in simulations, although the experimentally measured dielectric constant for non-polar polymers are greater than two. This is because the bond polarizability can also contribute significantly to the dielectric properties of non-polar polymers. When non-polar polymers are mixed with polar polymers, the missing contribution from the bond polarizability may enhance the electrostatic interactions in the blend (because the dielectric constant is smaller than reality). As a consequence, we need to correct the dielectric constant and the electrostatic interactions in order to obtain accurate $\chi$ for blends of polar and non-polar polymers.
Appendix A
Simplification of transfer matrix

The eigenvalues and eigenvectors of $T$ (eqn 2.2) are used to simplify eqn 2.4. The averaged transformation matrix $T$ has three eigenvalues, two of which contribute in the later calculations, namely $\lambda_1$ and $\lambda_2$:

\[
\begin{align*}
\lambda_1 &= \frac{1}{2} \left( \cos \theta - \cos \langle \cos \phi \rangle - 2 \sqrt{\langle \cos \phi \rangle + \cos \theta^2 \langle \sin \left( \frac{\phi}{2} \right) \rangle^4} \right) \\
\lambda_2 &= \frac{1}{2} \left( \cos \theta - \cos \langle \cos \phi \rangle + 2 \sqrt{\langle \cos \phi \rangle + \cos \theta^2 \langle \sin \left( \frac{\phi}{2} \right) \rangle^4} \right)
\end{align*}
\] (A.1)

The corresponding right eigenvectors are:

\[
\begin{align*}
e_1 &= \left\{ \frac{1}{2} (\cot \theta (1 + \langle \sec \phi \rangle) - 2 \csc \langle \sec \phi \rangle \langle \cos \phi \rangle + \cos \theta^2 \langle \sin \left( \frac{\phi}{2} \right) \rangle^4), 1, 0 \right\} \\
e_2 &= \left\{ \frac{1}{2} (\cot \theta (1 + \langle \sec \phi \rangle) + 2 \csc \langle \sec \phi \rangle \langle \cos \phi \rangle + \cos \theta^2 \langle \sin \left( \frac{\phi}{2} \right) \rangle^4), 1, 0 \right\}
\end{align*}
\] (A.2)

We can then write the vector $\{1,0,0\}$ in terms of the two eigenvectors:

\[
\hat{x} = c_1 e_1 + c_2 e_2
\] (A.3)

With the coefficients $c_1$ and $c_2$, eigenvalues $\lambda_1$ and $\lambda_2$ and eigenvectors $e_1$ and $e_2$, the second term on the right hand side of eqn 2.4 is simplified by assuming $n$
approaches infinity:

\[ \hat{x} \cdot \sum_{k=1}^{n} T^k \cdot \hat{x} = \sum_{k=1}^{\infty} (c_1 \lambda_k^1 e_1(1) + c_2 \lambda_k^2 e_2(1)) \]

\[ = \frac{1}{4} (\cos \theta + \langle \cos \phi \rangle ) \csc \left[ \frac{\theta}{2} \right]^2 \langle \csc \left[ \frac{\phi}{2} \rangle \rangle^2 \]

\[ = \frac{\cos \theta + \langle \cos \phi \rangle}{(1 - \cos \theta)(1 - \langle \cos \phi \rangle)} \quad \text{(A.4)} \]

Combining eqn A.4 and eqn 2.4, the final expression of the HR model (eqn 2.5) is obtained after some algebra.
Appendix B
Solving modified diffusion equation (eqn 3.8)

By expanding the propagator $Z(\mu; s)$ in eigenfunctions (eqn 3.9), we rewrite the diffusion equation (eqn 3.8) as

$$\epsilon_\alpha \psi_\alpha(\mu) = -D\nabla_\perp^2 \psi(\mu) + V(\mu)\psi(\mu) \quad (B.1)$$

The eigenfunctions $\psi_\alpha(\mu)$ (eqn 3.9) is further expanded in Legendre polynomials $P_n(\mu)$:

$$\psi_\alpha(\mu) = \sum_{n=0}^N c_{\alpha,n} \sqrt{\frac{2n+1}{2}} P_n(\mu) \quad (B.2)$$

in which $c_{\alpha,n}$ are the expansion coefficients for $\psi_\alpha(\mu)$. Both eigenfunction expansion of $Z(\mu; s)$ and Legendre polynomial expansion of $\psi_\alpha(\mu)$ are truncated at the same order $N$. The Legendre polynomials are orthogonal with respect to integration over all $\mu$: $\int_{-1}^{1} d\mu P_n(\mu) P_m(\mu) = 2\delta_{mn}/(2n+1)$.

By taking the inner product of $\sqrt{(2m+1)/2}P_m(\mu)$ with eqn B.1 and integrating both sides of the equation over $\mu$, we write the diffusion equation as:

$$\epsilon_\alpha c_{\alpha,m} = Dm(m+1)c_{\alpha,m} + \sum_n \langle m|V(\mu)|n\rangle c_{\alpha,n} \quad (B.3)$$

Here the “$|n\rangle$” represents $\sqrt{(2n+1/2)}P_n(\mu)$. The notation $\langle m|n\rangle$ denotes the inner product of $|m\rangle$ and $|n\rangle$, which by orthonormality is $\delta_{mn}$. Likewise, $\langle m|n\rangle$ denotes the angular average “matrix element” of $V(\mu)$ between $|m\rangle$ and $|n\rangle$. For convenience, we write the second term on the right-hand side of eqn B.3 as $V_{mn}$. 

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Using the recurrence relation of the Legendre polynomials $P_n$ [56], we simplify $V_{mn}$ (eqn 3.4,B.3) as:

$$V_{mn} = -\alpha q \left( \frac{3(n + 1)(n + 2)}{2(2n + 1)(2n + 3)} \delta_{m,n+2} + \frac{n(n + 1)}{(2n - 1)(2n + 3)} \delta_{m,n} + \frac{3n(n - 1)}{2(2n + 1)(2n - 1)} \delta_{m,n-2} \right)$$

$$- f \left( \frac{n + 1}{2n + 1} \delta_{m,n+1} + \frac{n}{2n + 1} \delta_{m,n-1} \right) \quad (B.4)$$

The right-hand side operator of eqn B.3 becomes an $N \times N$ matrix: $M_{mn} = Dm(m + 1)\delta_{mn} + V_{mn}$, for which the eigenvalues are $\epsilon_\alpha$ and the corresponding eigenvectors are $\{c_{\alpha,m}\}$. The eigenvalues $\epsilon_\alpha$ and eigenvectors $\{c_{\alpha,m}\}$ are used to construct the propagator $Z(\mu; s)$ (eqn B.2 and 3.9) so that the tangent distribution $\Pi(\mu)$ (eqn 3.6) and quadrupolar order parameter $q$ (eqn 4.3) can be determined self-consistently for a given $\alpha$. 

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Bibliography


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