Multiscale Modeling Structure and Super Structures of Dendronized Polymers

A dissertation submitted to
ETH Zürich

for the degree of
Doctor of Sciences

presented by
Ding Yi
Master of Science
Freie Universität Berlin

born 21.03.1981
citizen of P.R.China

accepted on the recommendation of
Prof. Dr. H. C. Öttinger, examiner
Prof. Dr. M. Kröger, co-examiner
Prof. Dr. A. D. Schlüter, co-examiner

Zürich, 2008
Abstract

The main goals of this thesis have been, on the phenomenological side, to (i) explore phenomena of the dendronized polymer chemistry including morphology and dynamics of single molecules and (ii) to describe supramolecular structures of many-molecule dendronized polymeric systems. As the author uses a computational modeling approach to attack the aforementioned goals, and due to the complexity of dendronized polymeric systems, a systematic multiscale modeling approach had been required. Its implementation constitutes the methodological goal of this thesis.

The two threads of thesis work, phenomena and methodology, proceed in parallel and are mutually benefiting from each other. Dendronized polymers provide a good playground for practicing multiscale modeling approaches. At the same time modeling results solve theoretical problems in dendronized polymer systems. The first chapter of the thesis introduces the background of the work, states some open problems in dendronized polymers at the time the thesis plan had been set up. The second chapter gives a brief introduction to the tools the author developed and used for modeling. The multiscaled models are presented in the chapters 3–5. In the end of the thesis the author gives a summary of the work and an outlook for some prospective further developments.
Acknowledgments

Firstly I would like to thank Prof. Dr. H.C. Öttinger for giving me the opportunity to conduct my PhD thesis in his Polymer Physics research group and to benefit from the research facilities. It is his constant encouragement and diligent teaching that lead me to the world of thermodynamics and polymer physics. He taught me how to think in a way as physicists do and how to conduct good research, which I will benefit life-long in my future career.

I express my sincere appreciation to Prof. Dr. M. Kröger, who directly supervised my research project, for his advice, encouragement and valuable guidance. The door of his office is always open for all my questions and problems. His helps come from not only scientific advising but also taking care of my study plan and career development. It is him that turned me from a greenhorn into an experienced computational physicist.

My sincere thanks go to Prof. Dr. A.D. Schlüter, who initiated this project. He showed me the fantastic world of dendronized polymer and the beauty of chemistry when I was a master student in Germany. He offered me the possibility to come to Zürich and have my PhD thesis on tackling open problems of dendronized polymers. I benefit from his support and care during the whole time of my thesis work. The fact that I could spend my whole PhD time in both Polymer Physics group of Prof. Öttinger and Polymer Chemistry group of Prof. Schlüter gave me the chance to learn not only physics but also other aspects in the chemistry of polymers and materials in general.

I owe my thanks to Dr. M. Hütter from Polymer Physics and Prof. P. Walde from Polymer Chemistry, with the help of whom I was involved in many teaching activities and gained valuable teaching experiences. I would also like to thank our secretaries Daniela and Patricia for their helps when I had administrative questions.

I would thank Prof. A. Halperin from CEA Grenoble for the very helpful discussions on scaling theory of polymers.

I am grateful to all my colleagues in both groups of Polymer Physics and Polymer Chemistry, who are too many to mention individually, but who have made these years so memorable. I will always recall the time taken sharing our thoughts and ideas, not only for the office time but also for the spare times like usual coffee breaks and trips to other cities.
In the last but not least, my thanks go to my parents for their ceaseless support and selfless affection from China, my home.
Contents

1 Introduction ................................................................. 1
   1.1 Background of the Work ........................................... 2
      1.1.1 Dendronized Polymers ........................................ 2
      1.1.2 Helical super-structures observed by Cryo TEM ........... 4
      1.1.3 Theoretical Explanations/Hypotheses ...................... 4
   1.2 Multi-scaled models for amphiphilic denpolys .................. 5

2 Tools and Methods ..................................................... 11
   2.1 BBT: A Particle-Based Multiscale Modeling Package .......... 12
      2.1.1 Linked cells structure ..................................... 12
      2.1.2 Data structure for system configuration .................. 13
      2.1.3 Numerical experiments as objects ........................ 14
   2.2 An example of BBT model: Fully atomistic model ............... 14

3 Rubik Cylinder Model .................................................. 19
   3.1 Introduction ...................................................... 20
   3.2 The Prototype of RC: Dendronized Polymers and Their Self-Assembly ..... 23
   3.3 The Rubik Cylinder (RC) model .................................. 24
   3.4 Simulation ....................................................... 27
      3.4.1 Implementation details ..................................... 28
      3.4.2 Phonebook move ............................................ 29
      3.4.3 Application of moves ..................................... 30
      3.4.4 Deterministic recoloring, Janus vector ................... 30
   3.5 Sampling, observables, and reference values ..................... 31
      3.5.1 Helicity and pitch angles .................................. 32
      3.5.2 Torsion angles ............................................. 33
      3.5.3 Phase separation index ................................... 33
      3.5.4 End-to-end distance, radius of gyration .................. 34
3.6 Results and Discussion ................................................. 34
3.7 Conclusions .............................................................. 39
3.8 Appendix ................................................................. 49

4 The Emergence of The Janus Chain Model 53
4.1 Introduction ............................................................... 54
4.2 Atomistic model for DP ............................................... 55
   4.2.1 Architecture ......................................................... 56
   4.2.2 Goals ................................................................. 57
   4.2.3 Solving the model .................................................. 58
   4.2.4 Coarse-graining and effective diameter ......................... 59
   4.2.5 Results and insights from atomistic model ....................... 59
4.3 Janus chain model ..................................................... 63
   4.3.1 Classical ingredients .............................................. 63
   4.3.2 Induced curvature .................................................. 64
   4.3.3 Effective solvent quality ......................................... 65
   4.3.4 Brownian dynamics simulation .................................. 66
   4.3.5 JC model parameters .............................................. 66
   4.3.6 Selected results, comparison with experiment .................... 67
4.4 Conclusions .............................................................. 69

5 Extensive Exploration of The Janus Chain Model 75
5.1 Introduction ............................................................... 76
5.2 The model ............................................................... 77
5.3 Phase Diagram for Dendronized Polymers in Different Solvents .... 80
5.4 Generalized JC: More Complex Phases ............................... 85

6 Conclusions and Outlook ................................................. 89

A Derivation of Bending and Torsion Forces 91
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>A schematic illustration of a fourth generation dendronized polymer (PG4).</td>
<td>2</td>
</tr>
<tr>
<td>1.2</td>
<td>The chemical structure of polymer (PG4) with aliphatic and aromatic interior and charged ammonium termini.</td>
<td>3</td>
</tr>
<tr>
<td>1.3</td>
<td>Motivation: beyond the super-structures of dendronized polymers</td>
<td>3</td>
</tr>
<tr>
<td>1.4</td>
<td>(a) The 3-D helical super structure from 3-D reconstruction. The raw Cryo-TEM image of the PG4, a network-like assembly is represented. (b) Class sum images obtained from several hundred individual fiber motifs. (c) Reconstructed 3D double helical structure of fibers.</td>
<td>4</td>
</tr>
<tr>
<td>1.5</td>
<td>Models in different coarse grained levels.</td>
<td>6</td>
</tr>
<tr>
<td>2.1</td>
<td>A macromolecule consists of 930 atoms, the space of simulation box is decomposed into $10 \times 10 \times 10 = 1000$ cells.</td>
<td>13</td>
</tr>
<tr>
<td>3.1</td>
<td>Rubik cube meets Rubik cylinder. Both objects are characterized by their surface pattern and hidden rules for performing changes.</td>
<td>21</td>
</tr>
<tr>
<td>3.2</td>
<td>Semiflexible Rubik cylinder with a number ($N_l$) of backbone segments $u_{i=1,2,...,N_l}$ (yellow backbone, here $N_l = 4$), faces $k = 1,...,N_r$ (red or white, here $N_r = 12$) at segment $i$ are represented by their center positions, denoted as $r_{i,k}$. The notation will be used in Sec. 3.3. Steric interactions between Rubik cylinders are calculated between backbones, amphiphilic interactions between faces. For comparison, the Janus chain model [6] is shown, whose Janus vectors (red arrows) can be seen to represent the charge distribution inside a Rubik cylinder segment.</td>
<td>22</td>
</tr>
<tr>
<td>3.3</td>
<td>A schematic illustration of a third generation (PG3) dendronized polymer. A single G3 dendron is also shown. Both neutral and charged dendronized polymers have been synthesized, usually terminal monomers of the dendrons carry charges [7] and the polymer is surrounded by solvent (and counterions).</td>
<td>23</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>3.4</td>
<td>Helicity index $\zeta$, defined in Sec. 3.5.1, for a system of two RCs, vs. Metropolis MC step. In each MC step all moves (i)-(vi) described in Sec. 3.4 had been applied, including the probabilistic recoloring scheme, as further described in the text part. The dashed line marks the value $\zeta = 1/\sqrt{2}$ for a double helix at the minimum pitch angle, $\gamma = \pi/4$, cf. Tab. 3.1 and App. 3.8. System parameters: $N_c = 2$ (RCs), $N_l = 80$ (segments), $B/A = C/A = -1$, $p_A = p_B = p_C = 1$ (energy parameters), $N_t = 12$ (faces per segment), $c = 0.4$ (coverage), $k_B T/A = 0.7$ (temperature), $r_{cut} = R$ (amphiphilic cutoff distance), $\theta = 0.14$ (bond angle) and $R/L = 4$ (or alternatively, flexibility parameter $\xi = 0.0392$, defined in Eq. 3.25).</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>Total energy for the system specified in Fig. 3.4.</td>
<td></td>
</tr>
<tr>
<td>3.6</td>
<td>Mean squared end-to-end distance among the $N_c = 2$ chains; system parameters as for Fig. 3.4.</td>
<td></td>
</tr>
<tr>
<td>3.7</td>
<td>Phase separation index $S$ for the system presented in Fig. 3.4. Notice that this parameter is unity by construction for the deterministic recoloring mode, cf. Sec. 3.4.4.</td>
<td></td>
</tr>
<tr>
<td>3.8</td>
<td>Helicity index $\zeta$ defined in (3.21a). Both Metropolis and Barker MC results for two RCs with $N_l = 40$ segments each, at coverage $c = 40%$. Remaining simulation parameters as for Fig. 3.4.</td>
<td></td>
</tr>
<tr>
<td>3.9</td>
<td>Energy vs. MC step. Same conditions as for Fig. 3.8.</td>
<td></td>
</tr>
<tr>
<td>3.10</td>
<td>Helicity index. Both Metropolis and Barker MC results for two RCs with $N_l = 80$ segments each, at coverage $c = 40%$. All other simulation parameters as for Fig. 3.4.</td>
<td></td>
</tr>
<tr>
<td>3.11</td>
<td>Energy vs. MC step. Same conditions as for Fig. 3.10.</td>
<td></td>
</tr>
<tr>
<td>3.12</td>
<td>Sample configurations from Barker MC, of two RCs with $N_l = 80$ at different coverages $c$, taken at MC step 120000, cf. Figs. 3.10, 3.11, 3.13, and 3.14. We see the equilibrium pitch angle dependence on the charge coverage ($c$). Potential energies ($E$) are also reported. Compare with Fig. 3.17.</td>
<td></td>
</tr>
<tr>
<td>3.13</td>
<td>Same as Fig. 3.13, now with $c = 30%$. Snapshots for the configurations at MC step 80000 are shown in Fig. 3.15. For the Barker scheme the helicity index $\zeta$ (3.21a) quickly approaches a value close to its maximum, $\zeta = 1$.</td>
<td></td>
</tr>
<tr>
<td>3.14</td>
<td>Same as Fig. 3.11, now with $c = 30%$. Snapshots for the configurations at MC step 80000 are shown in Fig. 3.15.</td>
<td></td>
</tr>
</tbody>
</table>
LIST OF FIGURES

3.15 Sample conformations obtained during Metropolis (left) and Barker (right) sampling. Same model parameters as for the outermost left graph in Fig. 3.12 at charge coverage \( c = 30\% \). At \( c = 40\% \), the differences between Metropolis and Barker schemes become less pronounced. 43

3.16 Equi-physics surfaces \( \Xi(\xi) \) in the geometrical parameter space of the RC. The surface are labelled by the flexibility parameter \( \xi \), and the surfaces are defined by \( R = 2\xi L/\theta^2 \), cf. App. 3.8. 50

3.17 Total potential energy vs. pitch angle for the double helical intercoiled superstructure, for a number of coverages (of the hydrophobic sites). \( (B = C = -A, p_{A-C} = 1) \). 51

4.1 Sample snapshot of a stretched part of a G3 DP during atomistic simulation. 57

4.2 a) Schematic drawing of the \( \supset \subset \)-configuration of two DP’s and the scanning sphere used to calculate profiles. b) Density profiles for all and charged beads, respectively for bent third generation dendronized polymers (G3 DP). c) Density profile and charge distribution of two contacting, \( \cup \)-shaped G3 DPs (chains 1 and 2) in \( \supset \subset \)-configuration. Charges migrate to the outer side of the contact region, neutral atoms to the inner side. 62

4.3 Two interwinded Janus chains. 64

4.4 Different complexations (phase diagram) obtained by varying the solvent quality parameters. 67

4.5 Simulated “cryo TEM image” in comparison with the experimental image. 68

5.1 Schematic representation of two semiflexible Janus chains approaching each other and characteristic types of polymeric conformations observed inside the helical network. 82

5.2 Phase diagrams of JCs with coverages \( c = 0.3, 0.5 \) and \( 0.7 \), in the \( \Delta \chi - \chi_0 \) plane. Gray stands for individual chains (I); light purple stands for the intermediate state (L) between individual chains (I) and helical network (H); bright red for helical network (H); green for the intermediate state (D) between helical network (H) and ball-like aggregate (O, Blue). 83

5.3 Sample snapshots showing the formation of helical network, taken at times \( t = 1, 20, 80, 200, \) and \( 500 \), for the case with solvent qualities \( \chi_0 = -8, \Delta \chi = 16 \), coverage \( c = 0.7 \), and nearest neighbor interactions \( (\alpha = \infty) \). 84

5.4 Three representative configurations for: (O) globule (solvent quality \( \chi_0 = +4, \Delta \chi = 8 \), coverage \( c = 0.7 \)), (H) helical network \( (-8, 16, 0.7) \), and (I) individual chains. \( (-32, 1, 0.7) \). 84
5.5 Semi-log plots of intra- and inter-chain pair correlation functions of JCs (here for coverage $c = 0.7$) are used to classify states into three representative phases (O, H, and I). ......................... 84

5.6 Shown are examples for (a) double helix at coverage $c = 0.35$ and $\alpha = 12$, (b) triple ($c = 0.4, \alpha = 2$) (c) quadruple ($c = 0.8, \alpha = 2$), and (d) quintuple helix ($c = 0.9, \alpha = 2$). Remaining simulation parameters are $k = 15$, $\chi_0 = 1, \Delta \chi = 32$, and $r_c = 2$. ......................... 85
List of Tables

3.1 Interpretation of helicity quantities ζ and ε defined in (3.21) ........................................... 33

4.1 Number of atoms $M_0$, and repeat units $M$ (dendrons), mean-squared end-to-end distance $\langle R_{ee}^2 \rangle$ of the DP, contour length $L$ of its centerline, lateral diameter $d_{\text{eff}}$, corresponding JC repulsion diameter $d_{\text{rep}} \equiv d_{\text{eff}}/2^{1/6}$, persistence length $l_p$, as well as results from charge distribution measurements: charged fraction of (all) surface beads $S_{\pm}$, overall fraction $S_o$ of surface beads, the coverage $\phi_0 \equiv M_0^+ S_{\pm}/(M_0 S_o)$ of charges on the DP surface, for the atomistic model at temperature $T = 1$ LJU. All dimensional quantities given in reduced units, cf. last column. The persistence length $l_p$ is determined from the centerline (itself obtained using the method described in the text part) using the analytical result [24, 25, 12] for the mean squared end-to-end distance $\langle R_{ee}^2 \rangle$ of a semiflexible chain, $\langle R_{ee}^2 \rangle = 2l_p L - 2l_p^2 [1 - \exp(-L/l_p)]$. The third table row clarifies the connection between atomistic and mesoscopic (JC) parameters. Each bead of a JC represents $M/N$ dendrons (and $M_0/N$ united atoms), $d_{\text{rep}}$ LJU $= J Cu$, $l_p/d_{\text{rep}} = \kappa/k_B T$ and so on, as further elaborated in the text part. According to this table, the G4 DP has a persistence length of $l_p = 635.6$ LJU $= 118.9$ nm. ........................................... 60
Chapter 1

Introduction
1.1 Background of the Work

1.1.1 Dendronized Polymers

Dendronized polymers (denpols) are quite a new class of comb polymers whose backbones carry dendrons (dendritic wedges) at each repeat unit [1, 2]. Denpols carry hyper-branched side groups which make them different from normal comb polymers with linear side chains. The branches diverge regularly, each diverging is called a generation, the end points of branches are called termini or the periphery of the denpol. The branches are called the interior of the denpol. A schematic illustration of a fourth generation dendronized polymer (PG4) is given in Fig. 1.1. The high bulkiness of dendrons confines the conformation of dendronized polymers, and thus renders long dendronized polymers as a cylindrical object.

The hyperbranched dendron offers much more efficient space filling, compared to the one achievable by linear side chains of brush polymers. Denpols with moderate generation (more than 2, as demonstrated by the quasi-atomistic modeling results in chapter 4) behave like dense solid cylinders, but brush polymers never provide high enough density. A direct comparing of compactness provided by dendrons and linear chains has been reported [3]. Linear polymer hairs were grafted to the periphery of a G2 denpol. The resulted hybrid denpol-brush was subjected to AFM visualization, which indicated a distinct compactness difference between the 2 parts.

The thickness of denpol adds more dimensions of freedom for its chemical versatility compared to conventional 1-D polymer threads.

![Figure 1.1: A schematic illustration of a fourth generation dendronized polymer (PG4).](image)

The periphery of a denpol can be chemically decorated with functional groups which are different from its interior. An example is a denpol with hydrophobic organic interior and hydrophilic periphery, whose chemical structure is shown in Fig. 1.2. Due to the hydrophilicity of its termini, denpol of this kind is water soluble.

It has been observed that some denpols (as shown in Fig. 1.2) can self-assemble in water solution and form novel 3-D supramolecular structures. This exciting observation pushes
1.1. BACKGROUND OF THE WORK

Figure 1.2: The chemical structure of polymer (PG4) with aliphatic and aromatic interior and charged ammonium termini.

The investigation of denpols onto a higher level. A well known analogy is the self-assembly of conventional block copolymers [4], as shown in Fig. 1.3. The versatileness of a block-copolymer is limited by its simple geometry: conventional polymers are 1-D objects on the molecular level, so that the amphiphilicity can only be chemically addressed with freedom in one dimension. In other words, the amphiphilicity can only be addressed block-wise. In contrary, denpols provide greater freedom for addressing the amphiphilicity. Apart from block-wise, more versatile patterns can be achieved such as sector-wise or core-shell-wise. The self-assembly of denpols is an almost unexplored field until now.

Figure 1.3: Motivation: beyond the super-structures of dendronized polymers
CHAPTER 1. INTRODUCTION

1.1.2 Helical super-structures observed by Cryo TEM

Cryo-TEM visualizes macromolecules in a frozen aqueous solution. It has been reported in an Cryo-TEM visualization experiment [5] an aqueous solution of 4th-generation denpol (PG4) with ammonium terminal groups, was frozen and subjected to Cryo-TEM measurement, following the well-established methods [36] for sample preparation and microscopy techniques. The chemical structure of the measured G4 polymer is given in Fig. 1.2. The number-average and weight-average of the degree-of-polymerization of the polymer are \( P_n = 460 \) and \( P_w = 830 \), respectively. The corresponding average lengths of the polymer (in a totally stretched conformation) are 120 nm and 210 nm respectively. The concentration of the polymer in solution is 45 mg/L.

The raw image of the investigated polymer (PG4) is given in Fig. 1.4a. This picture represents a network structure, which is attributed to the assembly/aggregate of single polymer chains. The internal structure of the ‘fibres’ in the net-work had been achieved by classification and averaging of the amplified ‘fibres’ images (Fig. 1.4b). Then a computer aided 3-D reconstruction indicated the helical super-structure of the ‘fibres’: the ‘fiber’ in the net-work is composed of double helically inter-coiled denpol chains (Fig. 1.4c).

![Figure 1.4: (a) The 3-D helical super structure from 3-D reconstruction. The raw Cryo-TEM image of the PG4, a net-work like assembly is represented. (b) Class sum images obtained from several hundred individual fiber motifs. (c) Reconstructed 3D double helical structure of fibers.](image)

1.1.3 Theoretical Explanations/Hypotheses

The mechanics of this double helical network formation was at that time unknown and became a main question for which an answer will be proposed in this thesis. Previous molecular simulation works [7] have shown that a chemically non-chiral single dendronized polymer chain takes helical conformation, because of the steric demand of dendrons. The basic idea can be explained as ‘cylindrically confined spheres’. If a number of spheres with diameter \( d \)
are confined in a cylindrical space, the diameter of which is $D$ and $d < D < 2d$, the spheres will pack with a helical pattern because of their own volume, due to excluded volume interactions. In case of dendronized polymers, the chemical bonding at the focal points produces cylindrical confinement, and dendrons may tend to pack in a helical manner as well, due to the steric demand of themselves.

The above arguments make the occurrence of helical conformations plausible. However, the network formation (Fig. 1.4a) must be a result from some kind of affinities but not (or not only) by volume repulsion, because double chain intertwining is involved. On the other hand, a ’cylindrically confined sphere’ model tends to overestimate the volume repulsion of dendrons. For dendrons with flexible branches (short alkyl or alkyleoxy chains as in Fig. 1.2), the possibility for interpenetrating between dendrons must be considered. Thus the author proposes another approach to explain the observed phenomena.

The author de-emphasizes the steric demand and rigidity of dendrons, but focuses on the effect of amphiphilicity, which has been well investigated theoretically [8, 9] for dendrimers. Dendrimers with organic interior (cores and branches) and water-soluble peripheries can take different conformations (due to the flexibility of dendron), which depend on the quality of solvent. Usually there are not adequate amount of peripheral groups to cover all the ’surface’ of the dendrimer molecule, so that there must be some part of organic interiors exposed. Accordingly, the ’surface’ of the dendrimer molecule should be covered partly by hydrophilic peripheral groups and partly by hydrophobic organic interiors.

In this case a similar ’surface patterning’ (as amphiphilic dendrimers have) is expected, which renders the denpol as an amphiphile. Helical super-structures and network formation are expected to result from amphiphilic self-assembly. What make the denpol distinct from conventional amphiphiles is the fact that the amphiphilic pattern of denpol is dynamic, due to the flexibility of dendrons. The author presents in this thesis a computational approach to tackle the self-assembly problem of denpols, utilizing multiscaled models.

### 1.2 Multi-scaled models for amphiphilic denpols

The philosophy of multiscale has been deeply embedded in the mind of human beings, in most cases undeliberately. Based on this philosophy the hierarchical structure of science had been established [11]. Elementary particle physics laws govern the behavior of any physical systems in the universe but “The ability to reduce everything to simple fundamental laws does not imply the ability to start from those laws and reconstruct the universe”. People always need physics that is on a suitable level above the elementary particle level to solve realistic problems. The atomistic information has been coarse grained into information on
CHAPTER 1. INTRODUCTION

higher physics level. In many cases due to the simplicity of the elementary particle physics, the coarse graining path from particle physics level to higher physics level appears to be so smooth and painless that people even do not realize a level-jumping is under way.

Now we come back to the amphiphilic denpol problem proposed in section 1.1. The particle physics in this case become much more complicated: it involves the many-body interactions between denpol and solvent molecules (amphiphilic interactions), the dynamics of the denpol’s internal structure and amphiphilic pattern and the dynamics of the denpol’s global conformation (supramolecular structure). The complexity of particle-particle interactions and the coexistence of different characteristic length(time) scales make analytical approaches infeasible and throw considerable difficulty to numerical approaches. It is unavoidable to employ multiscale models with different coarse grained levels in the computational investigation of denpols containing high-molecular weight, charged components with complex internal structures.

![Figure 1.5: Models in different coarse grained levels.](image)

As illustrated by Fig. 1.5 the author has developed 3 models with different levels of coarse graining. The whole thesis work does not take a strict bottom-to-top order of constructing/studying models, but rather in a shuffling manner. The model ‘Rubik Cylinder’ is where the thesis work started from. It is a simple toy model, built on the basis of intuitive understandings of dendronized polymer. It works as an entrance to the whole maze of supramolecular chemistry/physics of amphiphilic denpols. It later on served to bridge the other two models by providing concrete parameter feeding/demand scenarios. This may seem against to some readers’ intuition but represents the most natural way of exploring an
unknown territory: first to make a tentative attempt then to confirm the attempt and gain some confidence, in the end to spend solid effort for extensive exploration.

This thesis presents the author’s original attempt-confirm-explore philosophy for model development. Chapter 3 elaborates RC model as an attempt to pose the hypothesis of dynamic amphiphilicity and broken symmetry. In the following chapter 4 the assumption of dynamic amphiphilicity, based on which RC model is built, is confirmed from atomistic modeling of denpol. With the confidence established a new model, the Janus Chain model, which is more sophisticated and suitable for more extensive studies is developed. Chapter 5 presents the extensive explorations of JC model.
Bibliography


Chapter 2

Tools and Methods
CHAPTER 2. TOOLS AND METHODS

2.1 BBT: A Particle-Based Multiscale Modeling Package

A software package is developed for most of the computational studies involved in this thesis. The package utilizes object orientation (OO) modeling strategy and extensively makes use of STL (standard template library) data containers [1], in order to make it easily readable and maintainable. In a time when computing power becomes much cheaper than human power, the OO strategy makes attractive trade-off of computing speed versus human maintaining effort. In the computational studies involved in the thesis, BBT package demonstrates satisfactory computing efficiency.

The name of this package BBT is the abbreviation of its key data structure: Bead, Bond and Topology. The full information of a studied system is expressed by a set of beads bonded according to a certain topology. This basic idea of data structure has been widely used in many computational chemistry softwares. The beads can be either real physical particles like atoms (or united atoms) and molecules, or imaginary objects as information carriers like virtual particles used in Smooth Particle Hydrodynamics (SPH) [2] and Vortex Method [3] for fluid mechanics. Depending on the system to be studied, the bead objects can be connected by different kinds of bonds following a customizable topology. For example, Lennard Jones particles connected by finite elongate nonlinear elastic (FENE) bonds in a linear topology realize a classical FENE-B model for linear polymers.

2.1.1 Linked cells structure

The physical law that determines the behavior of particle based systems is many-particle interaction which involves calculating all pairs of interacting particles. The computing effort of this kind scales as $N^2$ while $N$ is the total number of particles. Most interactions are with a finite active range, they fade away to ignorable beyond this range. The limit of this range is called cut-off distance. The cut-off distance of 12-6 type LJ interaction $U(r) \sim (\sigma r)^{12} - (\sigma r)^6$ is usually taken as $2.5\sigma$, beyond which $U(r)$ becomes less than 2% of its extremal. For systems which explicit LJ form is not needed the cut-off distance can be set even smaller.

The existence of finite cut-off distance makes it possible to calculate not all $N^2$ pairs of $N$ particles but only the pairs that within the cut-off range. It is an efficient way to decompose the space of studied system into individual cells with the cut-off distance as their size, so that a particle interacts only with others locating in the same cell and the close neighboring cells. For 3D space decomposed into cubic cells as depicted in Fig. 2.1 every cell has $3^3 - 1$ close neighbors. If the cell size is much smaller than the system size, the computing effort scales no longer as $N^2$ but $N$. 
2.1. BBT: A PARTICLE-BASED MULTISCALE MODELING PACKAGE

Figure 2.1: a macromolecule consists of 930 atoms, the space of simulation box is decomposed into $10 \times 10 \times 10 = 1000$ cells.

In BBT package a cell is represented as a data type cell which contains the indices of its neighboring cells and a dynamic list of indices of particles locating in it. As the evolution of the system a particle may move from one cell to another, this can be updated by a simple eliminating of its index from the list of its old cell and at the same time inserting into the list of the new cell, without touching the un-moved particles and the cells they are in. Compared to the linked-list technique presented in classical text books which is realized by process orientated programming tools and involves recalculating of all cells and particles for every cell list updating, the BBT data structure provides a much faster updating of cells structure when only a few of particles change their positions.

A neighbor_list data type is defined in BBT. It contains the whole list of cell objects and another list pointing from particle indices to the cell indices. Different neighbor_list objects can be used in parallel for calculating interactions with different cut-off ranges and geometries (apart from cubic).

2.1.2 Data structure for system configuration

The key data structure of BBT has been highlighted in the beginning of this chapter: bead, bond and topology. A bead object contains basic information such as position, velocity...
and force of a particle. A bond object contains the indices of the two beads which a bond is connecting and type of bondage such as FENE or linear elastic chemical bond. topology contains lists addressing the connectivity of particles. All the three of data types give a full description of a model system configuration, which is captured by a single and more general data type config.

2.1.3 Numerical experiments as objects

Once a model configuration is established, various numerical experiments can be carried out on it. Examples are Monte Carlo, molecular dynamics and stochastic dynamics. All kinds of numerical experiments are defined as data types (for example monte_carlo) containing their own configuration data config and basic experiment operations and parameters. This allows us to conduct different numerical experiments in parallel and communicate with each other. Parallel tempering Monte Carlo experiment can be a good example: a number of Monte Carlo experiments at different temperature are conducted in parallel, 2 Monte Carlo threads are accepted to exchange configurations from time to time. BBT enable such operations by a simple command as in pseudo code swap(monte_carlo[1].x, monte_carlo[2].x).

2.2 An example of BBT model: Fully atomistic model

With the help of a well developed classic force field data base [4, 5, 6], we can build a fully atomistic model for all types of real molecules. The Hamiltonian of the system is defined in EQ.2.1. It contains the contributions from the stretching of chemical bonds ($U_{bond}$), the variation of bond angles ($U_{bend}$), rotating of chemical bonds ($U_{torsion}$) and LJ interactions. All parameters appear in EQ.2.1 are depending on the types of atoms involved and available from force field data base. Gradient of potential energy $\frac{\partial U}{\partial r}$ gives the forces acting on an atom locating at $r$. The derivation of bending force and torsion force are demonstrated in Appendix A. The macromolecule in Fig. 2.1 is a snapshot of a fully atomistic modeling of low molecular weight G2 dendronized polymer. Extensive study on fully atomistic model is beyond the scope of this thesis.

$$
U = U_{bond} + U_{bend} + U_{torsion} + U_{LJ}
$$

$$
U_{bond} = \sum_{bonds} K_b (b - b_{eq})^2
$$

$$
U_{bend} = \sum_{bondangles} K_\theta (\theta - \theta_{eq})^2
$$

$$
U_{torsion} = \sum_{dihedrals} \frac{V_n}{2} [1 + \cos(n\Phi - \gamma)]
$$

$$
U_{LJ} = \sum_{i<j} \frac{A_{ij}}{r_{ij}^n} \left[ \frac{1}{r_{ij}^{12}} - \frac{1}{r_{ij}^{6}} \right]
$$
Details about other models which have been extensively studied in this thesis can be found in the next chapters.
Bibliography


Chapter 3

Rubik Cylinder Model
CHAPTER 3. RUBIK CYLINDER MODEL

Abstract

The authors introduce the semiflexible “Rubik cylinder” (RC) model, a model for investigating and illustrating the self-assembly of fibular-like macromolecules with complex internal structure. It is inspired by actual molecular geometries of interest. The RC model allows to reproduce basic experimental findings for dendronized polymers and serves to motivate another coarse-grained model, the less detailed Janus chain model, which has been recently introduced to capture the dynamics and superstructure formation of dendronized polymers. The RC model is solved by applying off-lattice Monte Carlo using mostly conventional moves, but also some model–adapted ones, which can be of use for other polymeric systems. This includes a so-called “phonebook”-move (geometric bridge), where parts of chains are regrown by efficiently using a lookup-table. The table represents a whole (sub)chain conformation of arbitrary length (or arbitrary number of monomers) by a single integer, the seed value of the random number generator. The phonebook move constitutes an extension of the concerted rotation move, and does not require solving nonlinear equations for constraints. Quantities characterizing the RC model will be defined and monitored and set in relation with RC conformations.

3.1 Introduction

Amphiphilic self-assembly of macromolecules has continuously gained attention within a number of research areas, from polymer synthesis [1] to colloidal chemistry, from nanotechnology [2] to biological science [3]. Amphiphilicity between molecules arises from the different chemical nature, polarity and cohesion energy of the interfaces separating them. Hence, molecular interfacial properties, rather than intramolecular properties, play the dominant role in the process of amphiphilic self-assembly [10, 11].

Dendronized polymers (DPs), a new class of complex synthetic polymers, can display novel supramolecular properties due to their ability to functionalization and large size. The amphiphilicity of DPs inherently provides them with dynamic features, as opposed to the case of conventional detergents with fixed block-wise amphiphilicity. It has been observed experimentally that achiral DPs form helical shaped superstructures (more details about DPs will be presented in Sec. 3.2). In this manuscript we will propose a simple model to explain and investigate the mechanism of the formation of such helical structures. Its basic

---

1This chapter is adapted from: Y. Ding, M. Kröger, RUBIK CYLINDER MODEL FOR DENDRONIZED POLYMERS, J. Comput. Theo. Nanosci. in press with permission from ASP.
ingredients are geometrical constraints and its ability to allow for a dynamical repatterning of surface amphiphilic entities, which includes the symmetry breaking of surface patterns within cylinder slices.

Figure 3.1: Rubik cube meets Rubik cylinder. Both objects are characterized by their surface pattern and hidden rules for performing changes.

The Rubik cylinder (RC) model, to be introduced here, offers these features. Its name derives from the more famous “Rubik’s cube”, cf. Fig. 3.1, for which players change the color patterning of the cube’s surface, without considering what happens inside the cube, except that they have to perform allowed moves to not destroy the interior. In analogy, firstly, the RC skeleton does not allow for arbitrary moves reflecting geometrical or topological constraints arising from chemical structure on the molecular level. Secondly, the key feature of amphiphilic entities in solution concerning their assembly behavior is the pattern of amphiphilicity on the interface between entities and solvent. We may call any surface whose pattern (of amphiphilicity) may change and where the moves are constrained by hidden processes or parameters, a structure which falls into the Rubik class of models.

For this chapter we have chosen a Rubik model with cylindrical, semiflexible shape, because this corresponds to the important case of linear macromolecules with internal structure (such as dendronized polymers [7, 8], magnetic chains in ferro- and magnetoviscous [9, 10, 11, 14, 13, 16, 15, 24] or electrorheological fluids [17, 18], wormlike micelles [19, 10, 20, 21, 22], one-dimensional metal chains [23, 24]), and because the RC model can be used – in that setting – to motivate the Janus chain model, which consists of a linear backbone with attached vectorial degree of freedom representing charge distributions along the backbone. The situation is schematically depicted in Fig. 3.2. More generally, the RC model can be used to model objects with dynamical surface patterns such as spherical dendrimers,
Figure 3.2: Semiflexible Rubik cylinder with a number \(N_l\) of backbone segments \(u_i=1,2,...,N_l\) (yellow backbone, here \(N_l = 4\)), faces \(k = 1,..,N_r\) (red or white, here \(N_r = 12\)) at segment \(i\) are represented by their center positions, denoted as \(r_{i,k}\). The notation will be used in Sec. 3.3. Steric interactions between Rubik cylinders are calculated between backbones, amphiphilic interactions between faces. For comparison, the Janus chain model [6] is shown, whose Janus vectors (red arrows) can be seen to represent the charge distribution inside a Rubik cylinder segment.

micelles. It is suited to describe cylindrical amphiphiles as will become obvious from good agreement between the simulated model behavior and the experimentally observed phenomena of dendronized polymers [7, 8], where the structurally achiral, atactic dendronized polymers self-assemble in aqueous solution, and form helical fibular-like super-structure [3].

In this work we do not report about the effect of concentration on the phenomenology of the RC model, because the results tend to coincide with the ones obtained for the Janus chain model, cf. Fig. 3.2 and chapters 4–5. In particular, for (semi-)stiff RCs at very sufficiently large densities, the system can be expected to exhibit an isotropic to orientationally ordered state (nematic, smectic) transition, as is known from independent studies of semiflexible polymers and nematic liquid crystals, cf. [27, 28, 29, 30, 31, 37, 33, 34], where also the nonequilibrium phase diagram had been discussed.

Due to their relevance for the present work a brief introduction to dendronized polymers is given in Sec. 3.2. Section 3.3 introduces the RC model. Full implementation details including Monte Carlo moves can be found in Sec. 3.4, including the newly developed phonebook move, cf. Sec. 3.4.2. Section 3.5 defines several quantities which help characterizing the RC state, while the appendices offer some general considerations which effectively limit the parameter space in App. 3.8, report about the preferred energy state, App. 3.8, and provide analytically derived expectations about the behavior of the RC model, such as the minimum
pitch angle, in App. 3.8. Results and conclusions are collected in Secs. 3.6 and 3.7, respectively.

### 3.2 The Prototype of RC: Dendronized Polymers and Their Self-Assembly

Dendronized polymers are a new class of comb polymers whose backbones carry dendrons (dendritic wedges) at each repeat unit [7, 8], as schematically depicted in Fig. 3.3. The high bulkiness of dendrons confines the conformation of dendronized polymers, and thus renders dendronized polymers as cylindrical objects.

![Figure 3.3: A schematic illustration of a third generation (PG3) dendronized polymer. A single G3 dendron is also shown. Both neutral and charged dendronized polymers have been synthesized, usually terminal monomers of the dendrons carry charges [7] and the polymer is surrounded by solvent (and counterions).](image)

Dendronized polymers self-assemble into extraordinary three-dimensional super-molecular structures. The corresponding observations have been made using the cryo-transmission electron microscopy (Cryo-TEM) [35] setup, which is a TEM with a specimen holder capable of maintaining the specimen at liquid nitrogen or liquid helium temperatures. This allows imaging specimens prepared in vitreous ice, the preferred preparation technique for imaging individual molecules or macromolecular assemblies. In that particular experiment [3] an aqueous solution of 4th-generation dendronized polymer (PG4) with ammonium terminal groups was frozen and subjected to Cryo-TEM measurement, following the established methods [36] for sample preparation and microscopy techniques. The chemical structure of
the measured G4 polymer is given in Fig. 1.2. A computer aided 3-D reconstruction of the TEM image was conducted, and indicated a helical super-structure: 2 strands of dendronized polymer chains helically inter-wind with each other, form a double helical fiber.

In order to understand the mechanism of such super-structure formation for dendronized polymers it is useful to recall properties of their constituents, amphiphilic dendrimers. Dendrimers [37] are a type of macromolecules similar to, but simpler than dendronized polymers. Their amphiphilicity has been well investigated theoretically [38, 39]. Dendrimers with organic interior (cores and branches) and water-soluble peripheries can take different conformations (due to the flexibility of dendron), which depend on the quality of solvent. Usually there are no adequate amounts of peripheral groups to cover all the ‘surface’ of the dendrimer molecule, so that there must be some part of organic interiors exposed to the solvent atmosphere. Accordingly, the ‘surface’ of the dendrimer molecule should be covered partly by hydrophilic peripheral groups and partly by hydrophobic organic interiors. A similar ‘surface patterning’ (as amphiphilic dendrimers have) is also expected for dendronized polymers, which renders them as cylindrical amphiphiles. Hence, helical super-structure is expected to be a result of amphiphilic self-assembly.

This exciting observation pushes the investigation of dendronized polymers onto a higher level [8, 40]. A known analogy is the self-assembly of conventional block copolymers [2]. The versatility of a block-copolymer is however limited geometrically: conventional polymers are one-dimensional objects on the molecular level, so that the amphiphilicity can only be chemically addressed with freedom in one dimension. Expressed differently, the amphiphilicity can only be addressed in a block-wise manner. In contrary, dendronized polymers provide great freedom for addressing the amphiphilicity. Not only block-wise, but more versatile patterns can be achieved such as sector-wise or core-shell-wise textures. The self-assembly of dendronized polymer is an almost unexplored field until now, while novel directions and known potential applications for dendronized polymers have been summarized in [4, 8, 7, 42, 43, 40]. The unusual structure of dendronized polymers and the potential impact they may possess have attracted theoreticians to this class of polymers [6, 21, 44, 45].

### 3.3 The Rubik Cylinder (RC) model

The single RC is a semiflexible cylinder, constructed by a string of loosely connected unstretchable circular segments. Particles carrying different colors sit on each segment equidistantly spaced along the circular cross-section, as shown in Fig. 3.2. For the purpose of defining interaction potentials, parameters, and to set up a simulation code we introduce appropriate notation.
3.3. THE RUBIK CYLINDER (RC) MODEL

A RC system contains $N_c$ cylinders, each of which contains $N_l$ segments with (i) fixed bond angle $\theta$ between adjacent segments, and (ii) bond length $L$. Segment unit vector $\mathbf{u}_i^\alpha$, subsequent segments along the RC backbone obey

$$\mathbf{u}_i^\alpha \cdot \mathbf{u}_{i+1}^\alpha = \cos \theta,$$

(3.1)

and we can introduce $(N_l + 1)N_c$ node positions $r_i^\alpha$ between segments via

$$\mathbf{u}_i^\alpha = \frac{r_{i+1}^\alpha - r_i^\alpha}{L},$$

(3.2)

or, quite equivalently, $\forall i > k$ $r_i^\alpha = r_k^\alpha + L \sum_{j=k}^{i-1} \mathbf{u}_j^\alpha$, specifically, for $k = 1$: $r_1^\alpha = r_1^\alpha + L \sum_{j=1}^{i-1} \mathbf{u}_j^\alpha$, where $r_1^\alpha$ denotes the position of the first node of chain $\alpha$. In our notation, rod-like chains exhibit a bond angle $\theta = 0$. Additional $N_r$ particles orbiting each of the segments in a distance $R$ are assigned to be located at $r_{i,j}^\alpha = r_i^\alpha + L \sum_{i-1}^{i,j} \mathbf{u}_j^\alpha$, where $\boldsymbol{\Omega}_{i,j}^\alpha$ lies on a unit circle surrounding the segment $\mathbf{u}_i^\alpha$,

$$\boldsymbol{\Omega}_{i,j}^\alpha \equiv \mathbf{v}_i^\alpha \cos \frac{2j\pi}{N_r} + w_i^\alpha \sin \frac{2j\pi}{N_r},$$

(3.4)

and where the following abbreviations have been introduced:

$$\mathbf{v}_i^\alpha \equiv \frac{\mathbf{u}_i^\alpha \times \mathbf{u}_{i+1}^\alpha}{|\mathbf{u}_i^\alpha \times \mathbf{u}_{i+1}^\alpha|}, \quad \mathbf{w}_i^\alpha \equiv \mathbf{u}_i^\alpha \times \mathbf{v}_i^\alpha,$$

(3.5)

with $\mathbf{u}_{N_l+1}^\alpha \equiv -\mathbf{u}_{N_l-1}^\alpha$ for convenience. For rods, $\mathbf{v}_i^\alpha$ is randomly chosen perpendicular to $\mathbf{u}_i^\alpha$. All the orbiting particles (located at $r_{i,j}^\alpha$) carry either red (binary 1) or white (binary 0) color, where the fraction between the state of the bins (colors) is assumed to be fixed for each segment, i.e., each segment carries $N_r^{\text{red}}$ red and $N_r - N_r^{\text{red}}$ white particles. Colors represent hydrophilic and hydrophobic sites. The binary variable $c_{i,j}^\alpha \in \{0, 1\}$ holds this dynamic information, while $\forall i, \alpha \sum_{j=1}^{N_r} c_{i,j}^\alpha = N_r^{\text{red}}$ remains constant for all times. The ratio

$$c \equiv \frac{N_r^{\text{red}}}{N_r}$$

(3.6)

is called the coverage of hydrophilic sites on the RC surface. Having defined particle positions and their labels, the RC model consists – in addition to the constraints for bond angles and bond lengths – of specifying configuration (conformation- and color-) dependent interaction potentials.
The total potential energy $E$ is given as the sum of steric repulsion ($U_{\text{steri}}$) and amphiphilic interactions ($U_{\text{amphi}}$, depends on the color state), both radially symmetric potentials, as follows:

$$E = \sum_{\alpha,i} \sum_{(\beta,m)\neq(\alpha,i)} U_{\text{steri}}(|\mathbf{r}_i^\alpha - \mathbf{r}_m^\beta|) + \sum_{j,n} U_{\text{amphi}}(|\mathbf{r}_{i,j}^\alpha - \mathbf{r}_{m,n}^\beta|, \sigma),$$  \hspace{1cm} (3.7)

where the sum extends over all pairs of different particles along the backbone for the steric interaction, as well as over all pairs of colored sites on different segments for the amphiphilic interaction.

The steric repulsion is modelled as hard core interaction at distance $2R$, i.e., (which is the effective cylinder diameter),

$$U_{\text{steri}}(r) = \begin{cases} \infty, & r \leq 2R, \\ 0, & r > 2R. \end{cases} \hspace{1cm} (3.8)$$

Due to the colors (amphiphilicity) of particles, there are three kinds of amphiphilic interactions, because its strength depends on an interaction indicator defined as $\sigma = c_{i,j}^{\alpha} + c_{m,n}^{\beta}$, and $\sigma$ can take the values 0, 1, or 2,

$$U_{\text{amphi}}(r, \sigma) = \begin{cases} A \Phi_{pA}(r), & \sigma = 0 \quad \text{(white-white)}, \\ B \Phi_{pB}(r), & \sigma = 1 \quad \text{(red-white)}, \\ C \Phi_{pC}(r), & \sigma = 2 \quad \text{(red-red)}, \end{cases} \hspace{1cm} (3.9)$$

where $\Phi_p$ for any “power”$ p \in \{p_A, p_B, p_C\}$ is given as

$$\Phi_p(r) \equiv \left( \frac{r_0}{r} \right)^p - \left( \frac{r_0}{r_{\text{cut}}} \right)^p, \hspace{1cm} (3.10)$$

with $\Phi_p(r \geq r_{\text{cut}}) = 0$, such that the amphiphilic interaction vanishes for pairs of faces at distances larger than $r_{\text{cut}}$. The characteristic length $r_0$ in equation (3.10) can we identify with $L$, and the bond length $L$ and energy $A$ are used to define unit length and energies, respectively, in the simulation. We are left with five dimensionless parameters $B/A$, $C/A$, $p_{A-C}$ specifying the potential, (dimensionless) temperature $k_B T / A$ and coverage $c$ characterizing the phenomenology of the RC model, as well as with geometrical coefficients $R/L$ and $\theta$ characterizing the radius and flexibility, respectively, of the RC. Letting $A = 1$, the white-white interaction is hydrophobic (attractive), and $B$ and $C$ should be negative in order to capture charge-charge repulsion and hydrophilic interaction. In this work we will present results only for a type of electrostatic potential for which $p_{A-C}$ are set to unity; the
RC can certainly be applied to more general situations. As we have elaborated in App. 3.8, the dimensionless ratio between radius $R$ and persistence length $l_p$ of the RC can be used to replace the three dimensional geometrical parameters $R$, $L$, and $\theta$ by a single one, to be denoted as $\xi$, with

$$\xi \equiv \frac{R}{l_p} \approx \frac{R\theta^2}{2L}.$$ 

Since $l_p = -L/\ln \cos \theta$ for the freely rotating RC (and $l_p = 2L/\theta^2$ for the wormlike RC, which is a freely rotating RC at $\theta \ll 1$). In the limit of vanishing potential energy, $U = 0$, properties of the freely rotating RC can be analytically derived and found in textbooks [24, 47].

### 3.4 Simulation

The classical Metropolis Monte Carlo method, for introductions see [48, 31, 50, 51, 25], is used to explore the important configuration space of the model system and to sample from a canonical ensemble, as long as we are not interested in the realistic dynamics of the RCs. The rigid constraints are most efficiently implemented using the Monte Carlo approach. The required interaction potentials, system parameters and constraints had been defined above. Our Monte Carlo moves subjected to the Metropolis criterion are: (i) ‘recoloring’: change of the color (amphiphilicity) pattern of the cylinders surface, (ii) ‘translation’: translational movement of the RC without changing the relative position and the angular orientation of segments within the cylinder, (iii) ‘rotation’: rotation of one part of a cylinder along a randomly selected bond with a random angle; (iv) ‘reptation’: removal of a terminal segment of a cylinder and regenerating a new segment at its opposite end, (v) ‘reconnection’: breakage of a pair of RCs into two pieces (each) and exchange of pieces, (vi) ‘regrowth’: removal and regrowth of connected strings of segments within a RC, while keeping remaining parts of the RC unchanged (in close analogy to the ‘CONROT’ [53] move). These moves obviously share the feature that they leave all model constraints intact. At the same time, every state of the available configuration space can be potentially reached. Moves (ii)–(vi) are applied in MC with equal frequency, these moves are always associated with ‘recoloring’ moves.

Attempted moves successively chosen from the types (i)–(vi) will be accepted with the probability

$$\min(1, e^{-\beta \Delta U}),$$

where $\Delta U$ is the change of total energy during the attempted move, and $\beta = 1/k_B T$ denotes inverse temperature. Accordingly, the move is unconditionally accepted if a state with lower energy has been reached, $\Delta U < 0$, otherwise an additional random number is needed to implement a probabilistic decision about acceptance. If not accepted, the move is rejected. Averages are sampled from all accepted states. We next describe in detail these moves, which are devised to leave systems parameters, such as volume, number of particles, number of faces per segment $N_f$, coverage $c$, bond length $L$, cylinder radius $R$, chain lengths $N_l$, and bond angles $\theta$ unchanged.
### Implementation details

(i) Recoloring. This move changes the color pattern of a RC surface without changing its conformation. The algorithm is simply to exchange the colors of two randomly picked particles $j_1$ and $j_2$ from the same RC segment $i$ of cylinder $\alpha$:

$$c_{i,j_1}^\alpha \rightarrow c_{i,j_2}^\alpha.$$  

(ii) Translation. The whole RC $\alpha$ is displaced by a random vector $\Delta r$:

$$\forall i \; r_i^\alpha \rightarrow r_i^\alpha + \Delta r,$$

which implies $\forall i,j \; r_{i,j}^\alpha = r_{i,j}^\alpha + \Delta r$ according to (3.3).

(iii) Rotation. A randomly selected bond vector $u_k^\alpha$ serves as a rotation axis. Segments of RC $\alpha$ on one side (randomly picked) of this bond are rotated around this axis with a random angle $t$. The rotation is actually coded by applying a rotation matrix $D$ to the set $\{i\}$, containing either all $i > k$ or all $i < k$, as follows:

$$\forall i \in \{i\} \; u_i^\alpha \rightarrow D \cdot u_i^\alpha,$$

with rotation matrix

$$D = I + (1 - \cos t) S \cdot S - (\sin t) S,$$

where $I$ denotes the unity matrix, $\det(D) = 1$, and the components $S_{\mu\nu}$ of the matrix $S$ read, with the usual orthonormal cartesian basis vectors $e_{1,2,3}$: $S_{\mu\nu} = (e_\mu \times u)_{\nu}$, where $u$ is the rotation axis. Equations (3.3), (3.13) imply $\forall i \in \{i\} \forall j \; r_i^\alpha = r_k^\alpha + D \cdot (r_i^\alpha - r_k^\alpha)$, and corresponding changes to the updated $v_i^\alpha$, $w_i^\alpha$, and eventually also the location of the anchoring point $r_1^\alpha$ upon re-evaluation due to (3.13), using the definitions from the previous section.

(iv) Reptation. One new segment is generated at a (randomly selected) end of a RC, while the segment at its opposite end is removed. This corresponds to a shifting of labels plus the creation of a new segment which fulfills the angle constraint. The new vector $v$ is created by rotation – via $D$ from (3.14) with $t = \theta$ – of the cross product between a random unit vector and the terminal segment vector. The color of the new segment is taken over from the annihilated segment.

(v) Reconnection. Each of two randomly selected cylinders is cut into two pieces at a randomly selected contour position. The pieces are reconnected to form two new cylinders of original length. This move is done in two steps: firstly the exchanged pieces are rigidly displaced, secondly the pieces are rotated to achieve the correct bond angle.
(vi) Regrowth. This move renews the conformation of a string of successive segments without affecting the remaining parts of the RC, and while keeping the bond angle constraints intact (geometric bridge). Such a move poses, in general, a highly nonlinear problem to be solved only numerically. This is seen by considering a string of \( n \) segments (unit vectors labelled \( \mathbf{u}_1 \) to \( \mathbf{u}_n \) for convenience), they are a part of a longer chain, and connected to the remaining part of the chain via \( \mathbf{u}_0 \) and \( \mathbf{u}_{n+1} \). The newly generated conformation (\( n \) vectors) has to satisfy the following \( n + 4 \) equations for \( n \) unit vectors (i.e., \( 2n \) angles)

\[
\begin{align*}
\sum_{i=1}^{n} \mathbf{u}_i &= \mathbf{r}_{n+1} - \mathbf{r}_1 \\
\mathbf{u}_i \cdot \mathbf{u}_{i+1} &= \cos \theta \quad (i = 0, \ldots, n)
\end{align*}
\]

(3.15)

This move had been achieved, for certain \( n \), by the \textit{concerted rotation} (‘CONROT’) algorithm [53], which numerically solves the above equations. More precisely, when a good initial guess is available for the coordinates, these equations (3.15) may readily be solved in an iterative Newton-Raphson procedure. The Newton-Raphson solution procedure has the advantage of being very simply implemented, but suffers from the difficulty that all solutions cannot be readily determined. More recently, a symmetric solution of the geometric bridge has been carried out. A large number of elementary Monte Carlo moves for branched and chain molecules have been presented by Theodorou and coworkers, see, for example [54]. We next present both an alternative to the CONROT move, and an extension to arbitrary \( n \), which does not require solving any nonlinear equation and no initial guesses; our so-called \textit{phonebook} move.

### 3.4.2 Phonebook move

The phonebook move is an computationally efficient solution of the geometric bridge (3.15) for arbitrary \( n \), at the cost of the computer main memory. Most importantly, the memory and CPU cost do not depend on the number \( n \) of segments involved during the move. In other words, the (phonebook) solution of the nonlinear equation does not depend on the number of variables, which is very atypical not only for a set of nonlinear equations, but also for linear equations, for which algorithms usually scale at least linearly with \( n \). ‘Recoloring’ moves are applied to the newly generated chain segments.

The phonebook move is implemented as follows: A data base is firstly generated, which stores the relative orientation between \( \mathbf{u}_1 \) and \( \mathbf{u}_n \) (2 angles) as well as the end-to-end distance of the string \( \mathbf{r}_{n+1} - \mathbf{r}_1 \) (3 values) for each of a large number of random conformations with \( n \) segments, where \( n \) is arbitrarily chosen. The database requires a minimum (still large) amount of memory by indexing a whole conformation (for later re-construction) by its seed value (innovation #1). For each \( n \) we have a separate phonebook which has seldomly to
be updated or refreshed, but can be saved and loaded at the beginning of a simulation (and
this overhead becomes irrelevant for the sufficiently long simulation runs we have in mind).
Every time new segments are generated the old segments conformations are saved in the
phonebook, they can be used later as new entries. A phonebook is a five-dimensional (event-
tually sparse) discrete grid (2 angles, 3 coordinates) carrying the seed value (single integer)
for the conformation which belongs to these 5 values. The book allows us to find a string
satisfying (3.15) immediately, without going through the book, because it is – at the same
time – a lookup-table on a grid (reason for efficiency), where the grid resolution can be ad-
justed according to the maximum available memory (here memory replaces CPU time). A
single rotation matrix is required to rotate a suitable entry, which fulfills the requirements
(3.15) into the right position (an essential memory-saving step). Renewing a conformation
is therefore done by simply looking up solutions from the data base rather than solving a
nonlinear equation. The book is re-filled once it becomes too lightly filled to be used effi-
ciently (innovation #2). In order to keep bond lengths exactly at unit length during this step,
we allow for tiny deviations from the prescribed bond angle in a single connected pair of the
new segments. These ‘errors’, however, do not accumulate during the simulation because
the regrowth move ensures that incorrect bond angles heal in the course of time (innovative
feature).

3.4.3 Application of moves

All the above moves (ii)-(vi) can be attempted in a random fashion, since results seem to
not depend on the order or relative weight of attempts, as we have verified. There is one
exception. The recoloring (i) move should be performed immediately after each of the other
(ii)-(vi) moves in order to address the fact that the majority of particles (backbone plus sur-
face particles) is part of the RC surface.

3.4.4 Deterministic recoloring, Janus vector

In order to improve the efficiency further, we have (optionally) completely eliminated the
recoloring move (i) by a deterministic move which corresponds to applying the move (i)
infinitely often, at zero temperature, as will be described in the next paragraph. Even though
the MC does not have a physical time, the deterministic move can be considered as “realistic”
since equilibrium as regards to the motion of submolecular structures such as branches of a
dendron (on the microscopic scale) is reached considerably more rapidly than equilibrium
as regards to the motion of the whole dendronized polymer (cylindrical nano-object, the
3.5. _SAMPLING, OBSERVABLES, AND REFERENCE VALUES_

‘mesoscopic’ scale). Accordingly, we partially equilibrate the whole color state at each conformational state (“fast relaxation” of color variables).

Deterministic recoloring is done instantaneously, for all segments and all chains, as follows. We calculate the mean orientation $j^*$ of white colors for each segment, i.e., the set of so called Janus vectors $J_i^α$ which are identical with the set of $Ω_{i,j}^α$ unit vectors (3.4) with particular $0 \leq j^* \leq N_r$ values for each segment. We define the Janus vector for a site (which is a node $i$ on RC $α$) at position $r_i^α$ to be determined from the direction of a total effective force (denoted as $j$) if at least one interacting nonbonded neighbor exists (otherwise the Janus vector is left at random), and to be perpendicular to its segment vector $u_i^α$, more precisely, $J_i^α \equiv u_i^α \times (u_i^α \times j)$, subsequently normalized to have unit length. The vector $j$ is obtained as the mean vector of virtual forces $j = \langle Φ_1(s) \rangle s$ where $s$ stands for $r_i^α - r_j^β$, $s$ denotes the norm of $s$, and the average goes over all nonbonded pairs. The notation $Φ_n$, here for $n = 1$, had been introduced in (3.10), and involves the (same) cutoff distance.

The deterministic recoloring algorithm assumes a total phase separation at each segment (see also Sec. 3.5.3), and reduces the information carried by the RC to the one which inspired the Janus model [6]. We will discuss this point further in Sec. 3.7.

### 3.5 Sampling, observables, and reference values

Several observables $A$, to be specified in the following subsections, will be sampled via Monte Carlo (MC) simulation. The canonical, constant temperature ($β = 1/k_BT$) ensemble average $⟨A⟩$ of an observable $A(Γ)$ which is a function of positions and momenta, i.e. phase space coordinates $Γ = \{r^N, p^N\}$, is classically [31, 51, 48] expressed as

$$\langle A \rangle = \int dΓ A(Γ) e^{-βH(Γ)}/\int dΓ e^{-βH(Γ)},$$

(3.16)

and solely involves knowledge of the Hamiltonian $H(Γ)$ (total energy) of the system of interest. Since the Hamiltonian is the simple sum of kinetic ($K$) and potential ($U$) contributions, $H(Γ) = K(p^N) + U(r^N)$, and $K$ a quadratic function of momenta, the integration over momenta can be carried out analytically as long as $A$ does not depend on momenta. The MC method is employed to perform the integration over positions, that is to compute the average for $A(r^N)$, by Eq. 3.16 upon strictly replacing $H$ and $Γ$ by $U$ and $r^N$, respectively. With the probability distribution of states, $ρ(Γ) \equiv \exp(-βU)/\int \exp(-βU)dΓ$, the average of $A$ can be re-written as: $⟨A⟩ = \int ρA dΓ$, and since our MC algorithm realizes the canonical distribution, averages are easily estimated from $T$ realizations (MC trials) $A(τ)$ as

$$⟨A⟩ = \frac{1}{T} \sum_{τ=1}^{T} A(τ).$$

(3.17)
3.5.1 Helicity and pitch angles

If two cylinders intercoil with each other and form a double helix, the color pattern on the surfaces of both cylinders must also be helical. We hence formulate quantities ($\zeta$ and $\epsilon$) from the color patterning of individual cylinders, which, if used together as shown in Tab. 3.1, inform about the degree of helicity of the RC system. The two quantities are defined as follows. The center position of the $i$th segment of RC $\alpha$ is $q_\alpha^i = \frac{1}{2}(r_\alpha^{i+1} + r_\alpha^i)$. Hence unit vectors $e_\alpha^i$ characterizing the orientation of the centerline of the RCs are given by

$$e_\alpha^i = \frac{q_\alpha^{i+1} - q_\alpha^i}{|q_\alpha^{i+1} - q_\alpha^i|}.$$  (3.18)

To characterize the orientation of color patterning we consider the curve passing through all the (segment-wise) mass-centers of red particles. These mass-centers are denoted as $s_\alpha^i$ and calculated via

$$s_\alpha^i = \frac{1}{N_r} \sum_{j=1}^{N_r} c_{i,j}^\alpha r_{i,j}^\alpha,$$  (3.19)

because white colors are represented by $c_{i,j}^\alpha = 0$. The corresponding unit vectors are

$$f_\alpha^i = \frac{s_\alpha^{i+1} - s_\alpha^i}{|s_\alpha^{i+1} - s_\alpha^i|}, \quad z_\alpha^i \equiv e_\alpha^i \cdot f_\alpha^i.$$  (3.20)

In case of perfect helical conformations, the pitch angles $\gamma_\alpha^i \equiv \cos^{-1}(z_\alpha^i)$ between all corresponding unit vectors, also defined in (3.20), should be identical and independent of $i$, while the precise value and sign of $z_\alpha^i$ reflects the pitch angle and handiness of helix $\alpha$. The quantities $\zeta$ and $\epsilon$ are now defined to reflect a mean value and amount of fluctuation of these angles over the whole system:

$$\zeta \equiv \langle |z_\alpha^i| \rangle_{i\alpha},$$

$$\epsilon \equiv 4 \langle (|z_\alpha^i| - \zeta)^2 \rangle_{i\alpha},$$  (3.21a,b)

where the absolute value $|z_\alpha^i|$ is used to erase the information about handiness. These parameters are bound by definition to $0 \leq \zeta, \epsilon \leq 1$. For cylinders with undeformable intersections the maximum packing can be achieved with the helical conformation at pitch angle $\gamma = \pi/4$. Some illustrative comments about this statement have been swapped to App. 3.8. Hence in the ideal case, where two cylinders are perfectly packed at the minimum pitch angle, the corresponding helicity quantities $\zeta$ and $\epsilon$ should take the values of $1/\sqrt{2}$ and $0$, respectively. For totally separated cylinders, whose colors are randomly distributed, both quantities should vanish. Quite randomly packed cylinders possess small $\zeta$ and large $\epsilon$ values. Perfectly collateral cylinders are also characterized by vanishing $\zeta$ and $\epsilon$ values. A summary is given by Tab. 3.1.
3.5. SAMPLING, OBSERVABLES, AND REFERENCE VALUES

<table>
<thead>
<tr>
<th>conformation</th>
<th>$\zeta$</th>
<th>$\epsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>separated cylinders</td>
<td>$\ll 1$</td>
<td>none zero</td>
</tr>
<tr>
<td>parallel packed</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>randomly packed</td>
<td>$\ll 1$</td>
<td>none zero</td>
</tr>
<tr>
<td>perfect helix</td>
<td>$1/\sqrt{2}$</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 3.1: Interpretation of helicity quantities $\zeta$ and $\epsilon$ defined in (3.21).

3.5.2 Torsion angles

Another strategy towards characterizing the helicity of the RC is to re-consider the unit vectors $\mathbf{f}^\alpha_i$ from (3.20), they form a conceptual ‘chain’ (for each $\alpha$). These ‘chains’ should be helical if the cylinders self-assemble into double helices. For regular helical polymer chains, all the torsion angles should be identical. We therefore quantify the amount of helicity further by calculating the mean torsion angle and its variance. To this end we need to introduce yet another unit vector $\mathbf{n}^\alpha_i$ and the related torsion angles $\phi^\alpha_i$ via $\mathbf{n}^\alpha_i = \mathbf{f}^\alpha_i \times \mathbf{f}^\alpha_{i+1} / |\mathbf{f}^\alpha_i \times \mathbf{f}^\alpha_{i+1}|$, $\cos \phi^\alpha_i = \mathbf{n}^\alpha_i \cdot \mathbf{n}_{i+1}$. Torsion angles range from $-\pi$ to $\pi$ while the inverse cosine (arccos) function only returns the angles between 0 and $\pi$; we therefore calculate the correct torsion angles as follows: $\phi^\alpha_i = (\mathbf{f}^\alpha_{i+1} \cdot \mathbf{m}^\alpha_i) \arccos(\mathbf{n}^\alpha_i \cdot \mathbf{n}^\alpha_{i+1})$ with $\mathbf{m}^\alpha_i \equiv (\mathbf{n}^\alpha_i \times \mathbf{n}^\alpha_{i+1})/(|\mathbf{n}^\alpha_i \times \mathbf{n}^\alpha_{i+1}|)$. Similar to the helicity parameter $\zeta$ and $\epsilon$, the average and variance of the distribution of torsion angles is used to measure the helicity of the system. For a well helical intercoiled conformation, we expect a certain fixed value of $\langle \phi^\alpha_i \rangle$ and a very low variance.

3.5.3 Phase separation index

In order to quantify the amount of (color) phase separation on the surface of cylinders, in case the deterministic coloring method is inactive, we can analyze the distribution, and in particular, the anisotropy of orbital vectors $\Omega^\alpha_{i,j}$ for each segment, by defining (orientational) order parameters, while the maximum value of the order parameters depend on the number of red faces, or coverage $c$ simply, because at $c = 0$ and $c = 1$, any type of order parameter should vanish. Here, we introduce a phase separation index $S$ as follows. From the centers of mass of colored particles on each segment, already defined as $s^\alpha_i$ in (3.19), we calculate a dimensionless moment of inertia $S^\alpha_i$ of only the colored particles at segment $i$ of RC $\alpha$ as:

$$S^\alpha_i = \frac{1}{R^2 N^\text{red}_r} \sum_{j=1}^{N_r} c^\alpha_{i,j} (r^\alpha_{i,j} - s^\alpha_i)^2,$$

(3.22)
which receives the value \( S_\alpha^i = 1 \) for a fully colored segment, its maximum for equally distributed colors, and its minimum, to be denoted as \( S_{\text{min}} \), for fully clustered colors. During a process of phase separation, colored particles migrate to one side of the segment, so that the value of \( S_\alpha^i \) decreases. In order to have a single phase separation index \( S \) for the whole system, which takes the values 0 and 1 for the cases of randomly and perfectly phase separated color distributions, respectively, we apply the definition

\[
S \equiv \frac{1 - \langle S_\alpha^i \rangle}{1 - S_{\text{min}}},
\]

(3.23)

where \( \langle \ldots \rangle \) denotes an average over all segments and chains. Deterministic recoloring is characterized by \( S = 1 \), and \( S_{\text{min}} \) can be calculated as \( S_{\text{min}} = (R^2 N_{\text{red}}^{-1} \sum_{j=1}^{N_{\text{red}}} (r_{ij}^a - s_i^a)^2) \), which does neither depend on \( \alpha \) nor \( i \) and can essentially be rewritten as \( \sum_k e^{ik} \) with appropriate weights and bounds, which depend on \( c \) (3.6). For example, \( S_{\text{min}} \approx 1 - 3/\pi^2 \) and \( S_{\text{min}} \approx 1 - 15/(4\pi^2) \) for \( c = 1/2 \) and \( 1/3 \), respectively. For \( c > 1/3 \), \( S_{\text{min}} \) increases and asymptotically reaches \( S_{\text{min}} \rightarrow 1 \) for \( c \rightarrow 0 \).

3.5.4 End-to-end distance, radius of gyration

Two more quantities characterizing the RC, and the conformation of polymeric molecules in general, are the mean squared end-to-end distance \( \langle R_{ee}^2 \rangle \) and squared radius of gyration \( \langle R_{gyr}^2 \rangle \). They are defined as follows [47, 24, 25]:

\[
\langle R_{ee}^2 \rangle = \frac{1}{N_c} \sum_{\alpha=1}^{N_c} (r_1^a - r_{N_l+1}^a)^2,
\]

(3.24a)

\[
\langle R_{gyr}^2 \rangle = \frac{1}{N_c} \sum_{\alpha=1}^{N_c} \frac{1}{N_l+1} \sum_{i=1}^{N_l+1} (r_i^a - \bar{r}_a)^2,
\]

(3.24b)

where \( \bar{r}_a \) denotes the center of mass of RC \( \alpha \), viz. \( \bar{r}_a = \frac{1}{N_l+1} \sum_{i=1}^{N_l+1} r_i^a \). For the case of freely rotating RCs, these two quantities are exactly related to each other, cf. [47, 24]. Deviations from ideality are caused by the presence of steric and amphiphilic interactions, and can be used to define a persistence length of the RC. For the freely rotating RC, we can evaluate these quantities analytically, \( \langle R_{ee}^2 \rangle = N_l L^2 C_\infty \) with characteristic ratio \( C_\infty = (1 + \kappa)/(1 - \kappa) - (2\kappa[1 - \kappa N_l])/(N_l[1 - \kappa]^2) \), where \( \kappa = \cos \theta \) is the parameter of the RC model.

3.6 Results and Discussion

Figures 3.4–3.7 show results for a system with two RCs with 80 segments each, randomly placed in a periodic simulation box, large enough to clearly prevent any self-interactions and
3.6. RESULTS AND DISCUSSION

Figure 3.4: Helicity index $\zeta$, defined in Sec. 3.5.1, for a system of two RCs, vs. Metropolis MC step. In each MC step all moves (i)-(vi) described in Sec. 3.4 had been applied, including the probabilistic recoloring scheme, as further described in the text part. The dashed line marks the value $\zeta = 1/\sqrt{2}$ for a double helix at the minimum pitch angle, $\gamma = \pi/4$, cf. Tab. 3.1 and App. 3.8. System parameters: $N_c = 2$ (RCs), $N_l = 80$ (segments), $B/A = C/A = -1$, $p_A = p_B = p_C = 1$ (energy parameters), $N_r = 12$ (faces per segment), $c = 0.4$ (coverage), $k_B T/A = 0.7$ (temperature), $r_{cut} = R$ (amphiphilic cutoff distance), $\theta = 0.14$ (bond angle) and $R/L = 4$ (or alternatively, flexibility parameter $\xi = 0.0392$, defined in Eq. 3.25).

any finite size effects. Simulation parameters are given in the caption of Fig. 3.4. A single MC step involves all moves (ii)-(vi) described in Sec. 3.4, including the probabilistic recoloring scheme – move (i) – which is applied 200 times directly after each of the other moves, for the reasons discussed above. From the data we deduce, that the RCs tend to approach each other and form a double helical structure. The helicity index $\zeta$ overally increases from $\zeta \approx 0.3$ to about $\zeta \approx 1/\sqrt{2}$. At the same time the total potential energy $E$ decreases starting from zero, where RCs are not (yet) in contact. The temperature is apparently small enough to drive the system close to its energetically preferred state, cf. App. 3.8. Two more quantities introduced in Sec. 3.5 are the mean squared end-to-end distance $\langle R_{ee}^2 \rangle$ and phase separation index $S$, shown in Figs. 3.6 and 3.7, respectively. The phase separation index strongly correlates with the helicity index, supporting our expectations. For a freely rotating RC, we have, according to Sec. 3.5.4, and with $\theta = 0.14$ and $N_l = 80$: $\langle R_{ee}^2 \rangle / L^2 = 5006.37$. This value mostly exactly coincides with the value for this quantity at the beginning of the MC run; $\langle R_{ee}^2 \rangle$ decreases with MC time, reflecting the compactness of the double helical configuration. Concerning this quantity alone, the state after 1000 MC steps corresponds to the one
for a freely rotating RC at bending angle $\theta = 0.36$ to be compared with $\theta = 0.14$, which is the one actually realized (fixed once and forever via the start configuration). The huge discrepancy would hardly be achieved through fluctuations, and is just another hint towards the formation of a non-freely rotating conformation. All together, this first computer experiment demonstrates, that initially randomly placed RCs tend to form a double-helical configuration on a MC time scale of 1000 steps (for the given setting), and that we can conclude about the superstructure formation from the various scalar quantities defined in Sec. 3.5.

Next, we replace the probabilistic recoloring move by the deterministic one, otherwise keep all simulation parameters at their values. First of all, this replacement produces a speed-up of the simulation time per MC step by one order of magnitude. Most interestingly, the
3.6. RESULTS AND DISCUSSION

Figure 3.7: Phase separation index $S$ for the system presented in Fig. 3.4. Notice that this parameter is unity by construction for the deterministic recoloring mode, cf. Sec. 3.4.4.

results, except for the phase separation index which is unity by definition upon applying the deterministic move, remain quite unchanged and are therefore not shown. We could proceed showing results for the RC system upon variation of system parameters which can be obtained in a straightforward manner applying the Metropolis scheme, together with deterministic recoloring. By following the “dynamics” of the process we observe, that the Metropolis scheme, for our set of available MC moves, and independent of temperature and energy parameters, tends to only slowly visit states with a very small energy. This would not matter in the sense that we are going to extract ensemble averages, and because our set of moves ensure ergodicity, but we want to show the effect of replacing the Metropolis criterion by another one, the less famous Barker scheme, which also obeys detailed balance [55]. While the Metropolis scheme has a transition probability $p_{xx'} = \exp(-\beta \Delta E)$ for $\Delta E \geq 0$ and $p_{xx'} = 0$ otherwise for the transition from state $x$ to $x'$, the Barker scheme is defined by $p_{xx'} = \exp(-\beta \Delta E)/[1 + \exp(-\beta \Delta E)]$. Here $\Delta E$ denotes the energy difference between the initial and final states of the attempted MC move: $\Delta E = E(x') - E(x)$. As we can see from Figs. 3.8–3.11, the Barker criterion seems to offer both, advantages and disadvantages for our system in terms of efficiency and precision, respectively, and these properties depend on the chain length $N_l$ and coverage. For small chains with $N_l = 40$ segments, using the Barker scheme, the helicity index $\zeta$ reaches a large value after half of the MC steps required in a Metropolis scheme, but its variance does not decrease as quickly as for the Metropolis scheme. This is reflected by the energy shown in Fig. 3.9 which is relaxing faster upon applying the Metropolis scheme. For long chain, in contrary, the Barker scheme is more efficient, while simulation results for the helicity index are not affected by the choice of ac-
CHAPTER 3. RUBIK CYLINDER MODEL

Figure 3.8: Helicity index $\zeta$ defined in (3.21a). Both Metropolis and Barker MC results for two RCs with $N_l = 40$ segments each, at coverage $c = 40\%$. Remaining simulation parameters as for Fig. 3.4.

ceptance criterion. The reason for the Barker scheme to be efficient for long chains is routed in its property to not accept lower energy states ($\Delta E < 0$) with a 100% probability, as the Metropolis scheme does. There are several local minima, which are easily reached by the Metropolis scheme, but which make it improbable to realize a double helical superstructure over a large number of segments. That’s why the Barker scheme becomes efficient for long chains in terms of producing double helical structures as the ones shown in Fig. 3.12, for $N_l = 80$. Actually, this figure nicely supports the independently obtained results given in Fig. 3.17. With increasing coverage, the energy tends to increase, and the minimum pitch angle – which corresponds to the most ideal double helical structure, cf. App. 3.8 – is obtained at low coverage. The differences between Metropolis and Barker schemes are enhanced at coverage $c = 30\%$, as demonstrated in Figs. 3.13 and 3.14. Here, not only the energies are different during the first 100000 MC steps, but also the helicity indices. These features are supported by inspecting the snapshots given in Fig. 3.15. For the long chains studied for these figures, the Barker scheme tends to produce more ideal helices.

To summarize, we have clearly observed the formation of more or less ideal double helical structures, independent of the sampling scheme, at a large range of temperatures, bond angles, energy parameters as long as $B$ and $C$ are negative (repulsive interaction), the cutoff distance for the amphiphilic interaction is smaller or of the order of $R$, and for all chain lengths. A single RC, if long enough, would obviously tend to backfold if its rigidity does not prevent the self-association at given temperature and energy parameters to become a measurable event [56].
3.7 Conclusions

We have introduced the semiflexible RC model, given full implementation details, and derived a number of limiting values for quantities characterizing the conformation of RCs. The RC model is simple, and incorporates the principle of topological constraints induced by internal structure. In particular, charges are constrained to be conserved at each segment, which is one of the main properties ultimately influencing the properties of dendronized polymers. The RC model allows for the calculation of intermolecular energies and other observables from a quite detailed picture of dendronized polymers, which takes into account surface charges not only in an approximate fashion. The RC model therefore serves to motivate the potentials used in the Janus model [6, 21] for these polymers. Moreover, the deterministic recoloring move which we have introduced and compared with results for the probabilistic recoloring scheme, directly motivate the Janus vector, defined in Sec. 3.4.4, as the single vectorial degree of freedom to be added for each segment. This vector carries information about the orientation of charge distributions along the RC backbone. In the Janus chain model, this vector has also a length. In contrary to this model, the presented RC model carries surface charges explicitly, and the interaction between two RC segments is determined from $N_s(N_s - 1)$ distance vectors rather than a single distance vector plus two orientations. Insofar, while a Janus vector at a segment carries all information about location of charges, and the interaction between RCs can be calculated using only backbone coordinates and Janus vector orientation, the effective interaction between Janus vectors cannot be trivially deduced. This feature is routed in the fact that the RC model has a finite and important cutoff distance. If the cutoff distance were removed from the RC model, we could calculate effective interactions between Janus beads using a Taylor expansion, for example, or we could try to perform...
the integrations (for the limit $N_l \to \infty$ at constant $c$) analytically. There is, however, no analytic solution to this problem, and the RC model can actually be regarded as an efficient, and physically meaningful, discrete implementation of this problem. The RC model is the prototype of the Janus chain model, where interactions are inspired by the physical situation of interest, and it gives a qualitative impression, or even approximate expressions, for the interaction potentials for the more coarse-grained level of description. Without deterministic recoloring, it carries information far beyond the Janus chain model, and it is important to also mention here that we have found, that results for the RC model are essentially unaltered if we switch between deterministic and probabilistic recoloring schemes.

Nearly every computational study of any physical problem requires the development of clever, memory or CPU time-saving computational tricks; however, for one of these tricks to be mentioned in the abstract of these chapter, it should constitute a significant advance and be useful to a wide range of researchers. We believe that the presented “phonebook” move, described in Sec. 3.4.2, exhibits the required feature. It can be applied to any system containing linear polymers in order to relax a large amount of $n$ connected segments simultaneously, in a concerted fashion. Usually, small amounts ($n \in [2, 7]$ segments) are rotated simultaneously, and the related nonlinear equations had to be solved numerically. For the classical approaches, the complexity strongly increases with $n$. While small $n$ are the easiest to implement, they do not significantly alter the configuration, and vice versa. A large $n$ seriously modifies the conformation at the cost of computational resources. In dense and monodisperse polymeric systems, intramolecular conformational changes are of upper-
most importance, while for dilute polymers and polydisperse systems the phonebook move should not be the method of choice; there is a large number of alternate methods available [57, 58, 59, 54]. The phonebook move opens the possibility to find (and then operate at) an optimum $n$ as both the required memory and CPU time does not depend on $n$. It can be applied to the simulation of polymeric systems, not only in equilibrium, but also for situations where the segmental distribution function is anisotropic [32, 61], or subject to constraints (such as Lagrange parameters, cf. [62, 63]).

We have mentioned the connection between the RC model and the Janus chain model. There are several ways to modify the RC model. For example, the linear backbone could be replaced by a branched one. Intramolecular potentials could be added to account for charge-induced stiffness, effective hydrophobic or -philic interactions. The rules for color redistribution could be changed to allow for color transport along the backbone of the cylinder: In that case, however, we should not take over the label “Rubik” as one of the main characteristics of the RC model would have been released.

Figure 3.11: Energy vs. MC step. Same conditions as for Fig. 3.10.
Figure 3.12: Sample configurations from Barker MC, of two RCs with \( N_l = 80 \) at different coverages \( c \), taken at MC step 120000, cf. Figs. 3.10, 3.11, 3.13, and 3.14. We see the equilibrium pitch angle dependence on the charge coverage \( (c) \). Potential energies \( (E) \) are also reported. Compare with Fig. 3.17.

Figure 3.13: Same as Fig. 3.13, now with \( c = 30\% \). Snapshots for the configurations at MC step 80000 are shown in Fig. 3.15. For the Barker scheme the helicity index \( \zeta \) (3.21a) quickly approaches a value close to its maximum, \( \zeta = 1 \).
3.7. CONCLUSIONS

Figure 3.14: Same as Fig. 3.11, now with \( c = 30\% \). Snapshots for the configurations at MC step 80000 are shown in Fig. 3.15.

Figure 3.15: Sample conformations obtained during Metropolis (left) and Barker (right) sampling. Same model parameters as for the outermost left graph in Fig. 3.12 at charge coverage \( c = 30\% \). At \( c = 40\% \), the differences between Metropolis and Barker schemes become less pronounced.
Bibliography


3.8 Appendix

Geometric parameter space for the RC model

The geometry of the RC is defined by three parameters, viz. radius $R$, bond length $L$, and bond angle $\theta$. Its color state is parameterized by the coverage $c$. While $c$ is certainly an independent variable, results should not be affected qualitatively, if we just change the “zoom” factor of the whole experiment. To be precise, in the limit of small bond angles, where the freely rotating RC becomes a wormlike RC, the bond length a redundant parameter, and the bond angle can be replaced by a dimensionless persistence length, just the dimensionless ratio between radius and persistence (bond angle correlation) length should be regarded as an independent parameter whose value has an effect on the qualitative behavior of the RC system. As already mentioned in Sec. 3.3, this flexibility parameter we denote as $\xi$, with

$$\xi = R\theta^2/(2L),$$

which is the expression for $R/l_p$ in the limit of small bending angle, $\theta \to 0$. For larger bending angles, one has $l_p = -1/\ln \kappa$ with $\kappa = \cos \theta$ [24], and quantities like the dimensionless mean squared end-to-end distance can be expressed in terms of $\kappa$, as shown in Sec. 3.5.4.

In order to illustrate the meaning of the flexibility parameter, we explicitly show in Fig. 3.16 the surfaces $\Xi(\xi)$ of constant $\xi$ in the original, three-dimensional parameter space spanned by $R$, $L$, and $\theta$. All points belonging to the same surface $\Xi(\xi)$ represent systems which only differ from each other on the aspect of different zooming scales, or with different resolution of details. For example, at fixed radius $R$, moving the point $(R, L, \theta)$ along its surface $\Xi(\xi)$ will only change the detailness of a model (smoother or coarser central line and cylinder surface, see also [27, 28, 50, 66, 67, 68] for details on the coarsening of polymeric structures), but not the qualitative nature of the described cylinder. In order to investigate the effect of all three geometrical parameters of the RC model we therefore need to only study one arbitrarily selected point per surface.

Preferred energy states of RCs

For two semirigid cylindrical objects such as charged dendronized polymers, the double helical conformation is the energetically preferred configuration. In that case maximum contact is achieved which ensures that the hydrophobic sites (white faces, in the case of RCs) are fully in contact, and that the hydrophobic energy is minimized.

In order to see if the RC model exhibits this feature, and which type of helices (pitch angles, in particular) are preferably realized, we started several MC runs where double heli-
Figure 3.16: Equi-physics surfaces $\Xi(\xi)$ in the geometrical parameter space of the RC. The surface are labelled by the flexibility parameter $\xi$, and the surfaces are defined by $R = 2\xi L/\theta^2$, cf. App. 3.8.

Figure 3.17 presents the total potential energy vs. pitch angle of the double helices. It can be seen that a low pitch angle is energetically preferred at low and medium coverage of hydrophilic sites (charges), certainly caused by the high compactness which comes together with a small pitch angle. However, for larger coverages, the larger pitch angles seem to be energetically preferred. This effect if due to the electrostatic repulsion. These results are qualitatively unaffected by the precise choice of parameters of the RC model, as long as (i) the cutoff distance $r_{\text{cut}}$ does not exceed the diameter ($2R$) of a RC and (ii) the parameters $B$ and $C$ are positive; their absolute values are irrelevant.

**Minimum pitch angle for the RC**

As we know from the previous section, the compacted double-helical (self-assembled, in practise) configuration is the energetically most favored state for two semi-flexible RCs in contact. Helicities are measured by the pitch angle $\gamma$, cf Sec. 3.5.1. The smaller the pitch angle (the higher the helicity) the more efficient two RCs can contact. The extreme cases are: (i) zero helicity (pitch angle $\gamma = \pi/2$); two parallel, (weakly) contacting cylinders in contact, (ii) compacted double helical structure at the minimum possible pitch angle. In order to calculate this minimum angle analytically, we need to consider the steric demand of the RCs, as the intersections of (hard core) cylinders are assumed to be undeformable. We
Let us consider a circular intersection of a double helix. This intersection is perpendicular to the axis of this helix. We denote with $C_1$ and $C_2$ the cross points of the two cylinders (nos. 1 and 2) centerlines with this intersection. Now imagine moving along the centerline of cylinder no. 2, with an infinitesimal small distance to point $C_2'$. The vertical displacement we denote by $\delta z$, while $\delta a$ and $l$ denote the length of the projection of the vectors $C_2C_2'$ and $C_1C_2$, respectively, to this intersection. Hence the distance between the two points $C_1$ and $C_2'$, which should not be smaller than distance $C_1C_2$, obeys

$$
C_1C_2' = l^2 + \delta z^2 \geq l^2 + \delta a^2,
$$

(3.26)

such that

$$
\delta z^2 \geq \delta a^2,
$$

(3.27)

and $\delta z$ can be expressed in the following way, where $H = 2\pi R \tan(\gamma)$ is the pitch of the helix:

$$
\delta z = \frac{\delta \phi}{2\pi} H = \frac{\delta a}{2\pi R} H.
$$

(3.28)

Accordingly,

$$
\frac{\delta z}{\delta a} = \frac{H}{2\pi R} \geq 1,
$$

(3.29)

which implies $H \geq 2\pi R$, or equivalently, $\tan(\gamma) \geq 1$, or equivalently, $\gamma \geq \pi/4$. The minimum pitch angle $\gamma = \pi/4$ is reached for an ideally packed double helix. We see that infinite pitch, $H = \infty$, corresponds to $\gamma = \pi/2$. 

---

Figure 3.17: Total potential energy vs. pitch angle for the double helical intercoiled superstructure, for a number of coverages (of the hydrophobic sites). ($B = C = -A, p_{A-C} = 1$).
Chapter 4

The Emergence of The Janus Chain Model
Abstract

It is the purpose of this chapter to establish a bottom-up multiscale approach for dendronized polymers. Based on our understanding of the phenomenology of an atomistic model for this class of polymers we introduce a “Janus Chain” (JC) model, which adds a vectorial degree of freedom (Janus vector) – related to the sectorial amphiphilicity – to each segment of the linear backbone of a (classical) uncharged, semiflexible, multibead chain representation of a polymer. The JC features induced polymeric curvature and ultimately triggers complexation. JC parameters related to the topology and chemical details are obtained from the atomistic level. Available experimental observations including the formation of superstructures and double-helical conformations are well reproduced by the JC model. JC is efficiently solved via Brownian dynamics simulation, and can be seen as a member of a universality class which is one (two) levels above the atomistic denpol model. It therefore should allow to model not only dendronized polymers, but also structures belonging to the same class – exhibiting induced (or spontaneous) curvature – such as single stranded DNA and actin filaments.

4.1 Introduction

Dendronized polymers (DP) have recently been developed as novel macromolecules with unprecedented internal structure comprising a linear backbone to whose repeat units dendrons of varying generation are attached. Their applications span from single molecule chemistry all the way to surface patterning. Additionally, they allow for hierarchical structure formation both in solution and in bulk [7, 8, 3]. With their highly branched dendritic layer surrounding a linear backbone they have the highest level of structural complexity presently known for man-made polymers. The unusual structure of DPs and the potential impact they may have has attracted theoreticians to this class of polymers [4, 5]. The coexistence of different characteristic length scales, such as microscopic and mesoscopic scales, raises difficulties in modeling such complex polymers and their supramolecular properties [5, 7, 8]. It is unavoidable to employ multiscale models with different coarse-grained levels in the computational investigation of high-molecular weight polymeric systems containing charged components with complex internal structure.

1This chapter is adapted from: Y. Ding, et al., FROM ATOMISTIC SIMULATION TO THE DYNAMICS, STRUCTURE AND HELICAL NETWORK FORMATION OF DENDRONIZED POLYMERS: THE JANUS CHAIN MODEL. J.Chem.Phys. 127, 094904, (2007) with permission from AIP.
This chapter constructs a bridge between modeling levels and describes how the concept and physics of the JC model is motivated by insight from atomistic simulations of dendronized polymers. Because of its additional degrees of freedom compared to conventional linear polymer chain models, the JC model is intrinsically biaxial, and captures orientation and strength of sectorial amphiphilicity. It offers analogies with a one-dimensional version of the Helfrich Hamiltonian for membranes and modeling self-assembling structures [9, 10, 11]. Here, induced curvature will be essential. Each bead of the JC potentially carries a single Janus (unit) vector whose orientation is given by nonbonded interactions (including interaction between different chains and different segments of the same chain), and affects the local conformation of the polymeric backbone. The JC offers analogies with magnetic chain systems where a magnetic moment is attached to each of its segments [12, 13, 15, 16, 17, 14]. The Janus vector allows to widely capture peculiar intermolecular interactions which arise due to the complex internal structure of DP. The JC model carries its two main ingredients in its name: beads with two faces, a feature ascribed to the Roman god Janus, as well as connectivity and flexibility. Some complex polymers render their monomer units being Janus, due to the complexity of their side groups. Single stranded DNA offers JC features since it carries phosphate (hydrophilic) and nucleobase (hydrophobic) groups. As for many other bio- and synthetic macromolecules, their JC nature makes them potential candidates to participate in supramolecular assembly processes.

In order to develop and motivate the coarse-grained (JC) model and to estimate its parameters, we study, in Sec. 4.2, a rather atomistic model of DP for which experimental data are available. From the statistics of single DP chains with varying number of generations and molecular weights, and relevant quantities obtained from systems of interacting chains, we extract the information required on the JC level. Section 4.3 then contains the definition of the JC model, simulation details, as well as qualitative and quantitative results for supramolecular behavior, and comparisons to experiments.

### 4.2 Atomistic model for DP

The “atomistic” model of a single DP is a type of united-atom collection of connected “atoms” (mass centers), which fully captures the topology of a DP, i.e., of the regularly branched dendrons, and their connectivity through a polymeric backbone. The atomistic model is not based on quantum mechanical calculations, it neglects all chemical structures such as aromatic rings, amide connectivities of relevance for length scales below a typical distance between adjacent branching points; accordingly dihedral hindrances are not taken into account. All bond lengths between directly connected (united) atoms and all bond angles
between directly connected segments (edges), for which values are deduced from the experimentally available information, are constrained to prescribed values (but no preference of torsional angles). The network is then defined by specifying connectivity, particular bond lengths, bond angles for all nodes, as well as interaction potentials. In general, all segments belonging to the same node will be constrained to lie in a plane, and all angles between adjacent segments at the same nodes are chosen to be equal. A dimensionless, radially symmetric SHRAT [25, 19] – Lennard-Jones (LJ) type – potential \( U(r) = \frac{512}{27}(1 - r)(3 - 2r)^3, \quad r < 3/2, \quad U = 0 \) otherwise, implicitly carrying a characteristic length and energy – which we use to introduce dimensionless LJ units (LJu) – is active between all atoms to represent excluded volume interactions. As for charged dendrimers and polyelectrolytes [20, 21] we employ the Debye-Hückel potential, \( U_{\text{DH}} = k_B T l_B \exp(-\lambda r)/r \), with Bjerrum length \( l_B \) to approximate the repulsive Coulombic interactions. Under salt-free conditions, which we consider here, the screening parameter, \( \lambda \), is set to be zero. Moreover it is known [22] that the DP conformation, for \( G \geq 2 \), is not sensitive to salt but is determined by the bulkiness of the dendrons.

4.2.1 Architecture

Specifically, we are going to simulate a vinyl-type DP (cf. Fig. 2 of Ref. [3]). The backbone of this DP with \( 2M \) atoms carrying \( M \) repeat units (dendrons), is (a main) part of the network: a linear, freely rotating zig-zag chain with fixed bond length \( b_0 (= 1.54 \, \text{Å} = 0.82 \, \text{LJu}, \text{i.e.,} \, 1 \, \text{LJu} = 187 \, \text{pm}) \), and made from two types of alternating beads: those \( M \) being connected with a \( G \)th generation dendron (thus possessing three-fold connectivity), and those \( M \) “neighbors” which are just part of the linear chain (bond angle 109°28').

Each dendron is a generation tree with 3-fold connectivity at branching points, and linear connectivity along the freely jointed chain (branch) between each pair of branching points. The first branching point (atom b1 in Fig. 4.2.1), is three beads away from the backbone, and, at the same time the bifurcation point introducing the first generation. Every branch between bifurcation points is a linear chain with 5 beads, and fully characterized by the above values for bond lengths and angles. The five beads represent six monomers \([-\text{O}(\text{CH}_2)_3\text{NHCO}-]\) because one of the monomers carries a NH-CO group, restricting its rotational degrees of freedom. Inset of Fig. 4.2.1 depicts the topology of a DP with only a single generation, denoted as G1. The detailed comparison with the exact chemical structure [3] gives rise to the chosen mapping, which explicitly contained the occupied volume by the united atoms; the LJu had been specified above. Beside excluded volume interaction, there are important electrostatic interactions. According to the chemistry of DP, the terminal beads at each den-
4.2. ATOMISTIC MODEL FOR DP

Figure 4.1: Sample snapshot of a stretched part of a G3 DP during atomistic simulation. Color coding: backbone (blue), segments attached to branching points (green), attached to atoms carrying charges (red), otherwise (yellow). Inset: Topology of a G1 vinyl-type DP. Explicitly shown is only a single repeat unit (dendron) which is attached to the polymeric backbone of the DP (with $M$ repeat units). All relevant lengths and angles defining the geometry of the atomistic model are given in the text part.

...dron are hydrophilic and positively charged (ammonium), while the rest (roughly 90% of all beads independent on the number of generations) are hydrophobic and neutral. The single DP carries a net charge, (trifluoride acetic acid) counterions would rarely interpenetrate the DP due to their large size and have been neglected for the results to be presented, see also Sec. 4.2.5. We take the Bjerrum length $l_B$ as for room temperature and pure water [24, 25], which is $l_B = 3.74$ LJU. The atomistic model for a single chain therefore has no adjustable parameters, and we can vary the number of generations and dendrons (and the number of DPs, and concentration in a multi-chain system).

4.2.2 Goals

The atomistically detailed model should (i) quantify geometrical parameters such as lateral size, flexibility and “surface” charge coverage, and their dependence on molecular weight and number of generations; (ii) qualitatively approve the concept of sectorial phase separation, which renders DP a sectorial amphiphile. In order to resolve these “local” properties of the DP, the amphiphilic interaction, which is supposed to be the main driving force for the...
supramolecular self-assembly of DPs, and solvent quality, must not be taken into account.

In order to develop the JC model which will allow us to study large-scale dynamics, phase and scaling behaviors, we need to explore the effect of these parameters on potentially slow, mesoscopic variables which allow to capture the properties of single chains, and effect of nonbonded interactions. The united-atom model is limited to this level because a single DP with $G$ generations and $M$ dendrons has $M_0 = 4M + 11M \sum_{g=1}^{G} 2^{g-1} \approx 2^{G+3.5}M$ atoms, including $M_0^+ = 2^G M \approx M_0/11$ charged terminal beads, or one million atoms for only two “realistic” DPs with $M = 1500$ and $G = 5$. It may be worthwhile to mention, that basic packing considerations, practically valid for any given temperature, predict an upper limit for the number of generations. The ratio between occupied volume of the DP and its maximum available, cylindrical volume (stretched backbone, stretched dendrons), behaves as $\propto 2^G/G^2$ and has a minimum at around $G = 2$, and reaches unity at $G \approx 10$. Large (small) internal density should obviously be compatible with large (small) stiffness and large (small) lateral sizes, at least in the absence of electrostatic interactions, cf. below. Packing effects would be more pronounced, and the maximum number of generations and computational costs much reduced if we were studying a more abstract model without atoms along branches, but we are interested in calculating parameters for a coarse-grained model for a specific DP, and we made sure that interpenetration effects, charge distributions cannot be reproduced in sufficient detail using such an oversimplified model.

### 4.2.3 Solving the model

This model was solved using standard Metropolis Monte Carlo (MC), where the basic MC move is the rotation of all material (chemically, directly or indirectly) connected to either the head or tail of a randomly selected segment about the axis (a unit vector $\mathbf{u}$) of this selected segment at an arbitrary angle ($\vartheta$). This operation requires three equally distributed random numbers (segment number, head or tail, angle), involves a single rotation matrix [26] to be multiplied with the coordinates of all the affected atoms, leaves all constraints for angles and bond lengths intact (even at branching points, because a rotation does not alter any of the constrained angles). The approach is clearly ergodic because all states can be reached, if an isolated single chain is studied. For a multichain system we have to add a simple chain’s center of mass displacement move. The energy penalty due to (constrained) overlap between adjacent beads, even though unrealistic, and easily corrected, plays no role during the MC, because only energy differences enter the algorithm. The effective volume of an atom is then approximately 2.4 LJu, if the atom radius is taken as 1 LJu, i.e. more than 40% below the value for a sphere of the same radius.
4.2.4 Coarse-graining and effective diameter

An effective diameter is obtained by measuring the fraction of void volume $\phi_i$ within a sphere of diameter $d_s$ around each bead $i$. A “surface” bead has $\phi_i > \frac{1}{2} + \langle \phi \rangle$, with $\langle \phi \rangle$ the average void fraction for backbone beads. A useful $d_s$ is comparable in size with the diameter of the DP and not much larger than it. For the measurements reported here, $d_s = 10$ (LJu) for both G3 and G4 DPs (with $M = 100$ repeat units). By slowly increasing $d_s$ we can reach a point, $d^*_s$, where all beads are considered to be on “surface”. If we imagine the DP undertaking a cylindrical overall shape, its effective diameter is $d_{\text{eff}} = (1 - 2^{-2/3})^{1/2}d^*_s$, which essentially follows from the fact that a cylinder fitting exactly into hollow sphere occupies half of the sphere’s volume. The so obtained values for $d_{\text{eff}}$ reported in Tab. 4.1 well coincide with experimentally reported values [3]. The mean squared distance of (all) beads to the centerline of the cylindrical, homogeneously filled, “tube” is $\frac{1}{8}d_{\text{eff}, d}^2$. This value is further used to calibrate our contour smoothing procedure, whose application is essential to bridge between micro- and mesosopic levels because the large steric congestion of dendrons does not allow the fully extended all-trans zig-zag conformation for the backbone. The simple procedure, as described in Ref. [27, 28, 25] for linear polymers, generates a smooth centerline (coordinates $c_{i=1,M}$) of a DP with $M$ repeat units, i.e., of the center of mass coordinates $r_{i=1,M}$ of the individual dendrons. A mean squared distance from all beads to this centerline is determined as $N^{-1}\sum_{i=1}^{N}\min_{j=1}^{M}(r_i - c_j)^2$, and the smoothing parameter is calibrated such that these two distances coincide.

4.2.5 Results and insights from atomistic model

To resolve the effect of number of generations on the persistence length, globular shape, and charge distribution, we investigated systems of isolated DPs with 3 to 4 generations, 100 to 500 dendrons, cf. Tab. 4.1. We extensively investigate DPs with 3 and 4 generations, because those DPs can be considered to be cylindrical objects with reasonable densities. G2 DPs are too loose to be dense cylinders, because the average void, $\langle \phi \rangle \approx 0.5$. On the other hand, G5 DPs are believed to be very dense, and have not yet been successfully synthesized except for one case [29]. The ratio between the effective radius and the persistence length (Tab. 4.1) characterizes the flexibility of DPs and will be used on the JC level. Further, single G3 and G4 DPs with 50 repeat units were arbitrarily shaped into “∪” conformation in order to resolve the interplay between charge migration and the shape (bending) of the DP. Density profiles, plotted in Figs. 4.2.5b-c, are obtained by moving a “scanning sphere” with radius 4 LJu (shown in Fig. 4.2.5a) across the centerline of the “∪” turn, and counting the number of positively charged ($A^+$) and all particles ($A$) inside the scanning sphere separately. The
Table 4.1: Number of atoms $M_0$, and repeat units $M$ (dendrons), mean-squared end-to-end distance $\langle R_{ee}^2 \rangle$ of the DP, contour length $L$ of its centerline, lateral diameter $d_{\text{eff}}$, corresponding JC repulsion diameter $d_{\text{rep}} \equiv d_{\text{eff}}/2^{1/6}$, persistence length $l_p$, as well as results from charge distribution measurements: charged fraction of (all) surface beads $S_{\pm}$, overall fraction $S_0$ of surface beads, the coverage $\phi_0 \equiv M_0^{-1} S_\pm /(M_0 S_0)$ of charges on the DP surface, for the atomistic model at temperature $T = 1$ LJu. All dimensional quantities given in reduced units, cf. last column. The persistence length $l_p$ is determined from the centerline (itself obtained using the method described in the text part) using the analytical result [24, 25, 12] for the mean squared end-to-end distance $\langle R_e^2 \rangle$ of a semiflexible chain, $\langle R_e^2 \rangle = 2l_p L - 2l_p^2 [1 - \exp(-L/l_p)]$. The third table row clarifies the connection between atomistic and mesoscopic (JC) parameters. Each bead of a JC represents $M/N$ dendrons (and $M_0/N$ united atoms), $d_{\text{rep}} \text{LJu} = \text{JCu}$, $l_p/d_{\text{rep}} = \kappa/k_B T$ and so on, as further elaborated in the text part. According to this table, the G4 DP has a persistence length of $l_p = 635.6$ LJu = 118.9 nm.

<table>
<thead>
<tr>
<th></th>
<th>$M_0/M$</th>
<th>$\langle R_{ee}^2 \rangle/M$</th>
<th>$L/M$</th>
<th>$d_{\text{rep}}$</th>
<th>$l_p$</th>
<th>$l_p/d_{\text{rep}}$</th>
<th>$d_{\text{eff}}M/L$</th>
<th>$S_\pm$</th>
<th>$S_0$</th>
<th>$\phi_0$</th>
<th>$\langle \phi \rangle$</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>G3</td>
<td>81</td>
<td>148.1</td>
<td>0.652</td>
<td>18.0</td>
<td>274.2</td>
<td>15.3</td>
<td>31.0</td>
<td>2510</td>
<td>46%</td>
<td>7%</td>
<td>66%</td>
<td>27</td>
</tr>
<tr>
<td>G4</td>
<td>169</td>
<td>101.8</td>
<td>0.480</td>
<td>24.9</td>
<td>635.6</td>
<td>25.5</td>
<td>58.4</td>
<td>9870</td>
<td>60%</td>
<td>18%</td>
<td>31%</td>
<td>8.5</td>
</tr>
<tr>
<td>JC</td>
<td>1</td>
<td>$\kappa/k_B T$</td>
<td>$M/N$</td>
<td>$M_0/N$</td>
<td>$\phi_0$</td>
<td></td>
<td>$\langle \phi \rangle$</td>
<td>Unit</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$M_0/M$</th>
<th>$\langle R_{ee}^2 \rangle/M$</th>
<th>$L/M$</th>
<th>$d_{\text{rep}}$</th>
<th>$l_p$</th>
<th>$l_p/d_{\text{rep}}$</th>
<th>$d_{\text{eff}}M/L$</th>
<th>$S_\pm$</th>
<th>$S_0$</th>
<th>$\phi_0$</th>
<th>$\langle \phi \rangle$</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>G3</td>
<td>81</td>
<td>148.1</td>
<td>0.652</td>
<td>18.0</td>
<td>274.2</td>
<td>15.3</td>
<td>31.0</td>
<td>2510</td>
<td>46%</td>
<td>7%</td>
<td>66%</td>
<td>27</td>
</tr>
<tr>
<td>G4</td>
<td>169</td>
<td>101.8</td>
<td>0.480</td>
<td>24.9</td>
<td>635.6</td>
<td>25.5</td>
<td>58.4</td>
<td>9870</td>
<td>60%</td>
<td>18%</td>
<td>31%</td>
<td>8.5</td>
</tr>
<tr>
<td>JC</td>
<td>1</td>
<td>$\kappa/k_B T$</td>
<td>$M/N$</td>
<td>$M_0/N$</td>
<td>$\phi_0$</td>
<td></td>
<td>$\langle \phi \rangle$</td>
<td>Unit</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1: Number of atoms $M_0$, and repeat units $M$ (dendrons), mean-squared end-to-end distance $\langle R_{ee}^2 \rangle$ of the DP, contour length $L$ of its centerline, lateral diameter $d_{\text{eff}}$, corresponding JC repulsion diameter $d_{\text{rep}} \equiv d_{\text{eff}}/2^{1/6}$, persistence length $l_p$, as well as results from charge distribution measurements: charged fraction of (all) surface beads $S_{\pm}$, overall fraction $S_0$ of surface beads, the coverage $\phi_0 \equiv M_0^{-1} S_\pm /(M_0 S_0)$ of charges on the DP surface, for the atomistic model at temperature $T = 1$ LJu. All dimensional quantities given in reduced units, cf. last column. The persistence length $l_p$ is determined from the centerline (itself obtained using the method described in the text part) using the analytical result [24, 25, 12] for the mean squared end-to-end distance $\langle R_e^2 \rangle$ of a semiflexible chain, $\langle R_e^2 \rangle = 2l_p L - 2l_p^2 [1 - \exp(-L/l_p)]$. The third table row clarifies the connection between atomistic and mesoscopic (JC) parameters. Each bead of a JC represents $M/N$ dendrons (and $M_0/N$ united atoms), $d_{\text{rep}} \text{LJu} = \text{JCu}$, $l_p/d_{\text{rep}} = \kappa/k_B T$ and so on, as further elaborated in the text part. According to this table, the G4 DP has a persistence length of $l_p = 635.6$ LJu = 118.9 nm.
profiles reveal asymmetries. At the point of bending, the density of neutral particles is higher in the inner side of the curve, and the charges tend to migrate to the outer side. This can be described as sectorial phase separation, where charged and neutral particles separate along the sectorial direction of cylindrical objects. A consequence of such a process – which is actually enhanced in the presence of explicit counterions – is the difference of surface property along the sectorial direction, which renders cylinder-like DPs sectorial amphiphiles. From the density profiles of two contacting G3 DPs, cf. Fig. 4.2.5c, a kind of phase separation is clearly observed, as for the bending experiments. The contact–induced phase separation is observed also for G4 DPs and qualitatively unaffected by the mutual shapes of the two contacting chains. To summarize, we observe a contact induced phase separation, whose magnitude is controlled by bending. The correlation mainly originates from the different volume occupations of charged and neutral particles. Together with the geometrical parameters abstracted from the atomistic model, we are in the position to motivate the more coarse grained JC model.
Figure 4.2: a) Schematic drawing of the $\subset\subset$-configuration of two DP’s and the scanning sphere used to calculate profiles. b) Density profiles for all and charged beads, respectively for bent third generation dendronized polymers (G3 DP). c) Density profile and charge distribution of two contacting, $\cup$-shaped G3 DPs (chains 1 and 2) in $\subset\subset$-configuration. Charges migrate to the outer side of the contact region, neutral atoms to the inner side.
4.3 Janus chain model

The JC model neglects chemical details of the DP but captures its physical properties: contact induced phase separation and interplay between phase separation and bending. Correspondingly, the contact induced phase separation generates a neutral surface in the (inner side of the) region of close contact, leading to an effective hydrophobic (attractive) force between contacting DPs (includes backfolding). The above processes give rise to a self-stimulating, self-amplifying mechanism for the formation of helically inter-winded DP super-structures (thus render them as active systems), provided the system parameters exceed certain thresholds to be discussed below. The JC model for self-assembling DPs is based on the classical dynamical multi-bead FENE chain model \[12, 30, 25\] supplemented with LJ interactions, bending interactions, and an attractive part of the LJ potential which is parameterized by an effective solvent quality. It reduces to several known models for particular choices of its parameters.

4.3.1 Classical ingredients

A main ingredient of the JC model is the classical FENE (+LJ) model which consists of a multiple disconnected off-lattice path \((N\) nodes for each of the \(N_p\) subpaths) of LJ particles (“beads”) at each node interacting via \(U^{\text{LJ}}(r) = U^{\text{LJ}}(r; \chi) = \chi U^{\text{LJ}}(r)\) for \(r < r_{\text{WCA}}\) and \(U^{\text{LJ}}(r; \chi) = \chi U^{\text{LJ}}(r)\) for \(r_{\text{WCA}} < r < r_{\text{JC}}\), respectively, where \(r_{\text{WCA}} = 2^{1/6}\) denotes the minimum of the LJ potential, which, if truncated at \(r_{\text{WCA}}\), is known as WCA potential, and \(r_{\text{JC}}\) denotes a cut-off distance after which the (suitable shifted) LJ potential is identical to zero. The parameter \(\chi\) is known to model the effect of solvent quality \[31\] and will be specified below. Adjacent beads along the subpaths (polymer contours) are connected chain-like through anharmonic springs with a FENE force law \(F^{\text{FENE}}(s) = -H(s)s,\) for all the \((N - 1)N_p\) connectors \(s_i^a \equiv s_{i+1}^a - s_i^a\). The non-Hookean spring coefficient \(H(s)\) is chosen strong enough to ensure uncrossability as \(H(s) = k[1 - (s/s_{\text{max}})^2]^{-1}\), with \(k = 30\) and \(s_{\text{max}} = 1.5\) (LJu) as in Ref. \[30, 32\] such that also the preferred bond length \(\langle s \rangle\) of the FENE+LJ chain is very close to unity. Semiflexibility of chains without induced curvature is usually introduced (FENE-B model) by adding bending forces which derive from a bending potential \(V^{\text{bend}} = -\kappa \sum_{\alpha} \sum_i \hat{s}_i^a \cdot \hat{s}_{i+1}^a\) where the hat denotes, throughout this chapter, a unit vector, \(\hat{s} \equiv s/|s| = s/s\) for any \(s\). Here, \(\kappa\) is the bending coefficient which gives rise to a persistence length \(l_p \propto \kappa\) of an isolated semiflexible chain, cf. Refs. \[24, 12\].
4.3.2 Induced curvature

The JC model extends the FENE-B model to a bending potential with induced curvature, where so called Janus vectors $J_\alpha^i = \hat{r}_{\alpha i}^{\alpha'}$ (see Fig. 4.3), assigned to each interior bead $i$ in chain $\alpha$ – themselves instantaneously determined from a configuration – trigger induced curvature, twist rigidity, and have an effect on both bonded and nonbonded interactions.

Unit Janus vectors $\hat{J}_\alpha^i$ for each interior bead represent the local orientation of the uncharged (hydrophobic) material and are calculated, for each bead $i$ on chain $\alpha$, from the coordinate of its spatially nearest nonbonded bead (denoted as bead $i'$ on chain $\alpha'$, nonbonded beads either have $\alpha' \neq \alpha$ or $r_{\alpha i i'}^{\alpha} > r_{JC}$), i.e., $J^\alpha_i = \hat{r}_{\alpha i}^{\alpha'}$ where $r_{\alpha ij}^{\alpha'} = r_{ij} - r_i^\alpha$ denotes the vector pointing from bead $i$ in chain $\alpha$ to bead $j$ in chain $\beta$. The Janus vectors $J^\alpha_i$ are considered as fast, relaxed variables, whose dependence on coordinates are neglected when deriving forces from the JC potential. The JC potential, which adds to the LJ and FENE potentials, $U_{LJ+FENE} = \sum_{i,\alpha} U_{FENE}(s_i^\alpha) + \sum_{j,\beta} U_{LJ}(r_{ij}^{\alpha\beta}; \chi_{ij}^{\alpha\beta})$, reads

$$U_{JC} = -\kappa \sum_{\alpha=1}^{N_p} \sum_{i=2}^{N-1} (J_i^\alpha - \hat{s}_{i-1}^\alpha + \hat{s}_i^\alpha)^2,$$

(4.1)

with bending coefficient $\kappa$, and the coefficients $\chi_{ij}^{\alpha\beta}$ won’t be simple constants, cf. below.

While the orientation of the Janus vector had been defined above, $\hat{J}_i^\alpha = \hat{r}_{i i'}^{\alpha}$, the missing length $J_i^\alpha$ of the Janus vector $\mathbf{J}_i^\alpha = J_i^\alpha \hat{J}_i^\alpha$ to be used in (4.1) captures the strength of induced curvature and varies between zero (for interatomic distances $r_{i i'}^{\alpha} \geq r_{JC}$, and for completely neutral or completely charged chains where the Janus vector and the effect of induced curvature are absent) and unity (for $r_{i i'}^{\alpha} \leq r_{WCA}$ and partially charged chains), such that $\tilde{J}_i^\alpha$, together with the corresponding two segment vectors, cf. (4.1), tend to virtually form a three-
fold, in-plane junction. Since results are quite insensitive to the precise functional form, we simply assume that $J_i^\alpha$ linearly varies with distance and bilinearly with the (constant) fraction $\phi_0 \in [0, 1]$ of the neutral surface to arrive at $J_i^\alpha = 4\phi_0(1-\phi_0)(r_{JC} - r_{i\alpha'}^\alpha)/(r_{JC} - r_{WCA})$.

### 4.3.3 Effective solvent quality

The JC model has a second integral part, a configuration dependent (and Janus vector induced) expression for the effective solvent quality, i.e., for the strength of attractive/repulsive interaction beyond distances $r \geq r_{WCA}$. It reads

$$\chi_{ij}^{\alpha\beta} = \chi_0 \pm \phi_0(1-\phi_0)|g_{ij}^{\alpha\beta} g_{ji}^{\beta\alpha}| \Delta \chi,$$

(4.2)

with $g_{ij}^{\alpha\beta} \equiv (\hat{J}_i^\alpha \cdot \hat{r}_{ij}^{\alpha\beta} - \cos \phi_0\pi)/(1 - \cos \phi_0\pi)$ characterizing the orientational part, which vanishes for neutral and fully charged DPs. The plus sign in (4.2) applies when $g_{ij}^{\alpha\beta}$ and $g_{ji}^{\beta\alpha}$ are both positive, otherwise the minus sign applies; $\chi_0$ characterizes the solvent quality of the (dendronized) polymer at infinite dilution [31], and the solvent quality parameter varies in the range $\chi_{ij}^{\alpha\beta} \in [\chi_0 - \Delta \chi, \chi_0 + \Delta \chi]$ by construction, where $\Delta \chi \geq 0$ parameterizes the maximum effective departure from $\chi_0$ due to internal charge redistribution. Notice, that $g_{ij}^{\alpha\beta} = 1$ for $\beta = \alpha'$ and $j = i'$. We see, that for the case of both neutral or fully charged chains, the JC model reduces to the classical FENE-B model (with solvent quality $\chi_0$, choose $\chi_0 = 1$ for the original FENE-B model), where Janus interactions are absent. For the case of hydrophilic chains, $\phi_0 \approx 1$, $\chi_0 > 0$, the plus sign in (4.2) applies, beads tend to attract each other since $\chi_{ij}^{\alpha\beta} > 0$, while the strength of attraction depends on the relative orientation of chains and Janus vectors. For the case of hydrophobic chains, $\phi_0 \approx 0$, $\chi_0 < 0$, the minus sign applies. For a chain for which each bead carries a Janus vector, the bending angle is close to $\pi/3$ everywhere along the chain, and the dimensionless persistence length (for the JC model, bond length $\langle s \rangle \approx 1$ LJu) can therefore be approximated by the analytic expression

$$l_p = -1/\log(1/2) \approx 1.4427 \text{ or, alternatively [24], } \langle R_{ee}^2 \rangle = 3(N-1) - 4(1 - 2^{1-N}).$$

The JC model features many-body interactions. Microscopic origins for (4.1) and (4.2) are the internal degrees of freedom of the atomistic chain, in particular, the distribution of its hydrophilic sites. As we have seen above from the experiments with $U$-shaped DPs, the charge distribution becomes asymmetric, charges tend to populate the “outer” surface, and causes a repulsion between a pair of two interwinded, agglomerated chains and a third chain, which can approach and break this pair only by surmounting an energy barrier, captured by (4.2).
4.3.4 Brownian dynamics simulation

We use Brownian dynamics to study the Langevin equation for the JC model, as described in detail in textbooks [26, 25]. The Langevin equation of motion for such systems composed of FENE-B chains have been studied extensively, cf. Ref. [12, 5]. The FENE potential can also be replaced by constraints for bond lengths, which lead to constraint and metric forces as described in Refs. [34, 26]. Connectivity and topology, rather than chemical details allow to capture the “universal” physical properties of polymers using these models [24, 35, 25, 36]. Because of the short-ranged nature of forces in the JC model, the equations of motions can be integrated with computational effort which is linear in the total number \( N_pN \) of particles. With increasing concentration intermolecular interactions become more relevant, induce curvature, and essentially affect the flexibility of chains confined in a network or in mutual contact.

4.3.5 JC model parameters

The JC model parameters \( N, \kappa, \phi_0 \) are deduced for a specific DP from the atomistic model, evaluated for single chains, where all terms carrying the Janus vectors vanish on the JC level, except for the case of backfolding chains. Additional parameters defining the JC system are the volume fraction \( \phi \) (or concentration) of beads, number of chains \( N_p \), bare and excess solvent qualities \( \chi_0 \) and \( \Delta \chi \), respectively, and temperature \( T \). In the first part of this chapter we simulated the vinyl-type DP system, for which the formation of a double helical network was observed [3], for G3 and G4 DPs. We selectively present results for the G4 JC model below. All geometrical parameters of the JC model are fixed with respect to the G4 DP system (for given molecular weight) as follows. From corresponding simulations of atomistic G4 DP, collected in Tab. 4.1, we obtain \( \kappa = l_p/d_{\text{eff}} = 22.7 \) at \( T = 1, N = L/d_{\text{eff}} = M/29.2 \), as well as surface coverage \( \phi_0 = 31\% \). The length (reference) unit for this JC model is \( \text{JCu} = d_{\text{rep}} = 24.9 \text{ LJu} \approx 4.7 \text{ nm} \), the mass of 169 united atoms (UA) equals the molar mass of a dendron [3], approximately 4000 g/mol, thus \( m_{\text{UA}} = 23.6 \text{ g/mol} \), the mass of a single JC bead (i.e., the reduced JCu for mass) is given by \( \text{JCu} = M_0m_{\text{UA}}/N = (M_0/M)m_{\text{UA}}M/N = 233 \text{ kg/mol} \). Knowing that the phase separation process results from electrostatic interactions between charged components, we set the cut-off distance for Janus interactions equal to the Bjerrum length, precisely, \( r_{\text{JC}} = (1 + l_B/d_{\text{eff}})d_{\text{eff}}/d_{\text{rep}} = 1.273 \text{ [JCu]} \). The volume fraction is estimated as \( \phi = 2.7\% \), according to the Cryo-TEM image in Ref. [3]. Temperature is kept at unity, as for conventional FENE-B simulations [24, 12], and the friction coefficient is (arbitrarily) set to unity, too, which, in turn, sets the reference time scale for the JC model depending on the viscous-
4.3. JANUS CHAIN MODEL

ity of the solvent. All JC parameters have been fixed concretely except the (dimensionless) solvent quality parameters $\chi_0$ and (positive) $\Delta \chi$, which characterize the amphiphilic interactions of DPs in solution.

4.3.6 Selected results, comparison with experiment

In order to explore the corresponding phase diagram we systematically vary the JC parameters $\chi_0$ and $\Delta \chi$. Figure 4.3.6 highlights the behaviors of DPs under different solvent quality conditions. Figure 4.5 is a simulated cryo TEM image of a double helical network JC system, which exhibits many similarities with the images taken from the real system, which we show for comparison. For the average pitch of helices we obtain approximately 2 JCu (9.4 nm), to be compared with 9.1 nm reported from experiments [3]. We observe, that the tendency of forming globular aggregates is increased by strengthening the inter-chain affinity which is achieved by decreasing the coverage $\phi_0$ of charged surface of the JC, and also by lowering the quality of the solvent, i.e., by increasing $\chi_0$. The presentation of a large amount of more quantitative results for the simple JC model must stay outside the scope of this chapter.

![Figure 4.4: Different complexations (phase diagram) obtained by varying the solvent quality parameters $\chi_0$ and $\Delta \chi$ in the JC model, while all remaining JC model parameters have been mapped from atomistic simulation for a vinyl-type G4 DP. As the value of absolute solvent quality $\chi_0$ increases (worsening solvent), the Janus Chains tends to aggregate irregularly. A sample snapshot for $(\chi_0, \Delta \chi) = (-2, 8)$ is provided in Fig. 4.5. Additional phases such as individual chains, or a nematic phase are expected [37] upon varying remaining parameters of the JC model: concentration, charge ratio, bending stiffness.](image)
CHAPTER 4. THE EMERGENCE OF THE JANUS CHAIN MODEL

Figure 4.5: Simulated “cryo TEM image” of a JC system corresponding to the G4 vinyl-type DP of Fig. 4.2.1, for which the experimental cryo TEM image [3] is shown for comparison in the upper part of this figure. The simulated network is formed by 15 identical JCs made of $N = 45$ Janus beads each, in a cubic (periodic) simulation cell of size $24 \text{ JCu}$, i.e., volume fraction $\phi \approx 2.5\%$, $\chi_0 = -2$ (good solvent), $\Delta \chi = 8$, cf. Fig. 4.3.6. Snapshot of the helical network taken at time $t = 25 \text{ JCu}$, having started from a random, non-assembled, system. The mesh size, approximately 30 nm, well coincides with the experimental value. Notice the scale-bar and amount of coarse graining compared with the underlying atomistic model, cf. Fig. 4.2.1. (Experimental image reprinted with permission from Wiley InterScience). Animated sequences of the JC model systems have been collected at: www.complexfluids.ethz.ch/JC
4.4 Conclusions

The Janus chain (JC) model has been developed in Sec. 4.3 based on insight from atomistic simulation (Sec. 4.2). The JC model allows to study dynamical and structural properties of a given, atomistically detailed, dendronized polymeric structure. It resolves structures on length scales huge compared with the size of a single dendron, and down to a fraction of the typical pitch size of a helical network. Reconstruction methods may be applied to calculate, for example, structure factors from the conformation of the JC by making use of the atomistic model also introduced here. The JC network bears analogies to a randomly cross-linked gel [8], for which expressions for the static structure factor had been derived using replica field theory [38]. We proposed and applied a mapping procedure which allows us to calculate all parameters of the JC model related to the topology and chemical details of the molecules of interest. To this end we used i) a contour smoothing method to extract the contour length and persistence length of the atomistic structures, ii) a scanning sphere to explore the internal distribution of charges and to quantify the effect of bending on the charge distribution and to motivate the existence of induced curvature term in the Hamiltonian. In this paper we did not arbitrarily vary model parameters but offered and applied a route to extract them from an underlying atomistically detailed simulation. The JC model and underlying concepts, induced curvature and effective solvent quality, have been approved qualitatively by the fact that sectorial amphiphilicity occurs when atomistic DPs are in close contact. Under such conditions, the hydrophilic (terminal) and hydrophobic (internal) beads tend to segregate, and to exhibit a sectorial amphiphilical phase separation. Solvent quality and the corresponding strength of repulsive/attractive forces had been added on the level of the JC model, for which – without induced curvature – we profit from known results on related coarse-grained models [10, 25, 11, 24]. Due to its efficiency, the JC model allows to study the formation of superstructures, helical chains for DPs. The JC model is easy to implement, introduces a new class of models by adding a vectorial degree of freedom to each segment of a conventional coarse-grained model for polymers. If the Janus vector is constructed from intrachain coordinates, the otherwise unchanged model allows to capture spontaneous curvature. This approach is certainly not restricted to the class of DPs. Established routes [10, 24, 26, 25, 8, 38, 25] can now be followed to explore the correlation between architecture and static and time-dependent material properties of the JC model.
CHAPTER 4. THE EMERGENCE OF THE JANUS CHAIN MODEL
Bibliography


[26] The rotation matrix is calculated from the angle $\vartheta$ and orientation of the selected segment with axis $u$ as $R = 1 + (1 - \cos \vartheta)S^2 + (\sin \vartheta)S$, with matrix $S$ whose components are $S_{\mu\nu} \equiv \epsilon_{\mu\nu\kappa}u_\kappa = (e_\nu \times u) \cdot e_\mu$, unity matrix $1$, total antisymmetric tensor $\epsilon$ of rank three, or orthonormal Euclidean base vectors $e_{1,2,3}$.


Chapter 5

Extensive Exploration of The Janus Chain Model
CHAPTER 5. EXTENSIVE EXPLORATION OF THE JANUS CHAIN MODEL

Abstract

We show that the recently proposed “Janus chain” model for dendronized polymers with minor modifications is able to describe the self-assembly of achiral (as well as chiral) molecules into multi–helical complexes. These include single-stranded, double-, triple-, quadruple-helical, and more general quaternary structures and bundles. The Janus vectors, which add vectorial degrees of freedom to a semiflexible polymer characterizing polymer chains on a classical coarse-grained level, serve to effectively capture three-body effects and induced spontaneous curvature in a plausible and efficient manner. We report, for the first time, about phase behavior of the Janus chain model and clarify the role of its parameters and range of applicability. In particular, we discuss the effect of solvent quality on the dynamics and microscopic mechanisms of helical network formation.

5.1 Introduction

Spontaneous formation of helical structures on the supramolecular level, such as observed in many physical and biophysical networks (collagen, dendronized polymers) and exploring the properties of such systems, are important areas of research. Approaches to their understanding and manipulation usually involve the self-assembly of chiral molecular building blocks [1, 2], where the “internal” asymmetry of the building blocks is explicitly used. The more challenging question is on how to obtain helix formation in systems which do not contain any chiral centers. Evidence of such kind has been reported from both experiment [3, 4] and theory [5, 6]. The mechanism of helical formation had been attributed to local symmetry breaking. Here we propose a universal model for investigating the formation and properties of helically interwound fibrous structures based on achiral systems. It is based on the so-called Janus chain model recently introduced by us, and originally designed for high generation dendronized polymers [7, 8] which consist of a number of dendrons attached to a linear polymeric backbone. The main idea behind the model is the observation that polarities are different for the chemical groups on the dendron termini and interior. This polarity difference allows to consider them as amphiphiles, which are known to give rise to a great variety of supramolecular assemblies [9, 10]. Unlike conventional amphiphiles such as block copolymers, structurally more complicated dendronized polymers potentially exhibit a dynamical amphiphilic pattern on their solvent contacting interface [11, 12, 6]. The anisotropy related to the local symmetry breaking of amphiphilic pattern [12, 6] is effectively captured

---

1This section is adapted from: Y. Ding, M. Kröger, Phase Behavior and Dynamics of Helically Wound Networks: Generalized Janus Chain Model. submitted manuscript to Macromol.
5.2. THE MODEL

Apart from dendronized polymers, many helical fibrous structures are formed via amphiphilic self-assembly in solution (mostly water). Examples include actin filaments, DNA double strands and collagen gels [13, 14, 15]. In this letter we stress the universality of the Janus chain model and explore its range of applicability, which is seen to go beyond the case of double-helical dendronized polymer structures.

There are a number of simple mesoparticle models which capture the characteristics of gel-forming systems, such as irreversible gelation via sticky particle models [16, 17] or more recent network formation models employing (i) two and three-body interactions between beads, giving rise to directional bonds, cf. [18, 19], and (ii) the simple elastic Lennard-Jones model exhibiting filamentous structures and a sol–gel transition [20, 21]. None of these models has yet addressed the existence of the polymeric backbone present in real physical gels. It is worthwhile to mention that a system with purely radial interaction is prone to undergo a phase separation [22] and is therefore not a good model for a gel-forming system.

5.2 The model

Classical, linear polymers are usually modelled on the coarse-grained level by anharmonic multibead chains, where each linear chain consists of a number $N$ of beads connected by anharmonic, finitely extendable nonlinear elastic (FENE) springs with bond vectors denoted as $\mathbf{b}_i$, bond length $b_i$. Semiflexibility is introduced by adding a bending Hamiltonian, excluded volume and solvent quality is taken into account by a radially symmetric Lennard-Jones potential between all beads [23, 25, 24].

The solvent is either modelled by explicit solvent particles, or by Brownian dynamics, with or without hydrodynamic interactions [26, 27, 28].

The Janus chain model builds on a system of semiflexible excluded volume multibead FENE chains. The potential energy fully characterizing this system is a superposition of FENE, bending, and Lennard-Jones potential, more formally: $U = \sum_i U_{\text{FENE}}(b_i) + U_{\text{bend}} + \sum_j U_{\text{LJ}}^{\chi_0}(r_{ij})$ with the classical ingredients [25, 24] $U_{\text{FENE}}(b) = -\frac{k}{2} b_0^2 \ln[1 - (b/b_{\text{max}})^2]$ and bending potential $U_{\text{bend}} = -\kappa \mathbf{b}_i \cdot \mathbf{b}_{i+1}$, where $r_{ij}$ is the distance vector between beads $i$ and $j$ and the hat denotes the corresponding unit vectors. The $U_{\text{LJ}}^{\chi_0}(r) = 4f(r)(r^{-12} - r^{-6} - r_c^{-12} + r_c^{-6})$ contribution equals the classical Lennard-Jones potential, modified by a prefactor which depends on distance: $f(r) = 1, f(r) = \chi_0$ and $f(r) = 0$ for $r \leq 2^{\frac{1}{6}}, r \in [2^{\frac{1}{6}}, r_c]$, and $r \geq r_c$, respectively. In these expressions, $b_{\text{max}}$ is the maximum extensibility of a bond, and $r_c$ a finite cutoff distance. The long range attractive part of the LJ potential is weighted by $\chi_0$, the solvent quality parameter [25, 24]. Throughout this manuscript, units are reduced.
to LJ units, denoted as JCu for the present purpose [29]. For all results to be presented in this letter we have used $b_{\text{max}} = 1.5$ and $\kappa = 25$, and typically studied systems composed of 15 chains with 45 beads each. If not otherwise mentioned, $r_c = 1.275$, $k = 30$ and the bead number density is 5%.

Next, we add degrees of freedom to the classical FENE chain by introducing so-called Janus unit vectors $\{\hat{J}_i\}$ to each of the beads. A Janus vector characterizes the local anisotropy of an otherwise spherically symmetric bead. For amphiphilic systems, the Janus vector is considered as a dipol pointing from the hydrophilic center to the hydrophobic center. Within the generalized Janus chain model to be introduced here, the Janus vector $\hat{J}_i$ of bead $i$ is induced by the surrounding of bead $i$, much in the spirit of embedded atom theories, where the induced quantity is usually a scalar (representing electron density) rather than a vector. To be specific, the orientation $\hat{J}_i$ is given by a weighted sum over normalized connectors

$$\hat{J}_i = \frac{\sum_j w(r_{ij})\hat{r}_{ij}}{\sum_j w(r_{ij})},$$

with a finite–range weight function $w(r)$, which we choose as $w(r) = r^{-\alpha} - r_c^{-\alpha}$ with exponent $\alpha$ and cutoff distance $r_c$. The limiting cases $\alpha = 0$ and $\alpha \to \infty$, at large $r_c$, correspond to mean field and nearest neighbor weighting, respectively. The idea behind this simple treatment is that the hydrophobic and hydrophilic components are redistributed due to binary interactions, and that the resulting pairs of mutually corresponding Janus vectors effectively prevent the further assembly (into aggregates). In the figures to be presented in this letter, such as Fig. 5.1, besides the polymeric contour and beads, the massless Janus vectors will be drawn in red.

In an amphiphilic system, solvent shows different qualities to different components. For the case of an aqueous system, water acts as good (bad) solvent with respect to the hydrophilic (hydrophobic) components. Our model parameter $\Delta \chi \geq 0$, explicitely defined in the Janus–Janus interaction potential (5.2) below, captures this difference on solvent qualities, while $\chi_0$ acts as the mid-point solvent quality between the two extremes, or equally, the mean solvent quality of the two components. The isotropic LJ potential containing $\chi_0$ quantifies the effect of solvent on nonlocal (global) interactions. The anisotropic part containing $\Delta \chi$ together with the Janus vectors describe the amphiphilic interaction $U_{J-J}$ between Janus vectors $\hat{J}_i$ and $\hat{J}_j$ at bead–bead distance $r_{ij}$:

$$U_{J-J}^{J-J} = \pm c(1 - c)\Delta \chi |g_{ij}g_{ji}|U_{0}^{\text{LJ}}(r_{ij}),$$

$$g_{ij} = (\hat{J}_i \cdot \hat{r}_{ij} - \cos c\pi)/(1 - \cos c\pi),$$
5.2. THE MODEL

where \( U_{0}^{LJ}(r) \) is the purely attractive part of the LJ potential, and coverage \( c \in [0, 1] \) is the fraction of hydrophobic components; it appears not only in the geometric factor \( g_{ij} \) which derives from considering two consoidally labelled objects (cf. Fig. 5.1a) in contact, but also in the interaction strength, which must be symmetric with respect to the transformation \( c \to 1 - c \) and which vanishes when either \( c = 0 \) or \( c = 1 \), i.e., in the case of a single component. The plus sign in (5.2a) applies when the geometric factors \( g_{ij} \) and \( g_{ji} \) are both positive, otherwise the minus sign is used. The asterisk in the subscript of \( U_{*}^{J-J} \) indicates that only nonbonded pairs of beads are subjected to this Janus potential. Since our Janus vectors are instantaneously defined by the surrounding configuration, we implicitly regard the corresponding dynamical process of amphiphilicity redistribution to be much faster than the configurational dynamics of the Janus chain, i.e., we implicitly make use of time-scale separation underlying the multiscale approach. The Janus vectors represent the induced chemical asymmetry of a Janus bead, which is potentially pronounced for “thick” macromolecules with bulky side-groups. The asymmetry, once realized, induces spontaneous curvature of the Janus chain, in accord with a bending Hamiltonian of the form \( H \propto (\hat{J} + \hat{b}_{i} - \hat{b}_{i-1})^{2} \) as proposed in [6]. In view of the part absorbed by the above bending potential (involving \( \kappa \)) this effect is captured by the following additional intramolecular interaction

\[
U_{i}^{J-J, \text{bend}} = -\kappa_{J} \hat{J}_{i} \cdot (\hat{b}_{i} - \hat{b}_{i-1}),
\]

(5.3)

where \( \kappa_{J} \) expresses the strength of bending induced by Janus vectors. For results explicitly shown in this paper \( \kappa_{J} = \kappa \). At this point one may ask, how to choose or obtain the parameters of the generalized Janus chain model which serve to study a real system. The parameters \( b_{0}, b_{\text{max}} \) and bending stiffness \( \kappa \) characterizing the structureless polymer (\( \Delta \chi = 0 \)) result from the architecture of the polymeric backbone, length of spacers between monomers, and, for dendronized polymers, the generation-sensitive persistence length and thickness of the polymer. The latter two quantities can be estimated using a simple Flory-type approach, as done for dendrimers in [30], where the spherical volume in the interaction term is replaced by a cylindrical one. While \( \chi_{0} \) has been related to solvent quality, the coverage \( c \) is determined by the given chemistry. More precisely, it should be related to the functionality of junctions inside dendronized polymer. While a bottle-brush with one or a few terminal monomers per strand will be characterized by \( c \ll 1 \), a copolymer brush or dendronized polymer may be well characterized by large values for \( 0 \ll c < 1 \). For the DPs with three-functional junctions of [7, 8, 6, 20, 21], for example, approximately half of the monomers are hydrophilic. There is a route to estimate these parameters using atomistic simulation [6]. By inspecting the energies, we see that \( \Delta \chi \) quantifies the strength of Janus-Janus interaction, and \( \alpha \) the range of interaction between Janus beads, while \( \kappa_{J} \) quantifies the tendency of the molecule
to bend, as a result of redistribution of hydrophobic and hydrophilic components. A large \( \kappa_J \gg \kappa \) will therefore favor the formation of compact helices while a weak \( \kappa_J \ll \kappa \) will allow for the formation of gently bent multiple-bundles. However, as this approach cannot be successfully followed for complex molecules like DP in view of today’s computational possibilities, and because it would limit our presentation to a particular system, we here present the reverse strategy, and investigate the effect of model parameters \( \chi_0, \Delta \chi \), and \( c \) on the phase behavior.

By now, the force \( \mathbf{F}_i = -\partial E/\partial \mathbf{r}_i \) on particle \( i \) is immediately obtained from the model energy \( E = U + U^{J-J} + U^{J-J,\text{bend}} \). We refrain from writing down the full expression, but mention the useful identity \( \partial \hat{b}_k/\partial \mathbf{r}_i = b_k^{-1}(\delta_{i,k+1} - \delta_{i,k})(1 - \hat{b}_k \hat{b}_k) \), where \( \delta \) is the Kronecker symbol, \( \mathbf{1} \) the unity matrix, and \( \hat{b}_k \hat{b}_k \) a dyadic product. We apply conventional Brownian dynamics as described in textbooks [31, 26, 24] to study the Langevin equation for the Janus chain model. The equations of motion for a number of these chains (according to given concentration) confined in a cubic simulation cell are solved subject to periodic boundary conditions.

### 5.3 Phase Diagram for Dendronized Polymers in Different Solvents

Before we turn to structural properties of the many chain system and the phase diagrams, let us inspect typical single chain conformations formed inside the system made of a large number of Janus chains.

Three of them are shown in Figs. 5.1b–d. All chains shown in this figure are found in a helical confirmation, which results from the Janus-Janus interaction. Fig. 5.1b shows a backfolding helical chain, which can be observed if the energy penalty for the kink (due to the stiffness \( \kappa \)) is smaller than the energy gain stemming from amphiphilic Janus-Janus interactions in the backfolded part of the chain. Similarly, linear chains can aggregate into rings when their length over stiffness ratio and concentration are both small enough to give the hydrophobic interaction the possibility to become active, and to create a metastable physical bond between chain ends, or more generally, between parts of the same chain. Rings are formed in a two-step process. After touching and the formation of temporary junctions, bending energy is lowered by lateral motion of junction towards the chain ends. At the same time, the chain tends to lower the Janus–Janus bending energy (5.3) which favors the formation of helical chains with constant pitch.

A 3D phase diagram obtained from 144 simulations upon varying coverage \( c \) and solvent
quality parameters $\chi_0$ and $\Delta \chi$ is presented in Fig. 5.2. Snapshots showing the formation of helical network are shown in Fig. 5.3. Iso-coverage surfaces at $c = 0.3$, 0.5 and 0.7 leave a good impression about the whole phase diagram of Janus chain systems in the $\Delta \chi - \chi_0$ plane. By analyzing the inter- and intramolecular pair correlation functions (example given in Fig. 5.5) and also visual inspection we have classified all states into three main regimes: individual non–collapsed chains (phase I), helical network (H), and individual ball–like globule (O). Three representative and accordingly labeled configurations characterizing the three main phases are shown on the right part of Fig. 5.4. Notice, that these results have been obtained for a limiting case of our model, the one where the Janus vectors are determined by nearest neighbor segments ($\alpha = \infty$). Under this original setting of the Janus chain model, we find that double–helical network formation is favored upon multi-helical agglomeration. The latter we do not observe for range of parameters used to study phase diagrams in Fig. 5.2.
Figure 5.1: (a) Schematic representation of two semiflexible Janus chains approaching each other. Shown are the Janus beads interacting via radially symmetric LJ potentials, the bending coefficient $\kappa$, the distance vector $r_{ij}$, two Janus vectors $\hat{J}_i$ and $\hat{J}_j$, and the fraction $c$ of hydrophobic surface, interacting via the Janus–Janus potential (5.2a). (b-d) Characteristic types of polymeric conformations observed inside the helical network, where Janus vectors derive from nearest neighbor interactions ($\alpha = \infty$) and are drawn in red. (b) backfolded single polymer (solvent quality: $\chi_0 = -8$, $\Delta \chi = 32$, $c = 0.7$). (c) ring formation of a single polymer ($-2, 32, 0.5$). (d) cross-link point involving three chains ($-4, 16, 0.7$).
Figure 5.2: Phase diagrams of JCs with coverages $c = 0.3$, 0.5 and 0.7, in the $\Delta \chi - \chi_0$ plane. Gray stands for individual chains (I); light purple stands for the intermediate state (L) between individual chains (I) and helical network (H); bright red for helical network (H); green for the intermediate state (D) between helical network (H) and ball-like aggregate (O, Blue).
Figure 5.3: Sample snapshots showing the formation of helical network, taken at times $t = 1, 20, 80, 200, \text{ and } 500$, for the case with solvent qualities $\chi_0 = -8, \Delta \chi = 16, \text{ coverage } c = 0.7, \text{ and nearest neighbor interactions } (\alpha = \infty)$.

Figure 5.4: Three representative configurations for: (O) globule (solvent quality $\chi_0 = +4, \Delta \chi = 8, \text{ coverage } c = 0.7$), (H) helical network ($-8, 16, 0.7$), and (I) individual chains ($-32, 1, 0.7$).

Figure 5.5: Semi-log plots of intra- and inter-chain pair correlation functions of JCs (here for coverage $c = 0.7$) are used to classify states into three representative phases (O, H, and I).
5.4 Generalized JC: More Complex Phases

However, as we will demonstrate next, the presented model is well capable of capturing the dynamics and physics of more complex phases. A pertinent example elucidating the range of applicability of the same model is offered next. We have varied the range of interaction of ionic interactions, qualitatively captured by the parameter $\alpha$ of our model. While $\alpha = \infty$ corresponds to a maximally short range interaction, smaller powers $\alpha$ allow parts of the chains to interact not only with their nearest neighbor but with surrounding material in second and higher order shells. The double-helical chain is essentially stable due to the short-range interaction chosen in the previous examples as it effectively repulses any additional chain approaching the formed cluster. By probing finite values for $\alpha$, we are able to observe multi-helical structures, as demonstrated in Fig. 5.6.

As is evident from these snapshots, there is a tendency to form ideal multi-helices in the absence of surrounding chains, i.e., at low concentrations. Upon increasing concentration, the systems again develop into network-like structures. At sufficiently large concentrations, a percolated network is observed.

![Figure 5.6](image)

**Figure 5.6:** Shown are examples for (a) double helix at coverage $c = 0.35$ and $\alpha = 12$, (b) triple ($c = 0.4$, $\alpha = 2$) (c) quadruple ($c = 0.8$, $\alpha = 2$), and (d) quintuple helix ($c = 0.9$, $\alpha = 2$). Remaining simulation parameters are $k = 15$, $\chi_0 = 1$, $\Delta\chi = 32$, and $r_c = 2$.

Modeling of the mechanical properties of filamentous protein networks [13] has attracted noticeable attention [32, 33, 34]. We have evidence, that the intrinsic stiffness of bundles increases with the order of helicity and that their effect on mesoscopic structures largely affects the material behavior, mesh size, and other properties of the samples. To this end we subjected the equilibrated Janus chain systems to shear and elongational deformation (or flow) by applying methods presented elsewhere [25, 24, 35] (results not shown).

The dynamics of the network formation process has been animated and is permanently available online at http://www.complexfluids.ethz.ch/JC, where we have summarized supporting information, movies, in particular.

To summarize, the generalized Janus chain model seems to contain sufficient, but a min-
imum amount of ingredients to capture the internal structure of single fibrils (multi-helical bundles). We are not aware of the existence of an alternate, competitive coarse-grained model of 3D semiflexible (bio)polymer networks. The time and length scales [29] reachable by the presented model, when combined with atomistic simulation of specific chemistry (as exemplified in [6] for the unmodified Janus chain model) in order to estimate model parameters, may help to study the dynamics of network formation and material properties efficiently.
Bibliography

BIBLIOGRAPHY


[29] URL: http://www.complexfluids.ethz.ch/units


Chapter 6

Conclusions and Outlook
In this thesis, a series of multiscaled models for amphiphilic dendronized polymers have been developed and studied. A mechanism involving induced dipole and symmetry breaking for amphiphilic denpol self-assembly has been proposed and implemented on the various levels. The simulation results are in good agreement with experimental data.

To this end, a systematic multiscale modeling procedure has been outlined and followed. The approach is based on a parameter feeding and demanding philosophy and served to pass materials information from the atomistic level to the supramolecular level.

The basic structural information of denpols such as persistence length, thickness, bulk density and surface charge coverage were achieved by modeling on atomistic level. Based on these information the coarse grained model, Janus Chain model, was developed. The supramolecular structures of amphiphilic denpols depending on solvent qualities and charge coverage were predicted and summarized in a phase diagram, which was achieved via extensive studies of Janus Chain model.

As a side product of this work a long-time maintainable code package for all the models has been developed. More generalized multiscaled models can be realized based on the package. The Janus Chain model is a simple and universal dynamical model, via some appropriately selected model parameters, networks with single-stranded, double-, triple- and quadruple-helical and more general quaternary structures can be achieved. It is convenient to conduct mechanical and rheological computational experiments on these different network systems using the package. The well designed data structure of the package also allows complicated statistic samplings, like the direct calculation of Poisson and friction matrices, and energy and entropy generators in the GENERIC framework. This should lead to multiscale models with rigorous thermodynamics consistency. While the mathematical framework has been well established, the main challenge of rigorous GENERIC based coarse graining is computational power, which are to be tackled by effective computing algorithms and state-of-art data structure designs.
Appendix A

Derivation of Bending and Torsion Forces

Here I present the derivations of bending and torsion forces in detail. These force calculations are used in the dynamic simulations of Janus chain model (chapter 4 and 5) and the fully atomistic model (introduced in section 2.2). The force calculation is always in Cartesian coordinate system.

Bending Force

Bending forces are calculated for each bond angles (three-atom groups). For a group with atoms #0, #1 and #2 the chemical bond vectors are:

\[ \mathbf{b}_0 = \mathbf{q}_1 - \mathbf{q}_0 \]
\[ \mathbf{b}_1 = \mathbf{q}_2 - \mathbf{q}_1 \]  (A.1)

The bending potential and bending force are defined as:

\[ U^{\text{bend}} = -\mathbf{b}_0 \cdot \mathbf{b}_1 \]  (A.2)

\[ \mathbf{F}^{\text{bend}}_i = -\nabla U^{\text{bend}} = \frac{\partial (\mathbf{b}_0 \cdot \mathbf{b}_1)}{\partial q_i}, \quad (i = 0, 1, 2) \]  (A.3)

The derivative of unit bond vector \( \mathbf{b}_i \) to the position of a bead \( q_k \) is a tensor \((i, k = 0, 1, 2)\):

\[ \frac{\partial \mathbf{b}_i}{\partial q_k} = \begin{pmatrix} \frac{\partial b_{i,1}}{\partial q_{k,1}} & \frac{\partial b_{i,2}}{\partial q_{k,1}} & \frac{\partial b_{i,3}}{\partial q_{k,1}} \\ \frac{\partial b_{i,1}}{\partial q_{k,2}} & \frac{\partial b_{i,2}}{\partial q_{k,2}} & \frac{\partial b_{i,3}}{\partial q_{k,2}} \\ \frac{\partial b_{i,1}}{\partial q_{k,3}} & \frac{\partial b_{i,2}}{\partial q_{k,3}} & \frac{\partial b_{i,3}}{\partial q_{k,3}} \end{pmatrix} \]  (A.4)

\(^1\)Prefactor is omitted for simplicity.
The elements of the tensor in eq.A.4 are:

\[
\frac{\partial \hat{b}_{ij}}{\partial q_{i+1,j'}} = \begin{cases} 
\frac{1}{b_i} - \frac{1}{b_i^2} (q_{i+1,j} - q_{i,j})^2, & j' = j = 1, 2, 3 \\
-\frac{1}{b_i^2} (q_{i+1,j} - q_{i,j}) (q_{i+1,j'} - q_{i,j'}), & j' \neq j = 1, 2, 3
\end{cases} \tag{A.5}
\]

Obviously there is the relationship:

\[
\frac{\partial \hat{b}_{ij}}{\partial q_{i,j'}} = -\frac{\partial \hat{b}_{ij}}{\partial q_{i+1,j'}} \tag{A.6}
\]

For clarity, eq.A.5 and eq.A.6 are written in tensorial form:

\[
\frac{\partial \hat{b}_i}{\partial q_{i+1}} = \frac{1}{b_i} I - \frac{1}{b_i} \begin{pmatrix} \hat{b}_{1,1} & \hat{b}_{1,2} & \hat{b}_{1,3} \\ \hat{b}_{2,1} & \hat{b}_{2,2} & \hat{b}_{2,3} \\ \hat{b}_{3,1} & \hat{b}_{3,2} & \hat{b}_{3,3} \end{pmatrix}, \tag{A.7}
\]

\[
\frac{\partial \hat{b}_{1,1}}{\partial q_{i+1,1,1}} = \frac{\partial}{\partial q_{i+1,1,1}} \frac{q_{i+1,1} - q_{i,1}}{b_i}
= \frac{1}{b_i} + (q_{i+1,1} - q_{i,1}) \frac{\partial}{\partial q_{i+1,1,1}} \frac{1}{b_i}
= \frac{1}{b_i} + (q_{i+1,1} - q_{i,1}) \left[ -\frac{1}{2b_i^2} \frac{\partial^2}{\partial q_{i+1,1,1}} \right]
= \frac{1}{b_i} + (q_{i+1,1} - q_{i,1}) \left[ -\frac{1}{2b_i^2} \frac{\partial (q_{i+1,1} - q_{i,1})^2}{\partial q_{i+1,1,1}} \right]
= \frac{1}{b_i} - \frac{1}{b_i^2} (q_{i+1,1} - q_{i,1})^2
\]

\[
\frac{\partial \hat{b}_{1,1}}{\partial q_{i+1,2}} = \frac{\partial}{\partial q_{i+1,2}} \frac{q_{i+1,1} - q_{i,1}}{b_i}
= (q_{i+1,1} - q_{i,1}) \frac{\partial}{\partial q_{i+1,2}} \frac{1}{b_i}
= (q_{i+1,1} - q_{i,1}) \left[ -\frac{1}{2b_i^2} \frac{\partial^2}{\partial q_{i+1,2}} \right]
= (q_{i+1,1} - q_{i,1}) \left[ -\frac{1}{2b_i^2} \frac{\partial (q_{i+1,2} - q_{i,2})^2}{\partial q_{i+1,2}} \right]
= -\frac{1}{b_i^2} (q_{i+1,1} - q_{i,1})(q_{i+1,2} - q_{i,2})
\]

\[
^3 I = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \theta = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}
\]
\[
\frac{\partial \hat{b}_i}{\partial q_k} = -\frac{1}{b_i} I + \frac{1}{b_i} \begin{pmatrix}
\hat{b}_{i,1}^2 & \hat{b}_{i,1}\hat{b}_{i,2} & \hat{b}_{i,1}\hat{b}_{i,3} \\
\hat{b}_{i,2}\hat{b}_{i,1} & \hat{b}_{i,2}^2 & \hat{b}_{i,2}\hat{b}_{i,3} \\
\hat{b}_{i,3}\hat{b}_{i,1} & \hat{b}_{i,3}\hat{b}_{i,2} & \hat{b}_{i,3}^2
\end{pmatrix},
\] (A.8)

For \( k \neq i \) and \( k \neq i + 1 \) the bond vector and position vector are not correlated so:

\[
\frac{\partial \hat{b}_i}{\partial q_k} = 0, \quad k \neq i \text{ and } k \neq i + 1
\] (A.9)

As a conclusion of eq.A.7, A.8, A.9:

\[
\frac{\partial \hat{b}_i}{\partial q_k} = \frac{1}{b_i} (\delta_{k,i+1} - \delta_{k,i}) (I - \hat{b}_i \hat{b}_i^T)
\] (A.10)

Inserting eq.A.10 into eq.A.3 gives the bending forces.

**Torsion Force**

Torsional forces are calculated for each dihedrals (four-atom groups). For a group with atoms \# 0, \# 1, \# 2 and \# 3, the chemical-bond vectors are:

\[
\begin{align*}
\mathbf{b}_0 &= \mathbf{q}_1 - \mathbf{q}_0 \\
\mathbf{b}_1 &= \mathbf{q}_2 - \mathbf{q}_1 \\
\mathbf{b}_2 &= \mathbf{q}_3 - \mathbf{q}_2
\end{align*}
\] (A.11)

The torsional angle \( \phi \) is defined as:

\[
\begin{align*}
\hat{n}_1 &= \frac{\mathbf{b}_0 \times \mathbf{b}_1}{|\mathbf{b}_0 \times \mathbf{b}_1|} \\
\hat{n}_2 &= \frac{\mathbf{b}_1 \times \mathbf{b}_2}{|\mathbf{b}_1 \times \mathbf{b}_2|} \\
\cos \phi &= \hat{n}_1 \cdot \hat{n}_2
\end{align*}
\] (A.12)

for save typing, the following notations are used:
\[
\hat{n}_1 = \frac{1}{|\mathbf{n}_1|}(A, B, C) \\
\hat{n}_2 = \frac{1}{|\mathbf{n}_2|}(D, E, F) \\
A = b_{0,z}b_{1,z} - b_{0,y}b_{1,y} \\
B = b_{0,z}b_{1,x} - b_{0,y}b_{1,z} \\
C = b_{0,z}b_{1,y} - b_{0,x}b_{1,x} \\
D = b_{1,x}b_{2,z} - b_{1,y}b_{2,y} \\
E = b_{1,x}b_{2,x} - b_{1,y}b_{2,z} \\
F = b_{1,x}b_{2,y} - b_{1,y}b_{2,x}
\] (A.13)

The torsional Hamiltonian of this dihedral is defined as:
\[
H^{\text{tor}} = \frac{V_n}{2} [1 + \cos(n\phi - \gamma)]
\] (A.14)

The torsional force on atoms are:
\[
f_{0}\text{tor} = \frac{\partial H}{\partial q_0} = \frac{\partial H}{\partial \phi} \frac{\partial \phi}{\partial q_0} = \frac{nV_n}{2\sin \phi} \sin(n\phi - \gamma) \frac{\partial \cos \phi}{\partial q_0}
\]
\[
f_{1}\text{tor} = \frac{\partial H}{\partial q_1} = \frac{\partial H}{\partial \phi} \frac{\partial \phi}{\partial q_1} = \frac{nV_n}{2\sin \phi} \sin(n\phi - \gamma) \frac{\partial \cos \phi}{\partial q_1}
\]
\[
f_{2}\text{tor} = \frac{\partial H}{\partial q_2} = \frac{\partial H}{\partial \phi} \frac{\partial \phi}{\partial q_2} = \frac{nV_n}{2\sin \phi} \sin(n\phi - \gamma) \frac{\partial \cos \phi}{\partial q_2}
\]
\[
f_{3}\text{tor} = \frac{\partial H}{\partial q_3} = \frac{\partial H}{\partial \phi} \frac{\partial \phi}{\partial q_3} = \frac{nV_n}{2\sin \phi} \sin(n\phi - \gamma) \frac{\partial \cos \phi}{\partial q_3}
\] (A.15)

The derived results are shown below:
\[
\frac{\partial \cos \phi}{\partial q_0} = \hat{n}_2 \cdot \left\{ -\frac{1}{|\mathbf{n}_1|^3} \begin{pmatrix}
Bb_{1,z} - Cb_{1,y} \\
-Ab_{1,z} + Cb_{1,x} \\
Ab_{1,y} - Bb_{1,x}
\end{pmatrix}
\begin{pmatrix}
A \\
B \\
C
\end{pmatrix}
+ \frac{1}{|\mathbf{n}_1|} \begin{pmatrix}
0 & b_{1,z} & -b_{1,y} \\
-b_{1,z} & 0 & b_{1,x} \\
b_{1,y} & -b_{1,x} & 0
\end{pmatrix}\right\}
\] (A.16)
\[
\frac{\partial \cos \phi}{\partial q_1} = \hat{n}_2 \cdot \left\{ -\frac{1}{|\mathbf{n}_1|^3} \begin{pmatrix}
-B(b_{0,z} + b_{1,z}) + C(b_{1,y} + b_{0,y}) \\
-A(b_{1,x} + b_{0,x}) - C(b_{0,x} + b_{1,x}) \\
-A(b_{0,y} + b_{1,y}) + B(b_{1,x} + b_{0,x})
\end{pmatrix}
\begin{pmatrix}
A \\
B \\
C
\end{pmatrix}
+ \frac{1}{|\mathbf{n}_1|} \begin{pmatrix}
0 & -b_{0,z} - b_{1,z} & b_{1,y} + b_{0,y} \\
-b_{1,x} + b_{0,z} & 0 & -b_{0,x} - b_{1,x} \\
-b_{0,y} - b_{1,y} & b_{1,x} + b_{0,x} & 0
\end{pmatrix}
\right\} (A.17)
\]

\[
\frac{\partial \cos \phi}{\partial q_2} = \hat{n}_1 \cdot \left\{ -\frac{1}{|\mathbf{n}_2|^3} \begin{pmatrix}
-E(b_{1,x} + b_{2,x}) + F(b_{2,y} + b_{1,y}) \\
-D(b_{2,z} + b_{1,z}) - F(b_{1,x} + b_{2,z}) \\
-D(b_{1,y} + b_{2,y}) + E(b_{2,x} + b_{1,x})
\end{pmatrix}
\begin{pmatrix}
D \\
E \\
F
\end{pmatrix}
+ \frac{1}{|\mathbf{n}_2|} \begin{pmatrix}
0 & b_{2,z} & -b_{2,y} \\
-b_{2,s} & 0 & b_{2,x} \\
b_{2,y} & -b_{2,x} & 0
\end{pmatrix}
\right\} (A.18)
\]

\[
\frac{\partial \cos \phi}{\partial q_3} = \hat{n}_1 \cdot \left\{ -\frac{1}{|\mathbf{n}_2|^3} \begin{pmatrix}
Eb_{1,z} - Fb_{1,y} \\
-Db_{1,z} + Fb_{1,x} \\
Db_{1,y} - Eb_{1,x}
\end{pmatrix}
\begin{pmatrix}
A \\
B \\
C
\end{pmatrix}
+ \frac{1}{|\mathbf{n}_2|} \begin{pmatrix}
0 & b_{1,z} & -b_{1,y} \\
-b_{1,x} & 0 & b_{1,x} \\
b_{1,y} & -b_{1,x} & 0
\end{pmatrix}
\right\} (A.19)
\]

Inserting eqA.16–A.19 into eqA.15 gives the torsion forces.
Curriculum Vitae

**Birthplace**

Born March 21, 1981 in Beijing, P.R. China.

**Education**

<table>
<thead>
<tr>
<th>Year Range</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2005.10 – 2008.10</td>
<td>PhD degree in Department of Materials, ETH Zürich. Working on computational polymer physics</td>
</tr>
<tr>
<td>2003.10 – 2005.8</td>
<td>Master of Science, Joint Polymer Science Master Program of Free University Berlin, Humboldt University Berlin, Technical University Berlin and University of Potsdam, Germany</td>
</tr>
<tr>
<td>1999.9 – 2003.7</td>
<td>Bachelor of Engineer, Department of Materials Science and Engineering, Beijing University of Chemical Technology, P.R. China</td>
</tr>
</tbody>
</table>

**Publications**

**APPENDIX A. DERIVATION OF BENDING AND TORSION FORCES**


**Ding, Y.; Kröger, M.:** Phase behavior and dynamics of a generalized Janus chain model for multi-helical complexes, *submitted to Macromolecules*

### PRESENTATIONS

<table>
<thead>
<tr>
<th>Year</th>
<th>Event Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2006.3</td>
<td>MiniSymposium of Dendronized Polymers, Berlin, Germany (oral presentation)</td>
</tr>
<tr>
<td>2006.9</td>
<td>Industry Day, Zürich, Switzerland (poster)</td>
</tr>
<tr>
<td>2007.8</td>
<td>The 5th International Dendrimer Symposium, Toulouse, France (poster)</td>
</tr>
<tr>
<td>2007.10</td>
<td>The 1st International Soft Matter Conference, Aachen, Germany (poster)</td>
</tr>
<tr>
<td>2008.7</td>
<td>Invited lecture from Universität für Bodenkultur Wien, Institut für Verfahrens- und Energietechnik, Vienna, Austria (oral presentation)</td>
</tr>
</tbody>
</table>
2008.8  Invited lecture from ETH Zürich, Department of Computer Science, CSE lab Zürich, Switzerland (oral presentation)

## Teaching Experience

<table>
<thead>
<tr>
<th>Semester</th>
<th>Course Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winter 2006</td>
<td>Practical laboratory course IV (ETH Zürich)</td>
</tr>
<tr>
<td>Summer 2007</td>
<td>Programming and Simulation techniques for Materials Science (ETH Zürich)</td>
</tr>
<tr>
<td>Winter 2007</td>
<td>Polymer Physics (ETH Zürich)</td>
</tr>
<tr>
<td>Summer 2008</td>
<td>Programming and Simulation techniques for Materials Science (ETH Zürich)</td>
</tr>
</tbody>
</table>