

# **Large Scale Brownian Dynamics Simulation of Dilute and Semidilute Polymeric Solutions**

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*This dissertation is dedicated to my wife Fatemeh, who has helped and encouraged me in the toughest moments of our life. I am deeply indebted to her for all of her unconditional devotions and very thankful for having her in my life.*

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*All human beings are in truth akin,  
All in creation share one origin.  
When fate allots a member pangs and pains,  
No ease for other members then remains.*  
-Sa'adi (Classis Persian Poet, 1210-1290 AD)

# Abstract

Excluded Volume (EV) and Hydrodynamic Interactions (HI) play a central role in static and dynamic properties of macromolecules in solution under equilibrium and nonequilibrium settings. The computational cost of incorporating HI in mesoscale Brownian dynamics (BD) simulations, particularly in the semidilute regime has motivated significant research aimed at development of high-fidelity and efficient techniques.

In this study, I have developed several algorithms for the mesoscale bead-spring representation of a macromolecular solution in dilute and semidilute regimes. The Krylov subspace method enables fast calculation of single chain dynamics with simulation time scaling of  $\mathcal{O}(N_b^2)$  [order  $N$  subscript b squared], where  $N_b$  is the number of beads in the chain. For simulations of multichain systems, a matrix-free approach is implemented which leads to  $\mathcal{O}(N \log N)$  scaling of simulation time, where  $N$  is the number of beads in the periodic box.

The Krylov and predictor-corrector schemes are used to study the behavior of dilute solutions of high molecular weight flexible macromolecules, and in particular Polystyrene (PS). The influence of HI and EV on the extensional hardening of the macromolecular solutions is considered. It is demonstrated that the combination of HI and successive fine-graining results in a remarkable prediction of rheological properties of solutions containing 1.95, 3.9, and 10.2 million molecular weight PS.

Further, a bead-spring model is developed to overcome the deficiencies of the current mesoscale worm-like chain models, i.e., to accurately describe the correlation along the backbone, segmental length, and the force-extension behavior even at the limit of 1 Kuhn

step per spring. The new model is utilized to examine the relaxation and stretching behavior of linear and comb DNA molecules. The BD computational results are in good agreement with single molecule visualization experiments in a cross-slot device (planar extensional flow).

For interacting multichain systems, the fidelity of the matrix-free algorithm is demonstrated by evaluating the asymptotic value of center of mass diffusivity at low concentrations and the radius of gyration as a function of number of beads in  $\theta$  [theta] and good solvent conditions. Our results are consistent with blob theory, which is commonly used to describe the concentration dependence of polymer solution properties.

# Table of Contents

|          |                                                          |           |
|----------|----------------------------------------------------------|-----------|
| <b>1</b> | <b>Introduction</b>                                      | <b>1</b>  |
| 1.1      | Polymer solutions . . . . .                              | 1         |
| 1.1.1    | Polymer flexibility . . . . .                            | 2         |
| 1.1.2    | Solvent quality . . . . .                                | 4         |
| 1.1.3    | Hydrodynamic interactions . . . . .                      | 6         |
| 1.1.4    | Concentration regimes . . . . .                          | 7         |
| 1.2      | Theoretical description of polymeric solutions . . . . . | 9         |
| 1.2.1    | Blob theory . . . . .                                    | 9         |
| 1.2.2    | Kinetic theory . . . . .                                 | 10        |
| 1.3      | Simulation methods . . . . .                             | 11        |
| 1.3.1    | Atomic-scale technique . . . . .                         | 11        |
| 1.3.2    | Mesoscale techniques . . . . .                           | 11        |
| 1.4      | Experimental characterization methods . . . . .          | 13        |
| <b>2</b> | <b>Methodology</b>                                       | <b>15</b> |
| 2.1      | Infinitely dilute solutions (isolated chains) . . . . .  | 15        |
| 2.1.1    | Introduction . . . . .                                   | 15        |
| 2.1.2    | Governing equations . . . . .                            | 17        |
| 2.1.3    | Numerical simulation steps . . . . .                     | 21        |
| 2.1.4    | Results and discussion . . . . .                         | 29        |
| 2.1.5    | Conclusions . . . . .                                    | 38        |

|          |                                                                              |           |
|----------|------------------------------------------------------------------------------|-----------|
| 2.2      | Semidilute solutions (interacting multichain systems)                        | 39        |
| 2.2.1    | Introduction                                                                 | 39        |
| 2.2.2    | Governing equations                                                          | 42        |
| 2.2.3    | Ewald representation of infinite sums                                        | 44        |
| 2.2.4    | SPME representation of infinite sums                                         | 46        |
| 2.2.5    | Optimal features of the matrix-free algorithm                                | 51        |
| 2.2.6    | Results and discussion                                                       | 53        |
| 2.2.7    | Conclusions                                                                  | 60        |
| <b>3</b> | <b>BDpack project</b>                                                        | <b>62</b> |
| <b>4</b> | <b>Extensional rheology of high <math>M_w</math> polystyrene</b>             | <b>66</b> |
| 4.1      | Introduction                                                                 | 66        |
| 4.2      | Parameter selection                                                          | 69        |
| 4.2.1    | Free-draining condition                                                      | 69        |
| 4.2.2    | Successive fine-graining (SFG) in the presence of HI and EV                  | 71        |
| 4.3      | Results and discussion                                                       | 73        |
| 4.3.1    | Effect of fine-graining                                                      | 73        |
| 4.3.2    | SFG in the presence of HI                                                    | 75        |
| 4.3.3    | Comparison of BD predictions using SFG in the presence of HI with experiment | 80        |
| 4.3.4    | Effect of EV with soft Gaussian potential                                    | 84        |
| 4.4      | Conclusions                                                                  | 88        |
| <b>5</b> | <b>Improved bead-spring model for semiflexible chains</b>                    | <b>90</b> |
| 5.1      | Introduction                                                                 | 90        |
| 5.2      | BD scheme for bead-spring models                                             | 91        |
| 5.3      | Mesoscopic bead-spring chain with bending potential                          | 92        |
| 5.4      | Determination of WLC-SK parameters                                           | 99        |
| 5.5      | Relaxation modes of WLC-SK                                                   | 101       |

|          |                                                                    |            |
|----------|--------------------------------------------------------------------|------------|
| 5.6      | Conclusions . . . . .                                              | 104        |
| <b>6</b> | <b>Dynamics of comb DNA molecules</b>                              | <b>105</b> |
| 6.1      | Introduction . . . . .                                             | 105        |
| 6.2      | Methodology . . . . .                                              | 107        |
| 6.3      | Result and discussions . . . . .                                   | 109        |
| 6.3.1    | Parameter Selection . . . . .                                      | 109        |
| 6.3.2    | Stretching dynamics: A comparison with experimental data . . . . . | 110        |
| 6.3.3    | Relaxation dynamics of comb DNA with long branches . . . . .       | 116        |
| 6.4      | Conclusions . . . . .                                              | 119        |
| <b>7</b> | <b>Conclusions</b>                                                 | <b>120</b> |
| <b>8</b> | <b>Future prospects</b>                                            | <b>123</b> |
| 8.1      | Physical problems . . . . .                                        | 123        |
| 8.1.1    | Universal transient stretching in planar shear flow . . . . .      | 123        |
| 8.1.2    | Concentration dependence of coil-stretch hysteresis . . . . .      | 123        |
| 8.2      | Further modeling options . . . . .                                 | 124        |
| 8.2.1    | Polydispersity . . . . .                                           | 124        |
| 8.2.2    | Polyelectrolyte solutions . . . . .                                | 124        |
| 8.2.3    | Complex polymer architectures . . . . .                            | 124        |
| 8.3      | Enhancing fidelity and computational power . . . . .               | 125        |
| 8.3.1    | Force-extension for flexible polymers in good solvent . . . . .    | 125        |
| 8.3.2    | Preventing chain crossings . . . . .                               | 125        |
| 8.3.3    | GPU enabled BDpack . . . . .                                       | 126        |
|          | <b>Bibliography</b>                                                | <b>127</b> |
|          | <b>Appendices</b>                                                  | <b>146</b> |
|          | <b>Appendix A Decomposition algorithms</b>                         | <b>147</b> |

|                                                                          |     |
|--------------------------------------------------------------------------|-----|
| Appendix B Further results on frequency of updating the diffusion tensor | 151 |
| Appendix C Calculation of bending force                                  | 153 |
| Appendix D Properties of real WLC                                        | 155 |
| Vita                                                                     | 157 |



# List of Tables

|     |                                                                                                                                                                                                                                                                                                                                                                                                                 |    |
|-----|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 2.1 | (%)Error in $\langle R_g^2 \rangle$ of polymers with 50 beads and $h^* = 0.15$ obtained with various time steps and update intervals relative to the results of Cholesky with unit block dimension and $dt = 1 \times 10^{-3}$ . . . . .                                                                                                                                                                        | 32 |
| 2.2 | (%)Error in transient fractional extension of molecules with $N_b = 50$ in planar extensional flow at $Wi = 1.5$ obtained with various time steps and update intervals relative to the results of Cholesky with unit block dimension and $dt = 1 \times 10^{-3}$ . . . . .                                                                                                                                      | 35 |
| 2.3 | Comparison of overall computational time in seconds required for simulating a chain with different number of beads under uniaxial extensional flow at $Wi = 10$ . A period of $\lambda_1^*$ along with $dt = 0.1$ and $\lambda_{RPY} = 1$ are considered for these tests. The amount of computational saving when the Cholesky is replaced by the Lanczos or the Chebyshev are reported in parenthesis. . . . . | 37 |
| 2.4 | The simulation parameters for multi-chain systems at different concentrations. $L$ is obtained using the analytical radius of gyration of polymers in $\theta$ -solvent. The simulation results of end-to-end distance and radius of gyration is given for both the Ewald and the matrix-free algorithms. . . . .                                                                                               | 56 |
| 2.5 | The parameters of the dilute and the semidilute multi-chain systems determined based on the diffusivity, the radius of gyration and the end-to-end distance of the chains in the infinitely dilute solution. . . . .                                                                                                                                                                                            | 58 |
| 3.1 | The numerical algorithms implemented in BDpack. . . . .                                                                                                                                                                                                                                                                                                                                                         | 63 |

|     |                                                                                                                                                                                                                                                                                                                                                                                          |     |
|-----|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 4.1 | Molecular parameters calculated by Li <i>et al.</i> [95] to simulate free-draining bead-spring chains with 19 segments. $\lambda_1^{\text{ext}}$ is the longest relaxation time obtained for macromolecules in $\theta$ -solvent and assuming $N_b, N_K \rightarrow \infty$ . $\lambda_1^{\text{exp}}$ is the experimental relaxation time measured by Gupta <i>et al.</i> [50]. . . . . | 70  |
| 4.2 | $h^*$ as a function of $N_b$ reported by Hsieh and Larson [58]. In this table, $\tilde{h}_K^*$ is calculated by fitting the values of $\tilde{h}^*$ vs. $N_b$ to a power function and extrapolating to $N_K + 1$ . . . . .                                                                                                                                                               | 80  |
| 6.1 | Molecular properties of DNA fragments which comprise the backbone and branches of comb macromolecules. . . . .                                                                                                                                                                                                                                                                           | 109 |
| B.1 | (%)Error in $\langle R_g^2 \rangle$ obtained with various time steps and update intervals relative to the results of Cholesky with unit block dimension and $dt = 8 \times 10^{-4}$ . . . . .                                                                                                                                                                                            | 151 |
| B.2 | (%)Error in transient fractional extension of molecules in planar extensional flow obtained with various time steps and update intervals relative to the results of Cholesky with unit block dimension and $dt = 8 \times 10^{-3}$ . . . . .                                                                                                                                             | 152 |

# List of Figures

|     |                                                                                                                                                                                                                                                                      |    |
|-----|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 1.1 | 6-12 Lennard-Jones potential. . . . .                                                                                                                                                                                                                                | 5  |
| 1.2 | The hydrodynamic interaction for multi-bead representation of a polymer chain in solution. $F$ is a point force applied to one of the beads and its effect is propagated through the solvent media (This figure is taken from the reference [31]). . . . .           | 6  |
| 1.3 | The physical interpretation of the overlap concentration $c^*$ (This figure is taken from the reference [24]). . . . .                                                                                                                                               | 8  |
| 1.4 | Different concentration regimes of a polymer solution depicted as a function of monomer concentration $c$ and excluded volume strength $z^*$ (This figure is taken from the reference [68]). . . . .                                                                 | 10 |
| 1.5 | Time and length scales of different simulation techniques for polymer solutions. . . . .                                                                                                                                                                             | 12 |
| 2.1 | Hydrodynamic center of resistance (hcr) and center of mass (cm) diffusion coefficient as a function of $N_b$ . . . . .                                                                                                                                               | 34 |
| 2.2 | Time for generating $\lambda_{\text{RPy}}$ Brownian vector with $E^{(m)} = E^{(L)} = 0.01$ . . . . .                                                                                                                                                                 | 36 |
| 2.3 | Spreading the force on the regular mesh, where the cells represent the grid points. The filled cell is the nearest point to the particle and the cells bounded by the dash-dot line are $p^3$ grid points at which the force on the particle is distributed. . . . . | 49 |

|     |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |    |
|-----|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 2.4 | (a) The mean-square-displacement and (b) the diffusivity of center of mass in $\theta$ -solvent obtained using both Ewald and matrix-free techniques. The filled and open symbols represent the results for the Ewald and the matrix-free algorithms, respectively. . . . .                                                                                                                                                                                                                                                         | 55 |
| 2.5 | The mean-square radius of gyration as a function of number of beads in a multi-chain system with $c/c^* = 0.1$ and 5. The error bars are smaller than the symbols. . . . .                                                                                                                                                                                                                                                                                                                                                          | 57 |
| 2.6 | Execution time per time step for Ewald as well as matrix-free algorithms. . .                                                                                                                                                                                                                                                                                                                                                                                                                                                       | 59 |
| 3.1 | This figure shows a schematic of polymer types (flexible and semiflexible) which can be translated into the bead-spring micromechanical model for BD simulations with fluctuating hydrodynamic interaction and excluded volume forces. BDpack can be used to simulate the properties of polymeric solutions in different flow conditions such as elongational dynamics of single and multichain systems in microfluidic devices, planar shear in rotational rheometry and uniaxial extension in filament stretching device. . . . . | 64 |
| 4.1 | Effect of $N_b$ on $Tr$ vs. $\epsilon$ of chains with (a) $M_w = 3.9 \times 10^6$ and (b) $M_w = 10.2 \times 10^6$ using BD simulations in the absence of HI and at $Wi = 12.58$ for the former and $Wi = 39.96$ for the latter. . . . .                                                                                                                                                                                                                                                                                            | 74 |
| 4.2 | Effect of $N_b$ on non-equilibrium segmental PDF for chains with $M_w = 10.2 \times 10^6$ in the absence of HI at $Wi = 39.96$ . . . . .                                                                                                                                                                                                                                                                                                                                                                                            | 76 |
| 4.3 | Extrapolation of $U_{\bar{\eta}R}^+$ obtained for different levels of fine-graining to the limit $N_b \rightarrow N_K + 1$ for $\tilde{h}_K^* = 0.05$ (circles), $\tilde{h}_K^* = 0.15$ (squares), and $\tilde{h}_K^* = 0.25$ (diamonds). The data shown have been obtained for $M_w = 10.2 \times 10^6$ and $Wi = 39.96$ at different strains. . . . .                                                                                                                                                                             | 77 |
| 4.4 | Effect of SFG in the presence of HI with various $\tilde{h}_K^*$ values at $Wi = 39.96$ on the results of $Tr$ vs. $\epsilon$ for $M_w = 10.2 \times 10^6$ . The error bars are approximately equal or smaller than the symbols. . . . .                                                                                                                                                                                                                                                                                            | 79 |

|      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |    |
|------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 4.5  | Effect of SFG in the presence of HI with $\tilde{h}_K^*$ chosen based on Table 4.2 at different $Wi$ on the results of $Tr$ vs. $\epsilon$ for (a) $M_w = 1.95 \times 10^6$ , (b) $M_w = 3.9 \times 10^6$ , and (c) $M_w = 10.2 \times 10^6$ . . . . .                                                                                                                                                                                                                                                                                              | 81 |
| 4.6  | The SFG procedure for $M_w = 1.95 \times 10^6$ [from (a) to (c)], $M_w = 3.9 \times 10^6$ [from (d) to (f)], and $M_w = 10.2 \times 10^6$ [from (g) to (i)] at different strains. The SFG data for $M_w = 1.95 \times 10^6$ are provided at $Wi = 1.32$ (circles), 2.4 (inverted triangles), 8 (squares), and 11.65 (diamonds), while the ones for $M_w = 3.9 \times 10^6$ are obtained at $Wi = 9.55$ (circles) and 35.2 (diamonds). The SFG data for $M_w = 10.2 \times 10^6$ are determined at $Wi = 19.9$ (circles) and 47.9 (squares). . . . . | 82 |
| 4.7  | Effect of SFG in the presence of HI with $\tilde{h}_K^*$ chosen based on Table 4.2 at different $Wi$ on the results of $Tr$ vs. $\epsilon$ for (a) $M_w = 10.2 \times 10^6$ and (b) $M_w = 20 \times 10^6$ . . . . .                                                                                                                                                                                                                                                                                                                                | 83 |
| 4.8  | Effect of soft Gaussian potential EV on equilibrium PDF of segmental connector vector and end-to-end distance of chains with $M_w = 20 \times 10^6$ and $N_b = 191$ . . . . .                                                                                                                                                                                                                                                                                                                                                                       | 85 |
| 4.9  | Effect of soft Gaussian EV on $Tr$ vs. $\epsilon$ of chains with $N_b = 191$ and different molecular weights in the absence of HI with and without inclusion of EV at $Wi = 11.2, 12.58, 39.96$ , and $29.74$ for $M_w = 1.95 \times 10^6, 3.9 \times 10^6, 10.2 \times 10^6$ , and $20 \times 10^6$ , respectively. . . . .                                                                                                                                                                                                                        | 86 |
| 4.10 | Effect of soft Gaussian EV on probability distribution at different strains for chains with $M_w = 20 \times 10^6$ and $N_b = 191$ at $Wi = 29.74$ in the absence of HI. . . . .                                                                                                                                                                                                                                                                                                                                                                    | 87 |
| 4.11 | Effect of soft Gaussian EV with $z = 1$ and $3$ on $Tr$ vs. $\epsilon$ of chains with $M_w = 20 \times 10^6$ . The SFG is employed in the presence of HI with and without EV. . . . .                                                                                                                                                                                                                                                                                                                                                               | 88 |
| 5.1  | Schematic representation of a constant force ensemble of bead-spring chains with bending rigidity. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                          | 93 |

|     |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |     |
|-----|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 5.2 | The comparison of the theoretical correlation of nearest neighbors for the real long WLC and WLC-SK models with the results of BD simulations. Inset: the comparison of the squared segmental connectivity vector for the real WLC and WLC-SK models with the results of Brownian dynamics. Note that the WLC-MS and WLC-UD models assume $\left\langle \hat{\mathbf{Q}}_{s,i} \cdot \hat{\mathbf{Q}}_{s,i+1} \right\rangle_{\text{eq}} = 0$ at all coarse-graining levels. . . . . | 94  |
| 5.3 | Average fractional extension as a function of the applied force for the WLC-MS and WLC-UD bead-spring models using BD simulations. The results are shown at different coarse-graining levels and compared with the real long WLC. . . . .                                                                                                                                                                                                                                           | 96  |
| 5.4 | The relative error $\epsilon_{\hat{Q}} = \frac{ \langle \hat{Q}_s^2 \rangle_{\text{eq}} - \langle \hat{Q}_{\text{wlc}}^2 \rangle_{\text{eq}} }{\langle \hat{Q}_{\text{wlc}}^2 \rangle_{\text{eq}}}$ of segmental dimension at equilibrium for WLC-UD and WLC-SK compared to the real WLC model as a function of the number of Kuhn steps per spring. Inset: squared segmental connectivity vector for the real WLC, WLC-UD, and WLC-SK models. . . . .                              | 98  |
| 5.5 | Spring force as a function of fractional extension at different coarse-graining level for the WLC-SK bead-spring model. . . . .                                                                                                                                                                                                                                                                                                                                                     | 100 |
| 5.6 | Average fractional extension as a function of the applied force for the WLC-SK bead-spring model compared via BD simulation. The results are shown at different coarse-graining levels and compared with the real long WLC. Inset: relative error associated with BD simulations using the WLC-SK model with respect to the results of the real long WLC. . . . .                                                                                                                   | 102 |
| 5.7 | The top 4 figures demonstrate the correlation function of four selected modes, namely, 2, 10, 16, and 20, as a function of normalized time $t/\lambda_R$ , where $\lambda_R$ is the Rouse relaxation time. The bottom figure shows the Relaxation time of all modes for the real WLC, WLC-UD, and WLC-SK models. . . . .                                                                                                                                                            | 103 |

|     |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |     |
|-----|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 6.1 | The normalized fractional extension of linear DNA with 40 kbp backbone as a function of Hencky strain at $Wi = 4$ . Different conformation types, i.e., kinked (dashed green), half dumbbell (dash-dot black), dumbbell (thin solid blue), folded (thick solid red), coiled (thick solid gray), and extended (dash-dot purple) are formed during the transient coil-stretch transition. The classification in this figure is based on the automatic conformation sorting algorithm [87, 157] at $\epsilon = 3$ . . . . . | 111 |
| 6.2 | $X/L_c$ as a function of Hencky strain for linear and comb DNA molecules with 2 and 9 branches at $Wi = 2$ . The snapshots of colored trajectories are shown in Figure 6.4. The insets demonstrate the probability of different end-to-end distance at the steady state condition, i.e., $\epsilon$ in the range of 13 to 18. . . . .                                                                                                                                                                                    | 112 |
| 6.3 | The probability of different end-to-end distance at the steady state condition and $\epsilon$ in the range of 13 to 18. . . . .                                                                                                                                                                                                                                                                                                                                                                                          | 113 |
| 6.4 | Snapshots of colored trajectories represented in Figure 6.2. Linear chain in part (a) shows a smooth unfolding behavior, while the presence of 2 (part (b)) and 9 (part (c)) branches, act as a constraint for the translation of the fold apex along the backbone. The numbers above the snapshots are the corresponding strain values. . . . .                                                                                                                                                                         | 114 |
| 6.5 | Steady state fractional extension as a function of $Wi$ for linear and comb DNA polymers. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                        | 115 |
| 6.6 | Relaxation dynamics of linear and comb polymers. The normalized fractions extension is depicted as a function of time normalized by the longest relaxation of the linear chain $\lambda_{1,lin}$ . . . . .                                                                                                                                                                                                                                                                                                               | 117 |
| 6.7 | Relaxation dynamics of linear and comb polymers in the absence of HI and EV. The normalized fractions extension is depicted as a function of time normalized by the longest relaxation of the linear chain $\lambda_{1,lin}$ . Configuration snapshots for the colored trajectories are given in the inset. . . . .                                                                                                                                                                                                      | 118 |

# Chapter 1

## Introduction

### 1.1 Polymer solutions

Polymeric liquids under deformation exhibit properties which are intermediate between those of classical viscous liquids and ideal elastic solids. Hence, these class of fluids are called *viscoelastic* materials, and their characterization, modeling and simulation are challenging due to the intricate coupling between the micro-structure and the imposed external field. For instance, unlike Newtonian fluids, the viscosity of polymeric liquids depends on the strength of the applied deformation. A number of experiments shows viscoelastic nature of polymer liquids leads to peculiar observations not seen in Newtonian fluids, such as extrudate swelling, melt fracture, rod climbing, elastic jets, and etc.

Polymer solutions are a subclass of polymeric liquids which are composed of macromolecules dissolved in a low molecular weight solvent. Numerous industrial applications for polymeric solutions relies on using external fields such as fluid flow to control macromolecular stretch and orientation and hence the ultimate material properties. Examples include turbulent drag reduction, fiber spinning, blow molding, etc. Biological solutions also contain long macromolecules such as deoxyribonucleic acid (DNA) and proteins as their essential building blocks.



Hence, understanding the flow-microstructure coupling in polymeric solutions is of fundamental importance in many fields of science and engineering including polymer physics, rheology, biology, and polymer processing.

### 1.1.1 Polymer flexibility

A polymer is composed of smaller units called monomers which are its structural repeating units and are connected by covalent bonds. Consider the ideal conformation of the chain with no interactions between different monomers (see [section 1.1.2](#) for detailed description of different solution conditions). The simplest model for the ideal conformation is the freely jointed chain (FJC) model. In this model, the correlation of the neighboring bonds (average of the angle between the neighboring bonds) is zero. The squared end-to-end distance of a polymer that follows the FJC model is,

$$\langle R_{ee}^2 \rangle = nl^2, \quad (1.1)$$

where  $n$  is the number of bonds along the chain and  $l$  is the length of the bond, e.g., for polyethylene it is the distance between carbon atoms which is 1.54 Å. However, typical polymers have non-zero correlation of the neighboring bonds. There are two angles that identify the correlation along the backbone. First is the tetrahedral angle  $\theta$  which is the angle between neighboring bonds and the other is the torsional or dihedral angle  $\varphi$  for three consecutive bonds which is the angle between the two planes constructed by the first two and the last two bonds, respectively. Since the tetrahedral angle is almost a constant value, the variation in the torsional angle is the main reason for the flexibility of the chain. Freely rotating chain (FRC) model assumes a constant tetrahedral angle but no constraint on the torsional angle. The worm-like chain (WLC) model or *semiflexible* chain is a special case of the FRC model where the tetrahedral angle is very small, however, the flexibility of the chain originates from this non-zero value of  $\theta$ .

The other two ideal chain models are hindered rotation (HR) and rotational isometric state (RIS) models which assume constraints on the variation of the torsional angle. While

HR considers specific potential for all torsional states, RIS restricts the possible torsional conformations to three main states, i.e., trans, gauche-minus, and gauche-plus.

The corresponding end-to-end distance for ideal chain conformation models with non-zero correlation between the directions of different bond vectors can be shown to be [128],

$$\langle R_{ee}^2 \rangle = C_n n l^2, \quad (1.2)$$

where  $C_n$  is the Flory's characteristic ratio [40] which depends on the number of bonds along the chain and is always larger than unity. In the limit of very long macromolecules ( $n \rightarrow \infty$ ),  $C_n$  approaches an asymptotic value  $C_\infty$ . It is a characteristic number in the range of 4-10 for flexible macromolecules and is very large ( $\sim 1/\theta^2$ ) for semiflexible chains. It is very convenient to define a coarse-grained equivalent freely jointed chain which has the same contour length (maximum end-to-end distance)  $L_c$  and the same average equilibrium mean-square end-to-end distance as the actual chain, but is composed of  $N_K$  randomly oriented *Kuhn* steps each of length  $b_K$ . We can specify the  $N_K$  and  $b_K$  for this model as,

$$N_K = \frac{L_c^2}{C_\infty n l^2}, \quad (1.3)$$

$$b_K = \frac{C_\infty n l^2}{L_c}. \quad (1.4)$$

The equivalent freely jointed chain model is the most fine-grained description of the polymer chain that is considered in the rest of this dissertation. Hence, the smallest length scale that is the most important is the Kuhn length (or Kuhn monomer) which we will also refer to as monomers. An equivalent micro-mechanical model is commonly used where the polymer chain is described using beads as centers of hydrodynamic resistance connected by rigid rods where each rod represents a Kuhn length. This model is used for both flexible (Kramers chain [11]) and semiflexible chains (Kratky-Porod model) [159, 156].

### 1.1.2 Solvent quality

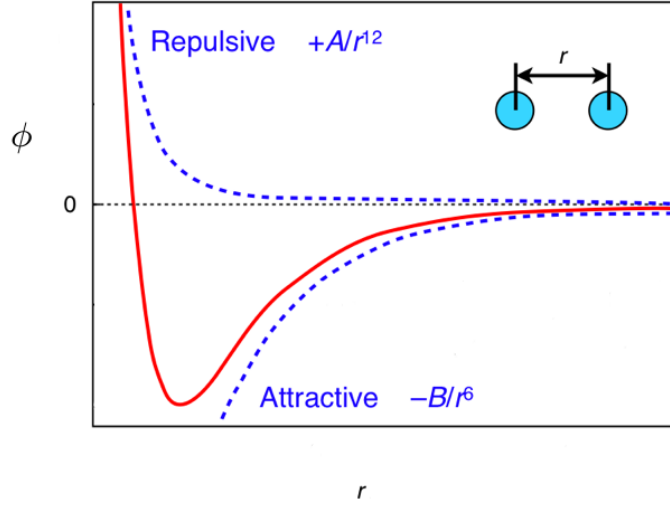
It is important to realize that the models considered in [section 1.1.1](#) are correct only under ideal conditions (no interaction), while the monomers of real uncharged macromolecules interact with other monomers of macromolecules as well as the solvent molecules in their vicinity. It is the sum of these interactions that determines the solvent condition or quality. If the effective interactions between monomers are repulsive, i.e., monomer-solvent interactions are more energetically favorable than monomer-monomer interactions, then the solvent is *good*. The opposite situation happens in a *poor* solvent, where the monomers of the chain effectively attract each other. In an intermediate case, the solvent is poor enough to cancel the effect of repulsive interactions between monomers (no net interaction) and the conformation of the chain is nearly ideal. This special condition is commonly referred to as the *theta* ( $\theta$ ) condition. Since the theta condition for a particular polymer-solvent pair happens at a certain temperature, this condition is also called the  $\theta$ -temperature,  $T_\theta$ . For instance, dioctyl phthalate (DOP) is a  $\theta$ -solvent for polystyrene at 22 °C. At temperatures higher than  $T_\theta$ , the macromolecules are in a good solvent condition and their conformation is expanded relative to the ideal conformation.

If the effective potential between the monomers that are a distance of  $r$  apart is  $\phi(r)$ , the net interaction between the monomers can be quantified using the *excluded volume* (EV) parameter  $v$ ,

$$v = \int (1 - \exp(-\phi(r)/k_{\text{B}}T)) \, \text{d}^3r, \quad (1.5)$$

where  $k_{\text{B}}$  is the Boltzmann constant and  $T$  is the absolute temperature. Typical monomers have a core repulsive interaction at small separations due to their steric repulsion. At large separations, however, there is a net attractive force since the monomers usually attract each other more than solvent when they are far apart. An example of this type of potential is the well-known 6-12 Lennard-Jones potential [\[91\]](#) (see [Figure 1.1](#)).

The EV parameter can take negative or positive numbers if the net interactions are attractive or repulsive, respectively and the theta condition is satisfied if  $v = 0$ . It should be noted that the limit of very good solvent (also termed athermal solvent) condition is attained



**Figure 1.1:** 6-12 Lennard-Jones potential.

if the potential has only the repulsive component, i.e., there is no energetic distinction between monomer-monomer and monomer-solvent interactions. Polymers in a chemically identical solvent is an example of an athermal solvent.

Another well established dimensionless parameter which represents of the excluded volume effects is,

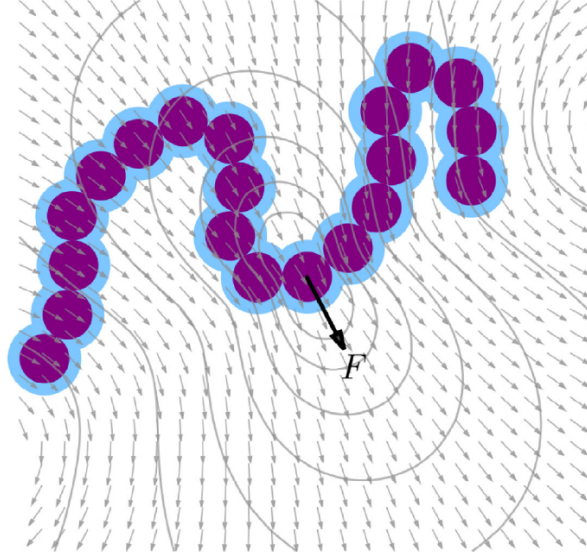
$$z \sim \frac{v}{b_K^3} N_K^{1/2}, \quad (1.6)$$

This parameter is extensively used in the perturbation expansion theory for macromolecules in good solvents [30] and is directly related to the average number of collisions taking place in the polymer coil. This parameter is also conveniently measured in experiments [83] and is very useful in comparison between theory/simulation and experiment.

Note that while the ideal conformation of the chain obeys random walk (RW) statistics, the real chain conformation in a better than theta solvent is swollen and follows a self avoiding walk (SAW). The scaling of the end-to-end distance in the two scenarios are,

$$R_{ee,RW} \approx b_K N_K^{1/2}, \quad (1.7)$$

$$R_{ee,SAW} \approx b_K N_K^{\nu_{eff}}, \quad (1.8)$$



**Figure 1.2:** The hydrodynamic interaction for multi-bead representation of a polymer chain in solution.  $F$  is a point force applied to one of the beads and its effect is propagated through the solvent media (This figure is taken from the reference [31]).

where  $\nu_{\text{eff}}$  is the effective exponent related to the solvent quality (EV interactions) which was theoretically found to be  $0.588 \pm 0.001$  for very large  $z$  values [30].

### 1.1.3 Hydrodynamic interactions

Upon movement of monomers in the solution, the solvent exerts hydrodynamic drag forces on the monomers. If the monomers are assumed to be spherical, the drag on an individual monomer follows Stokes force law [12]. However, the solvent flow field is perturbed due to the movement of all other monomers (see Figure 1.2) and hence the drag on a bead is changed as a result of this hydrodynamic interactions (HI). Assuming the monomers are point particles, the velocity perturbation at position  $\mathbf{r}$  due to force exerted on the solvent by a monomer at  $\mathbf{r}'$  is [129, 112],

$$\mathbf{v}'(\mathbf{r}) = \boldsymbol{\Omega}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{F}(\mathbf{r}'), \quad (1.9)$$

where  $\boldsymbol{\Omega}(\mathbf{r} - \mathbf{r}')$  is the Green's function of the Stokes equation. The simplest (monopole) solution to Stokes equation is known as Oseen-Burgers tensor,

$$\boldsymbol{\Omega}(\mathbf{r}) = \frac{1}{8\pi\eta_s r} \left( \boldsymbol{\delta} + \frac{\mathbf{r}\mathbf{r}}{r^2} \right). \quad (1.10)$$

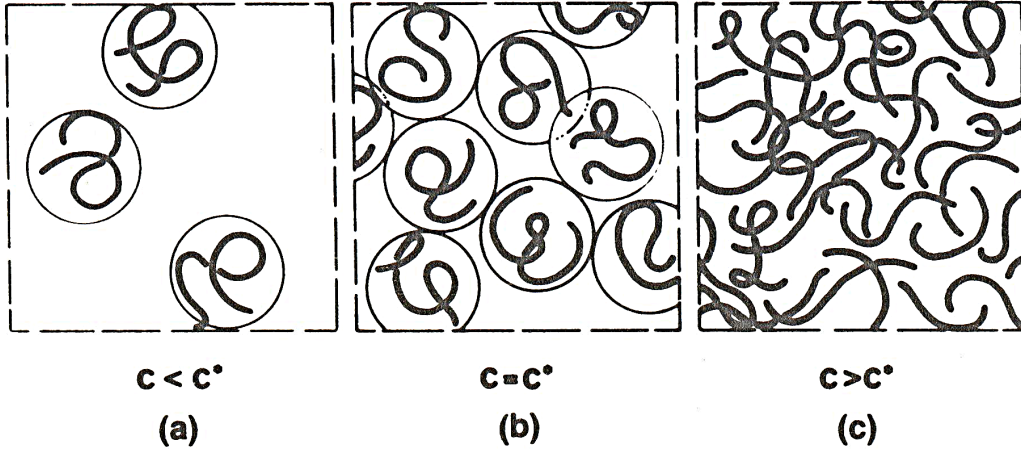
However, this solution can result in violation of semi positive definiteness of diffusion tensor. Moreover, for monomers with nonzero radius, a regularization is required to obtain correct solutions at small inter-particle distances. The Rotne-Prager-Yamakawa (RPY) tensor is the well-established example of such a solution which satisfies both conditions [164, 112].

It is important to mention that the hydrodynamic interaction (similar to electrostatic interactions) is long range, i.e., the additive effect of hydrodynamic forces ( $\int f^{\text{HI}}(r) d^3r$ , where  $f^{\text{HI}}$  is the effective hydrodynamic force at a particular distance) does not vanish at large distances. It is also important to understand that although HI does not alter the static properties of the system, it is essential in determining the polymer dynamics in solution.

#### 1.1.4 Concentration regimes

Other than the stiffness of macromolecules, the solvent quality, and hydrodynamic interactions, another factor that significantly influences the properties of polymer solutions is the concentration of the polymers in the solvent media. This is particularly important when one considers non-ideal solutions, as both inter-chain and intra-chain monomer interactions are present. At sufficiently low concentrations  $c$  (number of monomers per unit volume) the polymer solution is *dilute* in the sense that the average distance between the polymer coils is larger than their size and therefore they move with no short range interaction with other chains. Upon increasing the concentration, the polymer coils start to overlap at a special concentration called  $c^*$  which can be quantified based on the fact that this concentration is similar to the concentration of monomers inside the pervaded volume of a single coil,

$$c^* \approx \frac{N_K}{4/3\pi R_g^3}, \quad (1.11)$$



**Figure 1.3:** The physical interpretation of the overlap concentration  $c^*$  (This figure is taken from the reference [24]).

where  $R_g$  is the radius of gyration of the polymer chains.

The *semidilute* concentration regime begins where the monomer concentration is increased above  $c^*$ . At some larger value of concentration ( $c_e$ ), the dynamics of entangled regimes in the system becomes important and dominant in the behavior of the polymer solution. Upon further increasing the concentration to  $c^{**}$ , the system enters the concentrated regime where all excluded volume and hydrodynamic interactions are screened. The latter regime is not the subject of our study in this dissertation. It is important to mention that the transition between different regimes are smooth and does not occur at a singular experimental set of concentration and solvent quality. Many important static and dynamic properties such as polymer size, relaxation, and center of mass diffusivity of macromolecules in solution is a strong function of normalized concentration  $c/c^*$ . Moreover, the scaling of static and dynamic properties as a function of  $c/c^*$  or number of monomers in a chain is generally distinct in each concentration regime.

## 1.2 Theoretical description of polymeric solutions

### 1.2.1 Blob theory

The scaling theory (also known as blob theory) developed by de Gennes [24, 128] is a widely accepted scaling concept for long macromolecules under equilibrium and nonequilibrium conditions. The blob model is particularly useful in describing the concentration dependence of various properties in semidilute solutions [119, 15, 68].

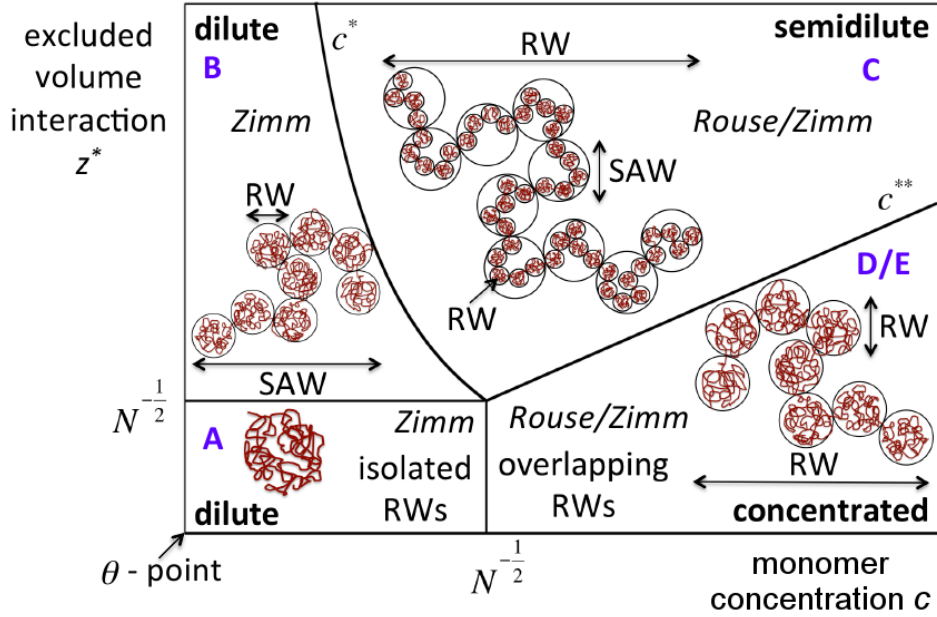
Using the blob concept, it is possible to construct a universal double crossover plot (see Figure 1.4), where the phase diagram and conformational properties can be understood based on the combined effect of solvent quality and the extent of molecule-molecule overlap (monomer concentration). Note that in this figure, the solvents are assumed to be in theta or better than theta condition. The effective strength of EV is measured using the parameter  $z^* = \epsilon/k_{\text{B}}T \left(1 - \frac{T_{\theta}}{T}\right)$ , where  $\epsilon$  is the energy of interaction between two monomers.  $z^*$  is directly related to the solvent quality, using Equation (1.6),

$$z = z^* N^{1/2} \quad (1.12)$$

For sufficiently dilute solutions, the crossover from RW to SAW statistics occurs at  $z \sim 1$ . For good solvent condition, there are two length scales that are important in the blob concept. The first one is the thermal blob size  $\xi_T$  which is the length scale up to which EV interactions are unimportant and hence the conformation is ideal. In the dilute concentration regime and for length scales larger than  $\xi_T$ , the conformation obeys SAW statistics. By increasing concentration above  $c^*$ , EV interactions become screened at a length scale shown by correlation or concentration blob  $\xi_c$ . For concentrations above  $c^{**}$ , the concentration blob completely shrinks down, i.e.,  $\xi_c \approx \xi_T$ .

In spite of the valuable information that can be drawn from blob theory (the scaling of static and dynamic properties in different concentration regimes), the blob model is for the limiting case of very long chains. Also as mentioned in section 1.1.4, the transition is smooth and the exact crossover concentration is not known *a priori*. Hence, the concentration





**Figure 1.4:** Different concentration regimes of a polymer solution depicted as a function of monomer concentration  $c$  and excluded volume strength  $z^*$  (This figure is taken from the reference [68]).

regimes and the crossovers should be determined via simulations. Most importantly, the properties of the solutions under nonequilibrium conditions and full fluctuating EV and HI are highly desired. To this end, implementation of reliable simulation techniques for polymeric solutions is essential.

### 1.2.2 Kinetic theory

Bird and coworkers [11] used kinetic theory for polymer solutions and introduced a framework to relate the macroscopic properties ( e.g., the stress tensor) and the ensemble average of the microscopic variables ( e.g., the chain end-to-end vector). In this theory, the evolution equation for the configurational distribution function, which is also called the Fokker-Planck or diffusion equation, is utilized to obtain the statistical average of the microscopic properties, such as the second moment of the chain end-to-end vector. However, it is often difficult to

solve the continuity equation for the moments exactly and hence it becomes indispensable to apply closure approximations.

To circumvent this issue, Öttinger [112] proved the existence of a stochastic differential equation (SDE) for the motion of polymers which is equivalent to the Fokker-Planck equation. This equation can be solved using appropriate simulation techniques. Brownian dynamics (BD) is a simulation method which is used in this work to obtain the configurational evolution of the chain.

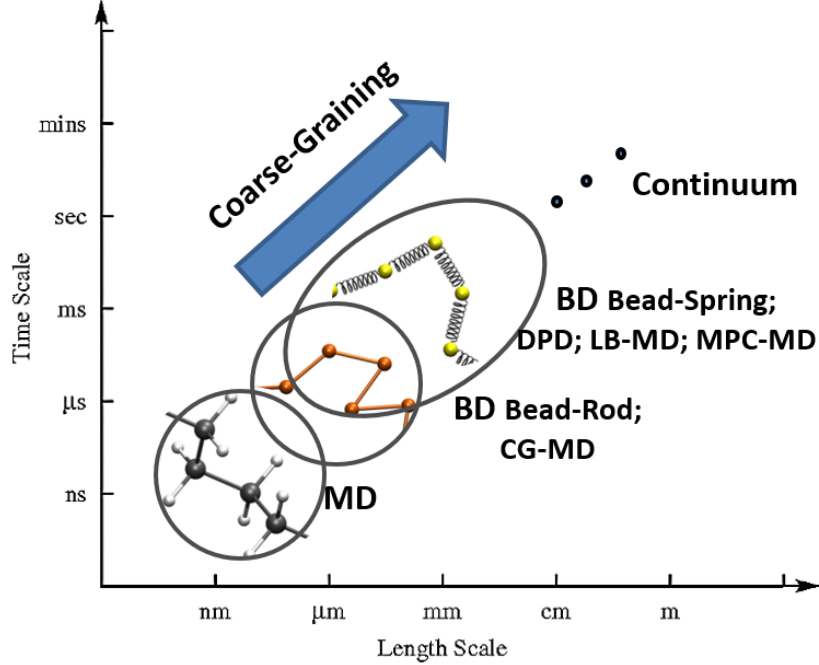
## 1.3 Simulation methods

### 1.3.1 Atomic-scale technique

Molecular dynamics (MD) is the most *fine-grained* simulation technique to obtain the configurational properties of a polymeric system in solution. In MD, the momentum conservation equation is solved for all atoms of the polymer chains as well as solvent molecules. However, the simulations on atomic length scales and time scales that account for explicit solvents are often not required and therefore movements of the *beads* which are composed of several chain repeating units suffice to describe the conformation of the macromolecules (see Figure 1.5). Coarse-grained *mesoscopic* techniques are reasonably accurate alternatives and are computationally much more efficient compared to all-atom MD.

### 1.3.2 Mesoscale techniques

In this category of simulation methods, a polymer is represented using a coarse-grained bead-spring micromechanical model [11, 112]. It is clear that the accuracy of the coarse-graining approach has a significant impact on the fidelity of the simulation results. To this end, the simulations using a bead-spring model and the corresponding parameterization should be performed systematically such that one recovers the behavior of the bead-rod model (the highest level of mesoscopic fine-graining) and experimental results. There are



**Figure 1.5:** Time and length scales of different simulation techniques for polymer solutions.

two subclasses in mesoscopic simulations. In the first one, the solvent is treated explicitly and therefore the hydrodynamic effects of solvent media on the solute is achieved through the momentum exchange between the entities. The dissipative particle dynamics (DPD), hybrid lattice Boltzmann-molecular dynamics (LB-MD), and the hybrid multi-particle collision-molecular dynamics (MPC-MD) are the examples of these methods. Note that in the latter two approaches, the solvent degrees of freedom are obtained using the LB and MPC methods, respectively, while the polymer chains are described using molecular dynamics.

In the other subclass which can be exemplified by Brownian dynamics, the solvent degrees of freedom are removed completely, while the long-range hydrodynamic effects are treated explicitly and exactly using the diffusion tensor. Due to high computational demand of calculating the diffusion tensor and Brownian displacements (in particular for polymers in semidilute solutions), the efficiency of BD algorithm is of crucial importance in order to use this method for large-scale systems. In [chapter 2](#) of this dissertation, the details of an

efficient BD technique are given. The resulting implementations of this novel technique are now available as an open-source package BDpack (see [chapter 3](#)).

## 1.4 Experimental characterization methods

For flexible macromolecules, the microstructural properties, i.e.,  $b_K$ ,  $N_K$ , and  $L_c$  are identified with the knowledge of the characteristic ratio  $C_\infty$  (known for different polymers) and the molecular weight  $M_w$ . For semiflexible chains, however,  $b_K$  and  $N_K$  are estimated by direct visualization of the chains.

Static and dynamic light scattering can be used to determine the quality of the solvent. The  $\theta$ -temperature is obtained using static light scattering by empirical evaluation of the second virial coefficient [128, 115]. Subsequently, dynamic light scattering is used to obtain the dimensions of the macromolecules and the solvent quality [115]. Moreover, the model variables related to the hydrodynamic drag on the chain is found using the approximate width of the chain [59, 58, 132].

Visualization of polymer microstructural evolution in presence or absence of flow has provided tremendous insight into behavior of polymeric fluids, including molecular individuality and its consequence on the macroscopic flow properties of this class of fluids [116]. Single molecule visualization is extensively used to describe the *individualistic* dynamics of long DNA macromolecules with different architecture [63, 138, 88, 96, 99]. In this study, the relaxation and stretching dynamics of comb DNA molecules are simulated and compared with experimental results (see [chapter 6](#)).

On the other hand, linear viscoelastic measurements under near equilibrium condition using small amplitude oscillatory shear flow can provide a bulk measure of material properties of polymer solutions [109]. Nonlinear rheology equipments can evaluate the polymer solution response far from equilibrium, for example under shear flows [52, 115] or uniaxial elongational flows [50, 105]. For instance, the filament stretching rheometer (FSR) can be used to probe the transient extensional viscosity of polymer solutions [152, 80, 50, 7, 105]. Specifically, in this device a well-controlled uniaxial extensional flow up to approximately 6 Hencky strains

is created that permits accurate measurement of the elongational properties of polymeric fluids. In [chapter 4](#), the extensional rheology of high molecular weight polystyrene is studied and compared with experimental measurements.

# Chapter 2

## Methodology

This chapter is based on the published papers:

- A. Saadat and B. Khomami. Computationally efficient algorithms for incorporation of hydrodynamic and excluded volume interactions in Brownian dynamics simulations: A comparative study of the Krylov subspace and Chebyshev based techniques. *J. Chem. Phys.*, 140:184903, 2014.
- A. Saadat and B. Khomami. Matrix-free Brownian dynamics simulation technique for semidilute polymeric solutions. *Phys. Rev. E*, 92:033307, 2015.

### 2.1 Infinitely dilute solutions (isolated chains)

#### 2.1.1 Introduction

The most time consuming operations involved in BD simulations in presence of HI is the decomposition of the diffusion tensor to obtain the Brownian displacement vector. A common technique for performing this decomposition is Cholesky factorization which for a bead-spring chain with  $N_b$  beads requires  $\mathcal{O}(N_b^3)$  [34] operations. In order to mitigate this poor scaling, Fixman [39] proposed an alternative method based on the Chebyshev polynomial approximation to the principle square root of the diffusion tensor (see [section 2.1.3](#)). Due

to the necessity of approximating the extreme eigenvalues of the diffusion tensor, different implementations of this method exist [70, 82, 69, 4]. The accuracy of this approximation is tuned on the basis of an error definition and the degree of polynomial, although the computational time generally scales with  $\mathcal{O}(N_b^{2.25})$ . The other technique to approximate the Brownian displacement vector is the Truncated Expansion Ansatz (TEA) proposed by Geyer and Winter [44]. This method assumes that the form of Brownian displacement vector is similar to the displacement originating from the deterministic force and that correlations between different units are weak and approximately equal. In spite of its computational efficiency ( $\mathcal{O}(N_b)$  operations [44]), the aforementioned assumptions of the algorithm could fail if  $N_b$  is large enough (see for example Table II of [135], where the relative error with respect to the Cholesky results is greater than 8% when  $N_b$  is  $\mathcal{O}(10^2)$ ) or when the hydrodynamic coupling is strong [135, 4, 29]. In contrast to the Chebyshev polynomial approximation technique, in cases where the coupling becomes strong during the simulation, an error reduction procedure does not exist for this method. Therefore, this method is not considered in this study.

Recently Ando *et al.* [4] have introduced an alternative algorithm to compute the correlated Brownian displacements based on Krylov subspaces. The great simplification over the Chebyshev based techniques is the elimination of the need for estimating the minimum and maximum eigenvalues of the diffusion tensor. Ando *et al.* [4], also examined the efficiency and the convergence of block versions of their decomposition algorithms for cases where the diffusion tensor changes slowly in comparison to the simulation time step.

The semi implicit predictor-corrector scheme has been proven extremely cost efficient for the time integration of the stochastic differential equation (SDE) of bead-spring micromechanical models [112, 147, 59, 138]. The algorithm is designed such that the overstretching of springs are prevented for simulations with large time steps. Hsieh *et al.* [59], have shown that the predictor-corrector scheme with time steps of approximately thousand times that of the explicit scheme can provide nearly equivalent results to the explicit scheme with only around 10% increase in computational time per time step. By applying the Gauss-Seidel iteration, the computational time of each time step can further be reduced as compared

to the semi implicit Newton’s method [59]. Hence, using the semi implicit predictor-corrector can lead up to few orders of magnitude speed up over the other alternatives based on selected  $N_b$  and  $Wi$  (see Table. 1 of [59]).

In this study, for the first time the semi implicit predictor-corrector scheme for BD of dilute polymer solution (bead-spring chains) in the presence of HI and EV is implemented in conjunction with a highly efficient large scale linear algebra package, namely, the Math Kernel Library (MKL), to allow large scale computations for  $\mathcal{O}(10^3)$  segments. As the configuration of each molecule evolves independently with respect to the other molecules, the simulation of the system is parallelized by employing message passing interface (MPI) for distributed-memory architectures. The main three decomposition techniques mentioned above, i.e. Cholesky, Chebyshev and Krylov, are studied to ascertain their efficiency and accuracy in both equilibrium and planar extensional flow field with varying block dimensions. For the Chebyshev polynomial approximation, the most effective and computationally efficient aspects of different implementations are selected and summarized into an algorithm which is outlined in the paper. Moreover, in the case of Krylov subspace method, additional refinements namely, reusing the unchanged part of tridiagonal matrix  $\mathbf{H}$  in iteratively updating the degree of the polynomial and introduction of a minimum number of polynomial terms which is updated throughout the simulation, are implemented towards increasing the efficiency of the algorithm. Finally, the most efficient simulation algorithm is employed to predict the measured material properties of high molecular weight dilute polystyrene solutions under uniaxial extensional flow [95].

### 2.1.2 Governing equations

In this section, the basic equations describing the dynamics of a molecule in dilute polymer solution are expressed using a coarse grained bead-spring model. The configurational state of a bead-spring chain, which consists of  $N_b$  identical beads connected by  $N_b - 1$  entropic springs, can be specified by the position vector of the beads, i.e.  $\{\mathbf{r}_\nu | \nu = 1, \dots, N_b\}$ . The probability distribution function is obtained by solving the corresponding Fokker-Planck



equation or an equivalent SDE [11]. Based on the convention used by Bird *et al.* [11] and Öttinger [112], the Greek indices represent the bead number (from 1 to  $N_b$ ) and the Latin indices represent the connector vector number (from 1 to  $N_b - 1$ ) throughout the paper. The Itô SDE of motion is [112],

$$\begin{aligned} d\mathbf{r}_\nu(t) = & \left[ \mathbf{v}_0(t) + \boldsymbol{\kappa}(t) \cdot \mathbf{r}_\nu(t) + \frac{1}{\zeta} \sum_{\mu} \boldsymbol{\Upsilon}_{\nu\mu} \cdot \mathbf{F}_\mu^\phi(t) \right] dt \\ & + k_B T \sum_{\mu} \nabla \cdot \boldsymbol{\Omega}_{\mu\nu} dt + \sqrt{\frac{2k_B T}{\zeta}} \sum_{\mu} \mathbf{C}_{\nu\mu}(t) \cdot d\mathbf{W}_\mu, \end{aligned} \quad (2.1)$$

where  $\mathbf{v}_0(t) + \boldsymbol{\kappa}(t) \cdot \mathbf{r}$  describes the homogeneous solvent flow field,  $\boldsymbol{\kappa}$  is a traceless tensor which is independent of position but may depend on time,  $k_B$  is the Boltzmann constant and  $T$  is the absolute temperature.  $\zeta$  is the bead friction coefficient, which relates the hydrodynamic radius of the bead  $a_b$  to the solvent viscosity  $\eta_s$  through the Stokes relation, i.e.  $a_b = \zeta/6\pi\eta_s$ .  $\boldsymbol{\Upsilon}_{\mu\nu}$  is the dimensionless diffusion tensor which is defined as

$$\boldsymbol{\Upsilon}_{\nu\mu} = \delta_{\nu\mu} \boldsymbol{\delta} + \zeta \boldsymbol{\Omega}_{\nu\mu} = \sum_{\mu'} \mathbf{C}_{\nu\mu'} \cdot \mathbf{C}_{\mu\mu'}^T. \quad (2.2)$$

here,  $\delta_{\nu\mu}$  is the Kronecker delta,  $\boldsymbol{\delta}$  is a  $3 \times 3$  unit tensor and  $\boldsymbol{\Omega}_{\nu\mu}$  is the tensor which describes hydrodynamic interaction between  $\mu^{\text{th}}$  and  $\nu^{\text{th}}$  bead. Note that the second equality in Equation (2.2) originates from fluctuation dissipation theorem [112, 146].  $\mathbf{F}_\nu^\phi = \mathbf{F}_\nu^{\text{spr}} + \mathbf{F}_\nu^{\text{EV}}$  is the net force on the  $\nu^{\text{th}}$  bead as a result of all conservative interactions, where  $\mathbf{F}_\nu^{\text{spr}}$  is the net spring force and the  $\mathbf{F}_\nu^{\text{EV}}$  is the total EV force due to the interaction with all other beads.  $\mathbf{W}$  is a  $3N_b$  dimensional Wiener process.

To non-dimensionalize the SDE, the characteristic time and length scales are defined as the relaxation time of a Hookean spring  $\lambda_H = \zeta/4H$  and one third of the Hookean spring equilibrium length  $l_H = \sqrt{k_B T/H}$ , with  $H$  being the Hookean spring constant. The non-dimensionalized variables using the time and length scales are identified with star superscript. Then,  $\boldsymbol{\Upsilon}_{\nu\mu}$  is expressed based on semi positive definite Rotne-Prager-Yamakawa (RPY) tensor in terms of non-dimensional distance between the beads  $\mu$  and  $\nu$ ,  $\mathbf{r}_{\nu\mu}^* = \mathbf{r}_\nu^* - \mathbf{r}_\mu^*$ , as

[121, 138]:

$$\mathbf{r}_{\nu\mu} = \begin{cases} \delta & \nu = \mu \\ \frac{3a^*}{4r_{\nu\mu}} \left[ \left(1 + \frac{2a^{*2}}{3r_{\nu\mu}^2}\right) \delta + \left(1 - \frac{2a^{*2}}{r_{\nu\mu}^2}\right) \frac{\mathbf{r}_{\nu\mu}\mathbf{r}_{\nu\mu}}{r_{\nu\mu}^2} \right] & \nu \neq \mu; \frac{r_{\nu\mu}}{2} \geq a^* \\ \left[ \left(1 - \frac{9r_{\nu\mu}}{32a^*}\right) \delta + \frac{3}{32a^*} \frac{\mathbf{r}_{\nu\mu}\mathbf{r}_{\nu\mu}}{r_{\nu\mu}} \right] & \nu \neq \mu; \frac{r_{\nu\mu}}{2} < a^*, \end{cases} \quad (2.3a)$$

$$\mathbf{r}_{\nu\mu} = \begin{cases} \frac{3a^*}{4r_{\nu\mu}} \left[ \left(1 + \frac{2a^{*2}}{3r_{\nu\mu}^2}\right) \delta + \left(1 - \frac{2a^{*2}}{r_{\nu\mu}^2}\right) \frac{\mathbf{r}_{\nu\mu}\mathbf{r}_{\nu\mu}}{r_{\nu\mu}^2} \right] & \nu \neq \mu; \frac{r_{\nu\mu}}{2} \geq a^* \end{cases} \quad (2.3b)$$

$$\mathbf{r}_{\nu\mu} = \begin{cases} \left[ \left(1 - \frac{9r_{\nu\mu}}{32a^*}\right) \delta + \frac{3}{32a^*} \frac{\mathbf{r}_{\nu\mu}\mathbf{r}_{\nu\mu}}{r_{\nu\mu}} \right] & \nu \neq \mu; \frac{r_{\nu\mu}}{2} < a^*, \end{cases} \quad (2.3c)$$

where  $r_{\mu\nu}^* = |\mathbf{r}_{\mu\nu}^*|$ . Note that  $h^*$  (the hydrodynamic interaction parameter) is related to dimensionless hydrodynamic radius as  $h^* = (1/\sqrt{\pi}) a^*$ . The dimensionless net spring force on the  $\nu^{\text{th}}$  bead,  $\mathbf{F}_{\nu}^{\text{spr}*}$ , is obtained from the tension in the neighboring springs  $\mathbf{F}_{\nu}^{\text{c}*}$  and  $\mathbf{F}_{\nu-1}^{\text{c}*}$  with  $\mathbf{F}_{\nu}^{\text{c}*}$  defined based on the connector vector between the adjacent beads,  $\mathbf{Q}_{\nu}^* = \mathbf{r}_{\nu+1}^* - \mathbf{r}_{\nu}^*$  and their corresponding force law:

$$\mathbf{F}_{\nu}^{\text{c}*} = \begin{cases} \frac{\mathbf{Q}_{\nu}^*}{1 - \mathbf{Q}_{\nu}^{*2}/b} & \text{FENE} \\ \frac{2\sqrt{b}}{3} \left[ \frac{1}{4(1 - \mathbf{Q}_{\nu}^*/\sqrt{b})^2} - \frac{1}{4} + \frac{\mathbf{Q}_{\nu}^*}{\sqrt{b}} \right] \frac{\mathbf{Q}_{\nu}^*}{Q_{\nu}^*} & \text{WLC} \\ \frac{1 - (\mathbf{Q}_{\nu}^*/\sqrt{3b})^2}{1 - (\mathbf{Q}_{\nu}^*/\sqrt{b})^2} \mathbf{Q}_{\nu}^* & \text{ILCCP}, \end{cases} \quad (2.4)$$

where  $Q_{\nu}^* = |\mathbf{Q}_{\nu}^*|$  and  $\sqrt{b}$  is the maximum dimensionless length of polymer springs. The WLC, FENE, and ILCCP refer to the worm like chain, Warner approximation to the Inverse Langevin Function (ILF), and the Cohen's Pade approximation to the ILF, respectively [139]. The dimensionless EV force  $\mathbf{F}_{\nu}^{\text{EV}*}$  is derived using the soft Gaussian potential  $E^*(\mathbf{r}_{\nu\mu}^*)$  introduced by Prakash and Öttinger [123] which is the regularized  $\delta$ -function potential,

$$\mathbf{F}_{\nu}^{\text{EV}*} = \sum_{\mu=1; \mu \neq \nu}^{N_b} \left( \frac{z^*}{d^{*5}} \right) \mathbf{r}_{\nu\mu}^* \exp \left( -\frac{\mathbf{r}_{\nu\mu}^{*2}}{2d^{*2}} \right), \quad (2.5)$$

where the parameter  $z^*$  is an indication of EV potential strength and  $d^*$  specifies the spatial range of the potential. In chapter 4, the rheological property of the system in uniaxial extensional flow is investigated. Therefore, the macroscopic stress tensor  $\boldsymbol{\tau}$  is expressed in term of mesoscopic model variables. The macroscopic stress tensor  $\boldsymbol{\tau}$  can be described by

the modified Kramer's expression in the absence of external forces [11, 121],

$$\boldsymbol{\tau} = -\eta_s (\boldsymbol{\kappa} + \boldsymbol{\kappa}^T) + (N_b - 1) n k_B T \boldsymbol{\delta} + n \sum_{\nu=1}^{N_b} \langle \mathbf{R}_\nu \mathbf{F}_\nu^\phi \rangle, \quad (2.6)$$

where  $n$  is the number of polymers per unit volume and  $\mathbf{R}_\nu = \mathbf{r}_v - \mathbf{r}_c$  is the relative distance of the bead positions with respect to the center of mass. The first term in Equation (2.6) represents the Newtonian solvent contribution to the stress and the second and third terms are the polymer molecules contribution. Note that the stress is non-dimensionalized with  $n k_B T$ .

In section 2.2.6 and chapter 4, the properties of polymer solution in planar and uniaxial extensional flow are investigated. In uniaxial extensional flow,  $\boldsymbol{\kappa}^*$  (non-dimensionalized using strain rate  $\dot{\epsilon}$ ) is defined as

$$\boldsymbol{\kappa}^* = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & -1/2 \end{pmatrix}.$$

The Trouton ratio is  $Tr = \frac{\eta_u^*}{\eta_0^*}$ , where  $\eta_u^*$  is the dimensionless uniaxial extensional viscosity and is defined as  $\eta_u^* = -\frac{\tau_{11}^* - \tau_{22}^*}{Pe}$  with  $Pe = \lambda_H \dot{\epsilon}$ . We also define  $Wi = \lambda_1 \dot{\epsilon} = \lambda_1^* Pe$ , where  $\lambda_1$  is the chain longest relaxation time.  $\eta_0^* = \frac{\eta_0}{(n k_B T) \lambda_H}$  is the dimensionless zero-shear viscosity. In dilute polymeric solutions  $\eta_0^* \approx \eta_s^*$ , hence,

$$Tr \approx 3 + \frac{\eta_p^*}{\eta_s^*}. \quad (2.7)$$

The Trouton ratio is usually depicted as a function of Hencky strain, which is defined as  $\epsilon = Pe \times t$ .

For planar extensional flow,

$$\boldsymbol{\kappa}^* = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

In the subsequent sections of this chapter, all the model parameters are nondimensionalized based on the aforementioned protocols. However, the star superscripts are primarily removed for simplicity, unless stated otherwise.

### 2.1.3 Numerical simulation steps

The evolution of the bead position vectors in a bead-spring chain can be obtained by performing matrix-vector operations in block format. The block diagonal matrix  $\mathbf{K}$  contains  $(N_b - 1) \times (N_b - 1)$  blocks of  $3 \times 3$  matrices and the diagonal blocks are equal to tensor  $\boldsymbol{\kappa}$  and the rest of the blocks are equal to  $\mathbf{0}$ . The diffusion matrix  $\mathbf{D}$  is also a block matrix which contains  $N_b \times N_b$  blocks and each block is the corresponding  $\boldsymbol{\Upsilon}_{\mu\nu}$  tensor. Furthermore, since we employ the Rotne-Prager-Yamakawa (RPY) HI tensor [112], the non-dimensionalized SDE does not contain the spatial derivative of the diffusion tensor. Hence, the evolution equation for the segmental connector vectors is ( $\mathbf{Q}$  is a block column vector consisting of  $N_b - 1$  connector vectors),

$$d\mathbf{Q} = \left[ Pe\mathbf{K} \cdot \mathbf{Q} + \frac{1}{4}\bar{\mathbf{B}} \cdot \mathbf{D} \cdot \mathbf{F}^\phi \right] dt + \frac{1}{\sqrt{2}}\bar{\mathbf{B}} \cdot \mathbf{C} \cdot d\mathbf{W}, \quad (2.8)$$

where  $\bar{\mathbf{B}}$  is the transformation matrix used by Bird *et al.* [11] to convert position vectors to connector vectors and is defined as,

$$\bar{\mathbf{B}} = \begin{bmatrix} -\delta & \delta & \mathbf{0} & \dots & \mathbf{0} \\ \mathbf{0} & -\delta & \delta & \dots & \mathbf{0} \\ \vdots & \ddots & \ddots & \ddots & \vdots \\ \mathbf{0} & \dots & \mathbf{0} & -\delta & \delta \end{bmatrix}_{N_b-1 \times N_b}. \quad (2.9)$$

$\mathbf{F}^\phi = \mathbf{F}^S + \mathbf{F}^{EV}$  is the block force vector defined based on  $\mathbf{F}_\nu^\phi$ , and  $\mathbf{C}$  is the coefficient matrix which satisfies the equation,

$$\mathbf{D} = \mathbf{C} \cdot \mathbf{C}^T. \quad (2.10)$$

Note that the solution to Equation (2.10) is not unique, i.e., any  $\mathbf{C}$  satisfying this equation can be used.

The semi implicit predictor-corrector scheme used in the earlier studies of Somasi *et al.* [147], Hsieh *et al.* [59], Schroeder *et al.* [138], and Prabhakar and Prakash [121] is used to obtain the internal configurations of the chains at each time step. Specifically, we utilize one predictor and two corrector steps as outlined in section 2.1.3. The evolution equation for center of mass as well as hydrodynamic center of resistance are given in section 2.1.3.

### Predictor step

In this step,  $\mathbf{Q}_{n+1}^\dagger$ , the initial estimate for  $\mathbf{Q}_{n+1}$ , which is the internal configuration of the chains at the end of  $n + 1$  time steps of size  $dt$ , is obtained by explicitly updating the configuration at the beginning of the time step, i.e.,  $\mathbf{Q}_n$ , using the Euler-Murayama method as follows,

$$\mathbf{Q}_{n+1}^\dagger = \mathbf{Q}_n + \left[ Pe \mathbf{K} \cdot \mathbf{Q}_n + \frac{1}{4} \bar{\mathbf{B}} \cdot \mathbf{D}_n \cdot \mathbf{F}_n^\phi \right] dt + \frac{1}{\sqrt{2}} \bar{\mathbf{B}} \cdot \Delta \mathbf{S}_n, \quad (2.11)$$

where  $\Delta \mathbf{S}_n = \mathbf{C}_n \cdot \Delta \mathbf{W}_n$ , is the correlated Brownian displacement vector which has a Gaussian distribution  $\mathcal{N}(\mathbf{0}, dt \mathbf{D})$ . The elements of the Wiener process increment vector  $\Delta \mathbf{W}_n$ , which are independent Gaussian random variables with zero mean and variance  $dt$ , are approximated by uniformly distributed random numbers [112]. The diffusion tensor  $\mathbf{D}_n$ , excluded volume force vector  $\mathbf{F}_n^{\text{EV}}$ , and tension in the springs  $\mathbf{F}_n^{\text{c}}$ , are readily calculated at the beginning of each time step based on  $\mathbf{Q}_n$ . The conservative spring force on the beads is obtained by using the relation  $\mathbf{F}_n^{\text{spr}} = -\bar{\mathbf{B}}^T \cdot \mathbf{F}_n^{\text{c}}$ .

In what follows in section 2.1.3, different techniques for decomposition of  $\mathbf{D}_n$ , calculation of error in approximating  $\Delta \mathbf{S}_n$  in iterative techniques, and application of MKL in large scale linear algebra involved in our simulations are described in more detail.

## Decomposition techniques

- (Block) Cholesky:

The Cholesky factorization of the diffusion tensor is considered as the standard technique for calculating  $\Delta \mathbf{S}$  [34, 135, 4], where  $\Delta \mathbf{S} = \mathbf{C} \cdot \Delta \mathbf{W}$ . In this method, the lower triangular matrix,  $\mathbf{C}$ , which satisfies Equation (2.10), is computed with the computational time scaling with  $N_b^3$ . In order to enhance the computational efficiency of this algorithm, it is assumed that the changes in the diffusion tensor is slow and then a block of  $s$  correlated vectors  $\Delta \mathbf{S}_{bl} = [\Delta \mathbf{S}^1, \dots, \Delta \mathbf{S}^s]$  is simultaneously computed as opposed to computing one vector at each time step [4]. The value  $s$  is also equivalent to the frequency of updating the diffusion tensor which is denoted by  $\lambda_{RPY}$  in this work.  $\Delta \mathbf{W}_{bl} = [\Delta \mathbf{W}^1, \dots, \Delta \mathbf{W}^s]$  denotes a block of  $s$  standard normal vectors and  $\Delta \mathbf{S}_{bl}$  is the corresponding correlated vectors.

- (Block) Krylov

The Krylov subspace method is used to approximate  $\Delta \mathbf{S} = \mathbf{D}^{1/2} \cdot \Delta \mathbf{W}$  based on the definition of the Krylov subspace,

$$K_m(\mathbf{D}, \Delta \mathbf{W}) = \text{span} \{ \Delta \mathbf{W}, \mathbf{D} \cdot \Delta \mathbf{W}, \dots, \mathbf{D}^{m-1} \cdot \Delta \mathbf{W} \}. \quad (2.12)$$

The approximation has the form  $\Delta \tilde{\mathbf{S}} = p_{m-1}^{Kr}(\mathbf{D}) \cdot \Delta \mathbf{W}$ , where  $p_{m-1}^{Kr}$  is a polynomial of degree of  $m-1$  or less. Similar to the block Cholesky method, a block variant of the Krylov can be used to further improve the efficiency of the algorithm. An additional benefit of using the block Krylov over the Krylov method is that the subspace constructed in solving for  $\Delta \mathbf{S}_{bl}$  is the combination of the subspaces for all vectors  $\Delta \mathbf{S}^i; i = 1, \dots, s$ . Indeed, the resulting subspace is larger than the subspace for the case of a single vector which will result in faster convergence of the block Krylov method [4].

Since the diffusion tensor is symmetric, the Lanczos approach is used to construct the orthonormal basis for the Krylov subspace, i.e.,  $\mathbf{V}_m$  for Lanczos and  $\mathbf{V}_{ms}$  for the Block Lanczos, with  $3N_b \times m$  entries for the former and  $3N_b \times ms$  for the latter. The matrix  $\mathbf{H}_m$  is a tridiagonal  $m \times m$  matrix which is automatically constructed in the Lanczos process and

its block version,  $\mathbf{H}_{ms}$  is a banded  $ms \times ms$  matrix produced in the block Lanczos method. Hence, the Krylov based decomposition algorithm can be interchangeably referred to as the Lanczos method. Further explanations and details on this method can be found in the paper by Ando *et al.* [4](see algorithms 1 and 2 of [4]). The main computational cost associated with this algorithm is the symmetric matrix-vector or matrix-matrix multiplication.

- (Block) Chebyshev

To approximate  $\mathbf{D}^{1/2}$ , Fixman [39] used Chebyshev polynomial of degree  $L$ ,  $p_L^{\text{Ch}}(\mathbf{D})$ , in the interval  $[-1, 1]$  and constructed  $p_L^{\text{Ch}}(\mathbf{D}) \cdot \Delta \mathbf{W}$  without explicitly computing  $p_L^{\text{Ch}}(\mathbf{D})$ . Assuming that the spectrum of matrix  $\mathbf{D}$  (i.e.,  $[\lambda_{\min}, \lambda_{\max}]$ ) lies within the interval  $[d_{\min}, d_{\max}]$ , a shifted matrix is defined as,

$$\mathbf{D}_{\text{sh}} = \frac{1}{a_-} \mathbf{D} - \frac{a_+}{a_-} \mathbf{I}, \quad (2.13)$$

where  $a_- = d_{\max} - d_{\min}/2$ ,  $a_+ = d_{\max} + d_{\min}/2$ , and  $\mathbf{I}$  denotes the identity matrix. Consequently the spectrum of  $\mathbf{D}_{\text{sh}}$  lies in the interval  $[-1, 1]$ . To approximate a general function  $F(\mathbf{D})$  which is the matrix square root in our case, the function  $G(\mathbf{D}_{\text{sh}})$  is defined such that it is equal to  $F(\mathbf{D})$ ,

$$G(\mathbf{D}_{\text{sh}}) = F(a_- \mathbf{D}_{\text{sh}} + a_+ \mathbf{I}). \quad (2.14)$$

$\Delta \tilde{\mathbf{S}}_{\text{Ch}}$  is then computed based on Chebyshev polynomial approximation to  $G(\mathbf{D}_{\text{sh}})$ , in which the polynomial expansion is up to degree  $L$ ,

$$\Delta \tilde{\mathbf{S}}_{\text{Ch}} = \left( \frac{c_0}{2} \mathbf{I} + \left[ \sum_{k=1}^L c_k \mathbf{T}_k(\mathbf{D}_{\text{sh}}) \right] \right) \cdot \Delta \mathbf{W} = \frac{c_0}{2} \Delta \mathbf{W} + \sum_{k=1}^L c_k \Delta \mathbf{V}_k, \quad (2.15)$$

here,  $\mathbf{T}_k$ s are the Chebyshev polynomials and  $\Delta \mathbf{V}_k = \mathbf{T}_k(\mathbf{D}_{\text{sh}}) \cdot \Delta \mathbf{W}$  which is obtained by following recursive formulas,

$$\begin{cases} \Delta \mathbf{V}_0 = \Delta \mathbf{W} \\ \Delta \mathbf{V}_1 = \mathbf{D}_{\text{sh}} \cdot \Delta \mathbf{W} \\ \Delta \mathbf{V}_k = 2\mathbf{D}_{\text{sh}} \cdot \Delta \mathbf{V}_{k-1} - \Delta \mathbf{V}_{k-2}. \end{cases} \quad (2.16)$$

The  $c_k$ s are the polynomial coefficients in the Chebyshev series expansion of shifted square root function  $g(x) = (a_-x + a_+)^{1/2}$  and  $x$  is in the interval  $[-1, 1]$ . The coefficients are given by,

$$c_j = \frac{2}{L+1} \sum_{k=1}^{L+1} g\left(\cos\left(\frac{\pi(k - \frac{1}{2})}{L+1}\right)\right) \cos\left(\frac{\pi j(k - \frac{1}{2})}{L+1}\right). \quad (2.17)$$

In order to have the eigenvalue spectrum for the shifted diffusion matrix in the domain  $[-1, 1]$ ,  $d_{\min}$  and  $d_{\max}$  should represent the correct bounds for all possible eigenvalues throughout the simulation. Exact calculation of the eigenvalues results in little or no additional computational saving of Chebyshev over the Cholesky method. Fixman [39] circumvented this difficulty by using the eigenvalues of the preaveraged RPY tensor. Kröger *et al.* [82] used  $d_{\min} = \frac{\lambda_{\min}^{\text{Zimm}}}{2}$  and  $d_{\max} = 2\lambda_{\max}^{\text{Zimm}}$  in their simulations. Recently Jain *et al.* [69] have proposed  $d_{\min} = \frac{\lambda_{\min}^{\text{Fixman}}}{2}$  and  $d_{\max} = 2\lambda_{\max}^{\text{Fixman}}$  where  $\lambda_{\min}^{\text{Fixman}}$  and  $\lambda_{\max}^{\text{Fixman}}$  are defined by the following expressions based on Fixman's suggestion,

$$\lambda_{\min}^{\text{Fixman}} = \frac{1}{3N_b} (\mathbf{u}_-^T \cdot \mathbf{D} \cdot \mathbf{u}_-), \quad (2.18a)$$

$$\lambda_{\max}^{\text{Fixman}} = \frac{1}{3N_b} (\mathbf{u}_+^T \cdot \mathbf{D} \cdot \mathbf{u}_+), \quad (2.18b)$$

where  $\mathbf{u}_+$  is a  $3N_b$ -dimensional vector whose entire elements are 1 and  $\mathbf{u}_-$  is a vector with the same size as  $\mathbf{u}_+$  but with alternating 1's and -1's.



## Definition of error in iterative decomposition techniques

In order to track the accuracy of the Lanczos and Chebyshev polynomial approximation methods, one has to define the error in estimation of correlated vectors. We used the error expression proposed by Ando *et al.* [4], based on two consecutive iterations,

$$E^{(m)} = \frac{\left\| \Delta \tilde{\mathbf{S}}^{(m)} - \Delta \tilde{\mathbf{S}}^{(m-1)} \right\|_2}{\left\| \Delta \tilde{\mathbf{S}}^{(m-1)} \right\|_2}. \quad (2.19)$$

The same expression holds for  $E^{(L)}$  by replacing  $m$  with  $L$ . For block version of the algorithms, the first column of  $\Delta \tilde{\mathbf{S}}^{(m)}$  was used to calculate the error. The convergence criteria is met when the value of error falls below a certain threshold. Based on the results presented by Ando *et al.* [4],  $E^{(m)} = E^{(L)} = 0.01$  was selected as an indication of sufficient accuracy to reproduce the results of Cholesky decomposition within the statistical error. It is clear that the number of iterations plays a key role in the efficiency of the algorithm. In this regard, we introduce the following additional considerations to enhance the computational efficiency of the algorithms:

- In iteratively updating the degree of polynomials, the part of the matrix  $\mathbf{H}_m$  (or  $\mathbf{H}_{ms}$ ) constructed in the previous iterations (which remains unchanged afterwards) is retained and reused for the current iteration.
- An appropriate initial degree of polynomial, i.e.,  $m_{\text{init}}$  or  $L_{\text{init}}$ , is used in the procedure of iteratively advancing the number of polynomial terms as opposed to starting from the minimum possible value ( $m = L = 2$ ). This value is then updated at some specific time intervals in the simulation. This is applicable for both Lanczos and Chebyshev methods.

These modifications are outlined in the Algorithms A.1-A.3 of Appendix A.

## Efficient linear algebra using the Intel Math Kernel Library (MKL)

The large scale linear algebra operations were performed using different levels (1 to 3) of the MKL\_BLAS library [1]. In particular, GBMV is used for banded matrix-vector products. SYMV and SYMM are used for cases in which one of the operands is a symmetric matrix, TRMV and TRMM are used when one of the operands is a triangular matrix, and GEMV, GEMM are called for the general matrix-vector and matrix-matrix multiplication, respectively. The QR factorization involved in the block Lanczos algorithm is done by GEQRF from the MKL\_LAPACK followed by ORGQR. The Cholesky decomposition is performed with the POTRF routine.

## First Corrector

The  $\mathbf{Q}_{n+1}^\dagger$  from the predictor is subsequently used in the first corrector as,

$$\bar{\mathbf{Q}}_{j,n+1} + \frac{1}{2}\bar{\mathbf{F}}_{j,n+1}^c dt = \bar{\mathbf{\Gamma}}_{j,n+1}, \quad (2.20)$$

here  $j$  specifies the segment index and the  $3(N_b - 1)$  component vector  $\bar{\mathbf{\Gamma}}_{n+1}$  is defined as,

$$\begin{aligned} \bar{\mathbf{\Gamma}}_{n+1} = \mathbf{Q}_n + \left[ \frac{1}{2}Pe \left( \mathbf{K} \cdot \mathbf{Q}_n + \mathbf{K} \cdot \mathbf{Q}_{n+1}^\dagger \right) + \frac{1}{2}\mathbf{F}_n^c + \frac{1}{4}\bar{\mathbf{B}} \cdot \mathbf{D}_n \cdot \mathbf{F}^{\text{spr}} \right. \\ \left. + \frac{1}{8}\bar{\mathbf{B}} \cdot \mathbf{D}_n \cdot \left( \mathbf{F}_n^{\text{EV}} + \mathbf{F}_{n+1}^{\text{EV}\dagger} \right) \right] dt + \frac{1}{\sqrt{2}}\bar{\mathbf{B}} \cdot \Delta \mathbf{S}_n, \end{aligned} \quad (2.21)$$

where  $\mathbf{F}_{n+1}^{\text{EV}\dagger}$  is evaluated based on the estimated configuration  $\mathbf{Q}_{n+1}^\dagger$ . Note that  $\mathbf{F}_\nu^{\text{S}} = \mathbf{F}_{\nu,n}^{\text{S}}$  if  $\nu \geq j$  and  $\mathbf{F}_\nu^{\text{S}} = \bar{\mathbf{F}}_{\nu,n+1}^{\text{S}}$  if  $\nu < j$ . Thus,  $\mathbf{F}^{\text{S}}$  contains the updated conservative forces from the previous segmental loops. The forces corresponding to the next segments are taken from the previous corrector step. The solution for  $\bar{\mathbf{Q}}_{j,n+1}$  is achieved by utilizing the cubic equation which is constructed by replacing the connector force  $\bar{\mathbf{F}}_{j,n+1}^c$  in Equation (2.20) by its definition in Equation (2.4),

$$\begin{cases} \text{WLC :} & x^3 - \left\{ \frac{\sqrt{b}(2+\frac{3}{4}dt)+G}{1+\frac{dt}{3}} \right\} x^2 + \left\{ \frac{b(1+\frac{1}{2}dt)+2\sqrt{b}G}{1+\frac{dt}{3}} \right\} x - \frac{b}{1+\frac{dt}{3}} G = 0 \\ \text{FENE :} & x^3 - Gx^2 - b \left( 1 + \frac{dt}{2} \right) x + bG = 0 \\ \text{ILCCP :} & x^3 - \left\{ \frac{G}{1+\frac{dt}{6}} \right\} x^2 - \left\{ \frac{b(1+\frac{1}{2}dt)}{1+\frac{dt}{6}} \right\} x + \frac{b}{1+\frac{dt}{6}} G = 0, \end{cases} \quad (2.22)$$

where  $x = |\bar{\mathbf{Q}}_{j,n+1}|$ , and  $G = |\bar{\mathbf{\Gamma}}_{j,n+1}|$ .

## Second Corrector

In this final step, an iterative procedure is implemented based on the results obtained from the first corrector,

$$\mathbf{Q}_{j,n+1}^{(k)} + \frac{1}{2} \mathbf{F}_{j,n+1}^{c,(k)} dt = \mathbf{\Gamma}_{j,n+1}^{(k-1)}, \quad (2.23)$$

here,  $k$  is the iteration index and  $\mathbf{\Gamma}_{n+1}^{(k-1)}$  is defined as,

$$\begin{aligned} \mathbf{\Gamma}_{n+1}^{(k-1)} = & \mathbf{Q}_n + \left[ \frac{1}{2} Pe \left( \mathbf{K} \cdot \mathbf{Q}_n + \mathbf{K} \cdot \mathbf{Q}_{n+1}^{(k-1)} \right) + \frac{1}{2} \mathbf{F}_{n+1}^{c,(k-1)} + \right. \\ & \left. \frac{1}{4} \bar{\mathbf{B}} \cdot \mathbf{D}_n \cdot \mathbf{F}_{n+1}^{\text{spr}} + \frac{1}{8} \bar{\mathbf{B}} \cdot \mathbf{D}_n \cdot \left( \mathbf{F}_n^{\text{EV}} + \mathbf{F}_{n+1}^{\text{EV}\dagger} \right) \right] dt + \frac{1}{\sqrt{2}} \bar{\mathbf{B}} \cdot \Delta \mathbf{S}_n, \end{aligned} \quad (2.24)$$

where  $\mathbf{F}_{\nu,n+1}^{\text{spr}} = \mathbf{F}_{\nu,n+1}^{\text{spr},(k-1)}$  if  $\nu \geq j$  and  $\mathbf{F}_{\nu,n+1}^{\text{spr}} = \mathbf{F}_{\nu,n+1}^{\text{spr},(k)}$  if  $\nu < j$ . To initialize the iteration, we use  $\mathbf{Q}_{n+1}^{(0)} = \bar{\mathbf{Q}}_{n+1}$ ,  $\mathbf{F}_{n+1}^{c,(0)} = \bar{\mathbf{F}}_{n+1}^c$ , and  $\mathbf{F}_{n+1}^{\text{spr},(0)} = \bar{\mathbf{F}}_{n+1}^{\text{spr}}$ . The cubic equation resulting from Equation (2.23) is solved in a same manner as in the first corrector step. Convergence is achieved when the relative error,  $\epsilon_{\text{pc}} = \frac{\|\mathbf{Q}_{n+1}^{(k)} - \mathbf{Q}_{n+1}^{(k-1)}\|_2}{\|\mathbf{Q}_{n+1}^{(k-1)}\|_2}$  is less than a specific value (e.g.,  $10^{-4}$ ).  $\|\cdot\|_2$  is the second norm, which is defined to be the square root of the sum of entries of a vector.

## The evolution equations for center of mass and hydrodynamic center of resistance

The evolution equation for the position of center of mass,  $\mathbf{r}_c = (1/N_b) \sum_{\nu} \mathbf{r}_{\nu}$ , can be written as,

$$r_{c,n+1}^q = r_{c,n}^q + \left[ Pe \sum_s \kappa^{qs} \cdot r_{c,n}^s + \frac{1}{4N_b} \sum_{\nu,\mu} \sum_s \Upsilon_{n,\nu\mu}^{qs} \cdot F_{\mu}^{\phi,s} \right] dt + \frac{1}{\sqrt{2}N_b} \sum_{\nu} \Delta S_{n,\nu}^q, \quad (2.25)$$

where  $\{q, s = 1, 2, 3\}$  and  $\Upsilon_{\nu\mu}^{qs}$  is the  $qs^{\text{th}}$  Cartesian component of  $\Upsilon_{\nu\mu}$ . The force in the third term on the right-hand side is the updated force at the end of second corrector step.

Then, the diffusion coefficient of center of mass is calculated in a straight forward manner as:

$$D_{\text{cm}} = \lim_{\tau \rightarrow \infty} \frac{\langle (\mathbf{r}_c(t + \tau) - \mathbf{r}_c(t))^2 \rangle}{6\tau}. \quad (2.26)$$

Note that the parameter used for non-dimensionalization of diffusion coefficient is the diffusion coefficient of a single bead,  $D_0 = k_B T / \zeta$ , as opposed to the characteristic time and length scales.

As the dynamics of center of mass and the position vectors are correlated [11, 112], the center of mass moves relative to the solvent even when there are no external forces acting on the chain. Nevertheless, the motion of the entire molecule can be described using the hydrodynamic center of resistance whose time-evolution is independent of molecule's internal degree of freedom. The position of the hydrodynamic center of resistance,  $\mathbf{r}_h$ , can be expressed in terms of bead positions as (Bird *et al.* [11], chapter 18)

$$\mathbf{r}_h = \sum_{\nu} \boldsymbol{\lambda}_{\nu} \cdot \mathbf{r}_{\nu}, \quad (2.27)$$

where  $\boldsymbol{\lambda}_{\nu}$  is the weight tensor and is defined in Table 16.1-2 of [11]. Then the evolution equation for  $\mathbf{r}_h$  can be written as

$$\mathbf{r}_{h,n+1} = \mathbf{r}_{h,n} + Pe \boldsymbol{\kappa} \cdot \mathbf{r}_{h,n} dt + \frac{1}{\sqrt{2}} \mathbf{L} \cdot \Delta \mathbf{S}_n, \quad (2.28)$$

and  $\mathbf{L} = [\boldsymbol{\lambda}_1, \boldsymbol{\lambda}_2, \dots, \boldsymbol{\lambda}_{N_b}]$ .

The diffusion coefficient of hydrodynamic center of resistance,  $D_{\text{hcr}}$ , is defined by replacing  $\mathbf{r}_c$  with  $\mathbf{r}_h$  in Equation (2.26).

### 2.1.4 Results and discussion

As mentioned earlier, one of the main goals of this chapter is to assess the computational fidelity and efficiency of different decomposition techniques for the diffusion tensor employed in BD simulations of bead-spring chains where the time integration of SDE for the segmental connector vectors is performed with the semi implicit predictor corrector scheme. Hence, much of the discussion below is centered around the determination of parameter set which gives the highest efficiency and the prescribed fidelity simultaneously. For this purpose, the effect of frequency of updating the diffusion tensor,  $\lambda_{\text{RPY}}$  (which also determines the dimension of the block in block versions of decomposition algorithms), is considered on the timing and accuracy of predicting the equilibrium and non-equilibrium properties of bead-spring chain micromechanical model.

#### Frequency of updating the diffusion tensor

In the block version of the aforementioned decomposition methods, the diffusion tensor is updated every  $\lambda_{\text{RPY}}$  time steps as opposed to every time step. The equilibrium squared radius of gyration and transient fractional extension have been used to ascertain the error associated with this simplification.

The HI and EV model parameters selection has been motivated by earlier studies [83, 151, 68, 146]. As the finite extensible springs are used in our simulations, the important non-dimensional parameter characterizing the EV interactions is  $\tilde{z}^*$ [151],

$$\tilde{z}^* = \frac{z^*}{\chi(b)^3}, \quad (2.29)$$

where  $\chi$  is the characteristic length of the spring in the units of  $l_H$ . For a FENE spring, this can be written as  $\chi = \sqrt{\frac{b}{b+5}}$  [11, 151], where  $b$  is the squared maximum extensibility of the spring. For other spring force models,  $\chi$  can be obtained numerically as a function of  $b$  [151], e.g., for the case of ILCCP force law it is given as,

$$\chi^2 = b^{1/3} \frac{\int_0^1 q^4 \left\{ (1 - q^2)^{b/3} \exp[-b/6q^2] \right\} dq}{\int_0^1 q^2 \left\{ (1 - q^2)^{b/3} \exp[-b/6q^2] \right\} dq}, \quad (2.30)$$

where  $q = Q/Q_{max}$  is the fractional extension and  $Q_{max} = \sqrt{b}$ . When  $b \rightarrow \infty$ , the Hookean spring behavior is recovered and  $\chi \approx 1$ . Clearly, The parameter  $\tilde{z}^*$  is related to solvent quality, i.e.,  $z$ , as  $\tilde{z}^* = z/\sqrt{N_b}$ .  $z$  depends on the absolute temperature and the molecular weight as follows:

$$z = \nu_0 (1 - T_\theta/T) \sqrt{M_w}, \quad (2.31)$$

where  $\nu_0$  is a chemistry dependent constant and  $T_\theta$  is the  $\theta$ -temperature.  $1 \leq z \leq 4$  is generally associated with good solvents [68]. For both equilibrium and non-equilibrium simulations reported in section 2.2.6,  $z = 1.4$  and the dimensionless range of the EV potential is taken as  $d^* = 2.5$ . In section 2.2.6, the EV potential parameters that are consistent for polymers with different length are selected following the strategy suggested by Kumar and Prakash [83], namely  $z^* = z\chi^3/\sqrt{N_b}$ , is used along with  $d^* = z^{*1/5}$ , and  $z\chi^3 = 1$  for  $N_b = 10$ . Note that when successively increasing the number of segments (or equivalently the molecular weight),  $z$  has to be increased according to scaling relationship in Equation (2.31). Moreover, the values of  $d^*$  according to this scheme permits the use of larger time steps in the numerical integration [83, 146]. The HI parameter can also be rescaled using  $\chi$  as  $\tilde{h}^* = \frac{h^*}{\chi}$ . Here,  $\tilde{h}^*$  must be reinterpreted as the ratio of the bead radius to the characteristic length of the finitely extensible spring. It is well-known that the physically acceptable values of  $h^*$  for a chain of Hookean springs lie in the range of  $0 < h^* \lesssim 0.5$  [112]. In section 2.2.6, hydrodynamic interaction parameter  $h^*$  is equal to 0.25 unless otherwise noted.

The longest dimensionless relaxation time is obtained by fitting a 3-parameter exponential to the decay of the mean square end to end distance [146]. For simulations in equilibrium

and under planar extensional flow in [section 2.2.6](#),  $\lambda_1^*$  was found to be equal to 117.74. In accord with earlier studies [\[55\]](#), the FENE force law was used with the maximum extension of each spring  $b = 20$  which results in  $\chi \approx 0.89$ .

### Effect of $\lambda_{\text{RPY}}$ on equilibrium behavior

In this section, the effect of  $\lambda_{\text{RPY}}$  and time step on the accuracy of predicted equilibrium radius of gyration  $\langle R_g^2 \rangle$  of the molecules is considered. The time step size is of particular interest when the semi implicit predictor-corrector scheme is used as large time steps do not result in unphysical overstretching of the chain segments [\[112, 147, 59\]](#); however, the accuracy of the predictions clearly depends on the magnitude of the time step. [Table 2.1](#) illustrates the error in the computed ensemble averaged squared radius of gyration  $\langle R_g^2 \rangle$  as a function of time step size and  $\lambda_{\text{RPY}}$  at  $h^* = 0.15$ . The ensemble averaged squared radius of gyration calculated using  $dt = 1 \times 10^{-3}$ ,  $\lambda_{\text{RPY}} = 1$  and Cholesky method is set as the reference value whose statistical error is 1.43%. Hence, the accuracy of results from all three decomposition methods and different sets of  $\lambda_{\text{RPY}}$  and  $dt$  will be determined based on comparison with this value. The relative error is defined as  $\text{Error} = |\langle R_g^2 \rangle - \langle R_g^2 \rangle_{\text{ref}}| / \langle R_g^2 \rangle_{\text{ref}}$ . The combined effect of  $dt$  and  $\lambda_{\text{RPY}}$  on the computational efficiency and fidelity is computed via  $\lambda_{\text{RPY}} dt$  [\[59\]](#). It is clearly observed that using the exact decomposition method, the Cholesky, as well as the approximation methods, the Chebyshev and the Lanczos result in accurate computations (Error < 3%) provided that  $\lambda_{\text{RPY}} dt \leq 0.1$ .

The results of the computations with  $h^* = 0.25$  are summarized in [Table B.1](#) of Appendix B. Clearly, the Lanczos method with  $dt$  less than 0.05 provides the equilibrium  $\langle R_g^2 \rangle$  with very small error. A comparison of different sets of  $dt$  and  $\lambda_{\text{RPY}}$  for fixed  $\lambda_{\text{RPY}} dt = 0.05$  and 0.5 shows that for similar  $\lambda_{\text{RPY}} dt$ , simulations with larger  $\lambda_{\text{RPY}}$  shows higher error. Similar to the case of  $h^* = 0.15$ , accurate results for  $\langle R_g^2 \rangle$  are obtained when  $\lambda_{\text{RPY}} dt \leq 0.1$  in the representative parameter range studied.

**Table 2.1:** (%)Error in  $\langle R_g^2 \rangle$  of polymers with 50 beads and  $h^* = 0.15$  obtained with various time steps and update intervals relative to the results of Cholesky with unit block dimension and  $dt = 1 \times 10^{-3}$ .

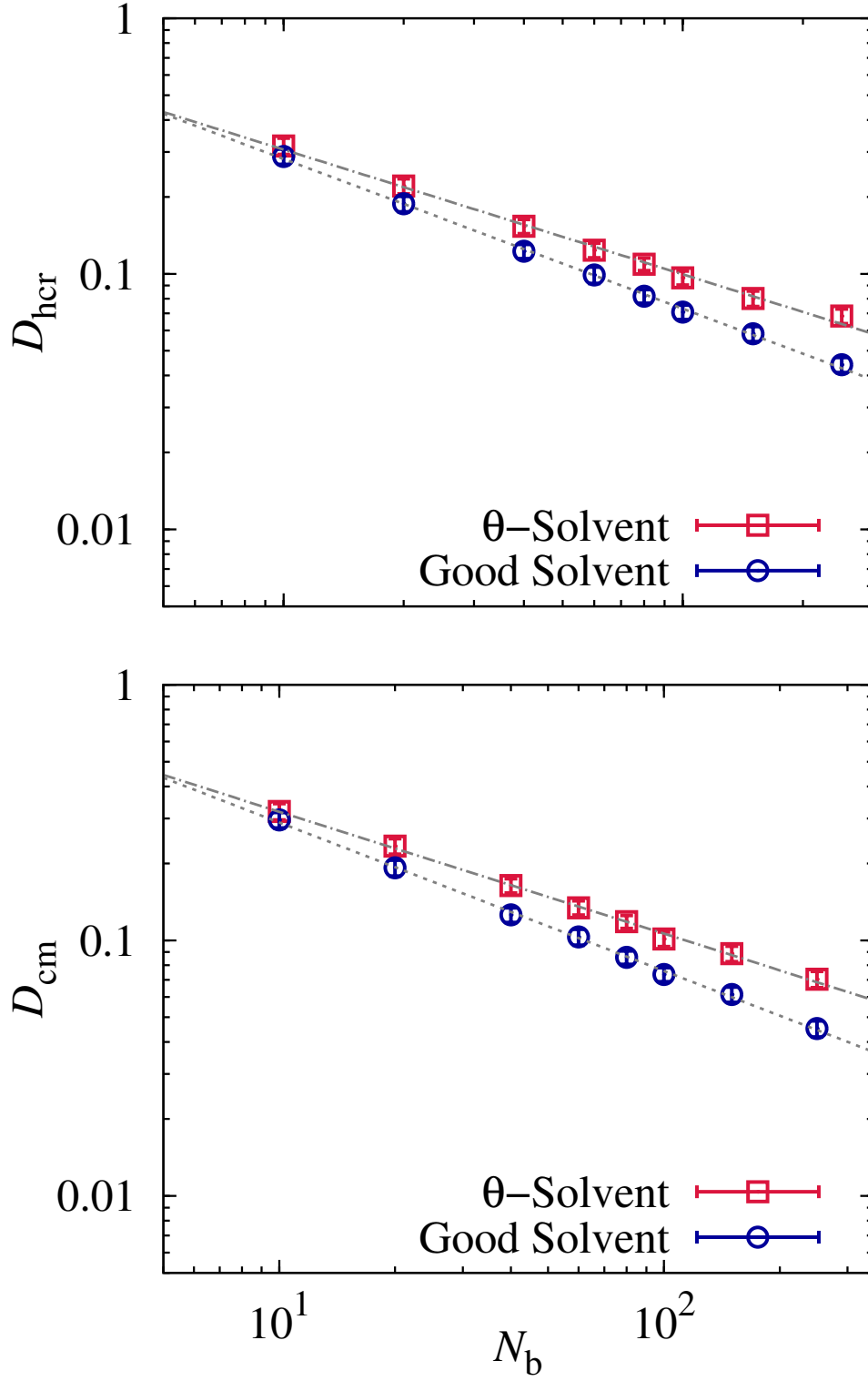
| Method    | $dt$               | $\lambda_{RPY}$ | $\lambda_{RPY}dt$  | $\langle R_g^2 \rangle$ | (%)Error        |
|-----------|--------------------|-----------------|--------------------|-------------------------|-----------------|
| Cholesky  | $1 \times 10^{-3}$ | 1               | $1 \times 10^{-3}$ | $26.12 \pm 0.37$        | Ref. $\pm 1.43$ |
| Cholesky  | 0.01               | 5               | 0.05               | $25.64 \pm 0.37$        | 1.84            |
| Lanczos   | 0.01               | 5               | 0.05               | $25.72 \pm 0.37$        | 1.51            |
| Chebyshev | 0.01               | 5               | 0.05               | $25.89 \pm 0.37$        | 0.90            |
| Cholesky  | 0.1                | 1               | 0.1                | $25.47 \pm 0.37$        | 2.5             |
| Lanczos   | 0.1                | 1               | 0.1                | $25.53 \pm 0.37$        | 2.26            |
| Chebyshev | 0.1                | 1               | 0.1                | $25.68 \pm 0.37$        | 1.68            |
| Cholesky  | 0.1                | 5               | 0.5                | $25.03 \pm 0.36$        | 4.19            |
| Lanczos   | 0.1                | 5               | 0.5                | $25.03 \pm 0.36$        | 4.16            |
| Chebyshev | 0.1                | 5               | 0.5                | $25.18 \pm 0.36$        | 3.61            |
| Cholesky  | 0.1                | 25              | 2.5                | $24.38 \pm 0.35$        | 6.63            |
| Lanczos   | 0.1                | 25              | 2.5                | $24.48 \pm 0.36$        | 6.3             |
| Chebyshev | 0.1                | 25              | 2.5                | $24.55 \pm 0.36$        | 6.00            |

### The diffusion coefficient scaling

In [Figure 2.1](#), logarithmic plots of  $D_{\text{hcr}}$  and  $D_{\text{cm}}$  are depicted as a function of  $N_b$  using the Lanczos algorithm for a  $\theta$ -solvent as well as a good solvent with  $dt = 0.05$  and  $\lambda_{RPY} = 1$ . As expected, the predictions of the Lanczos and the Chebyshev algorithms are quite close as both methods use polynomials to approximate the Brownian noise vector. The difference between these two algorithms and the Cholesky decomposition with  $dt = 0.01$  was within the statistical error of the latter method for the cases tested (data not shown).

The computed diffusion coefficients exhibit the expected scaling, i.e.,  $D_{\text{hcr}} \propto N_b^{-\nu_{\text{hcr}}}$  (or  $D_{\text{cm}} \propto N_b^{-\nu_{\text{cm}}}$ ). It is well known that for polymeric chains in a  $\theta$ -solvent  $\nu \approx 0.5$  [[11](#), [112](#)] and  $\nu \approx 0.588 \pm 0.001$  in a good solvent respectively [[93](#), [30](#)]. Specifically, consistent with theory and experiment, our computed exponents are  $\nu_{\text{hcr}} = 0.488 \pm 0.017$  ( $\nu_{\text{cm}} = 0.477 \pm 0.01$ ) and  $\nu_{\text{hcr}} = 0.586 \pm 0.01$  ( $\nu_{\text{cm}} = 0.581 \pm 0.01$ ) for macromolecules in a  $\theta$ -solvent and good solvents, respectively. It should be noted that an ensemble of 150 chains and  $\tau$  ranging from  $45\lambda_1^*$  to  $60\lambda_1^*$  were used to calculate the diffusion coefficients (see Equation [\(2.26\)](#)).





**Figure 2.1:** Hydrodynamic center of resistance (hcr) and center of mass (cm) diffusion coefficient as a function of  $N_b$ .

### Effect of $\lambda_{\text{RPY}}$ on chain extension in planar extensional flow

The fractional extension of the molecules as a function of time or Hencky strain is a good measure of the dynamics of polymer molecules in elongational flow [116, 138, 87]. This transient behavior at  $Wi = 1.5$  and  $h^*$  equal to 0.15 as well as 0.25 are considered in this section as another criteria to obtain a range for  $dt$  and  $\lambda_{\text{RPY}}$  in which the relative error with respect to the reference case is below an acceptable threshold. The relative error listed in Table 2.2 is defined as  $\text{Error} = \|R_{\text{ee}} - R_{\text{ee,ref}}\|_2 / \|R_{\text{ee,ref}}\|_2$ , where  $R_{\text{ee}}$  contains the chain end-to-end distance at different Hencky strains ranging from 0 to 7.5 and  $R_{\text{ee,ref}}$  is the corresponding reference data which is obtained using  $dt = 0.001$ ,  $\lambda_{\text{RPY}} = 1$ , and Cholesky decomposition, with the maximum statistical error 2.09 and 2.10 for  $h^* = 0.25$  and  $h^* = 0.15$ , respectively.

**Table 2.2:** (%)Error in transient fractional extension of molecules with  $N_b = 50$  in planar extensional flow at  $Wi = 1.5$  obtained with various time steps and update intervals relative to the results of Cholesky with unit block dimension and  $dt = 1 \times 10^{-3}$ .

| $h^*$ | Method    | $dt$               | $\lambda_{\text{RPY}}$ | $\lambda_{\text{RPY}} \times dt$ | (%)Error        |
|-------|-----------|--------------------|------------------------|----------------------------------|-----------------|
| 0.25  | Cholesky  | $1 \times 10^{-3}$ | 1                      | $1 \times 10^{-3}$               | Ref. $\pm 2.09$ |
| 0.25  | Cholesky  | 0.1                | 1                      | 0.1                              | 1.87            |
| 0.25  | Lanczos   | 0.1                | 1                      | 0.1                              | 2.47            |
| 0.25  | Chebyshev | 0.1                | 1                      | 0.1                              | 1.73            |
| 0.25  | Cholesky  | 0.01               | 50                     | 0.5                              | 2.73            |
| 0.25  | Lanczos   | 0.01               | 50                     | 0.5                              | 2.38            |
| 0.25  | Chebyshev | 0.01               | 50                     | 0.5                              | 1.74            |
| 0.15  | Cholesky  | $1 \times 10^{-3}$ | 1                      | $1 \times 10^{-3}$               | Ref. $\pm 2.10$ |
| 0.15  | Cholesky  | 0.01               | 5                      | 0.05                             | 1.85            |
| 0.15  | Lanczos   | 0.01               | 5                      | 0.05                             | 1.71            |
| 0.15  | Chebyshev | 0.01               | 5                      | 0.05                             | 1.71            |
| 0.15  | Lanczos   | 0.1                | 1                      | 0.1                              | 2.32            |
| 0.15  | Chebyshev | 0.1                | 1                      | 0.1                              | 2.21            |

On the basis of the results summarized in Table 2.2,  $\lambda_{\text{RPY}}$  and  $dt$  also affect the accuracy of predicting the unraveling of polymeric chains in planar extensional flow. Particularly, for all three decomposition techniques and different  $h^*$  values, error in predicting the unraveling dynamics at  $Wi = 1.5$  is less than 3% for  $\lambda_{\text{RPY}}dt$  up to 0.5.

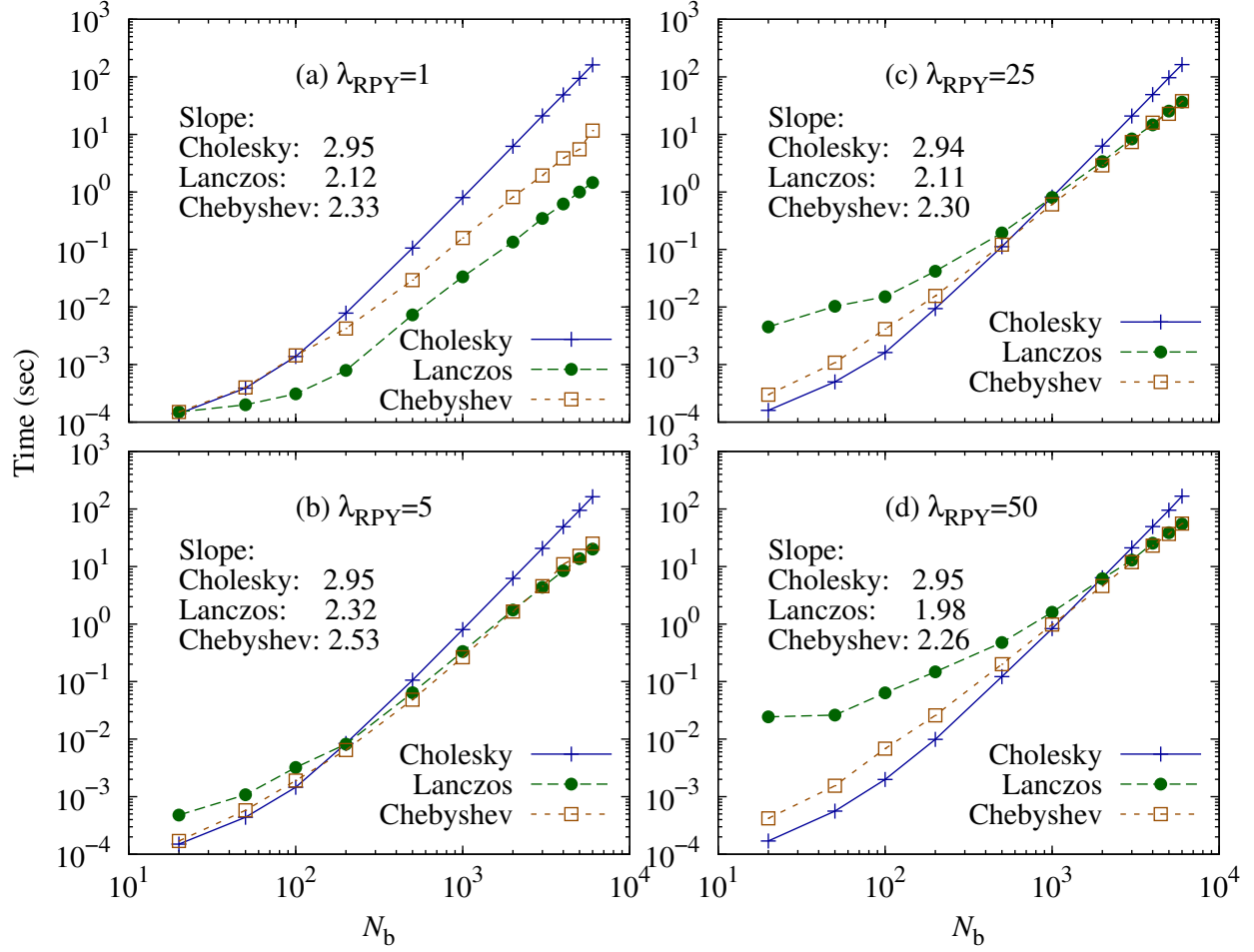
The results of similar tests at  $Wi = 0.65$  are reported in [Table B.2](#) of [Appendix B](#). Overall, our computations demonstrate that for equilibrium and/or flow condition at different  $Wi$  and HI strength, the simulations with  $\lambda_{\text{RPY}}dt \leq 0.1$  give rise to accurate results.

### Comparison of computational time

The computational efficiency of previously mentioned decomposition techniques were compared for different values of  $\lambda_{\text{RPY}}$ . The tests were performed on a quad-core Intel Xeon W3550 processor. [Figure 2.2\(a\)](#)-[Figure 2.2\(d\)](#) show the wall time (computed with `MPI_Wtime`) and the scaling of execution time with number of beads for generating 1, 5, 25, and 50 Brownian noise vectors, respectively. It should be noted that to report the slope in the linear region, the fitting was performed after  $N_b = 500$  for [Figure 2.2\(a\)](#)-[Figure 2.2\(c\)](#) and after  $N_b = 1000$  for [Figure 2.2\(d\)](#). Also note that both  $E^{(m)}$  and  $E^{(L)}$  are equal to 0.01.

As it can be observed in [Figure 2.2\(a\)](#), for the case of  $\lambda_{\text{RPY}} = 1$ , both Lanczos and Chebyshev algorithms are much more efficient than Cholesky even in the limit of small number of beads. It should be noted that the number of iterations range was in agreement with the corresponding reports by Ando *et al.* [\[4\]](#) (data not shown). The Lanczos algorithm is considerably faster than the Chebyshev for unit block dimension and their difference continuously grows for larger number of beads (see the slopes in [Figure 2.2\(a\)](#)). This is attributed to the smaller number of iterations required by the Lanczos algorithm [\[4\]](#).

There is another important characteristic behavior which has not been highlighted in the previous studies on cases with non-unit block dimensions. As it is illustrated in [Figure 2.2\(b\)](#) through [Figure 2.2\(d\)](#), there would be a cross-over point after which the Lanczos and Chebyshev become advantageous over the Cholesky method. The reason for this behavior is due to the fact that the main computational part of the Cholesky algorithm is the decomposition which does not change through increasing the block dimension. For the Lanczos method, however, the arithmetic operations in the time consuming part of Algorithm 1 (line 7) is  $\lambda_{\text{RPY}}$  times that of Algorithm 2 and there is a QR factorization involved in the block version of algorithm at each iteration. Hence, as can be seen in [Figure 2.2](#), there is a substantial difference between the computational timing of the block version of Lanczos



**Figure 2.2:** Time for generating  $\lambda_{\text{RPY}}$  Brownian vector with  $E^{(m)} = E^{(L)} = 0.01$ .

algorithm and the Lanczos algorithm. For the Chebyshev algorithm, the difference between the results of  $\lambda_{\text{RPY}}$  larger than one and  $\lambda_{\text{RPY}}$  equal to one only stem from larger number of arithmetic operations, particularly in line 12 of Algorithm 3. The cross-over  $N_b$  is around 200 for the case of  $\lambda_{\text{RPY}} = 5$ . As can be observed in Figure 2.2(b) through Figure 2.2(d), by advancing the block dimension size, the value of cross over point will be altered to larger number of beads. For the largest block dimension,  $\lambda_{\text{RPY}} = 50$ , although the scaling becomes  $\mathcal{O}(N_b^2)$  for Lanczos and  $\mathcal{O}(N_b^{2.25})$  for Chebyshev, the scaling for Cholesky remains at  $\mathcal{O}(N_b^{2.95})$ .

We have tabulated the comparison of CPU time of the entire simulation for a period of  $\lambda_1^*$  in [Table 2.3](#). In this table, the overall timings of different decomposition techniques are compared when the chain contains number of beads ranging from 58 to 476. The tests were performed for the polystyrene with 20 million molecular weight in the presence of HI and EV at  $Wi = 10$  under uniaxial extensional flow. Note that these experiments were performed on a twelve-core per node Intel Xeon X5660 cluster.

**Table 2.3:** Comparison of overall computational time in seconds required for simulating a chain with different number of beads under uniaxial extensional flow at  $Wi = 10$ . A period of  $\lambda_1^*$  along with  $dt = 0.1$  and  $\lambda_{\text{RPY}} = 1$  are considered for these tests. The amount of computational saving when the Cholesky is replaced by the Lanczos or the Chebyshev are reported in parenthesis.

| $N_b$ | $\lambda_1^*$      | Cholesky | Lanczos       | Chebyshev     |
|-------|--------------------|----------|---------------|---------------|
| 58    | $4.08 \times 10^2$ | 7.16     | 6.14 (14.2%)  | 7.54 (-5.3%)  |
| 96    | $1.02 \times 10^3$ | 58       | 48 (17.4%)    | 56 (3.4%)     |
| 134   | $1.83 \times 10^3$ | 249      | 196 (21.3%)   | 221 (10.9%)   |
| 191   | $3.10 \times 10^3$ | 1100     | 863 (21.5%)   | 975 (11.4%)   |
| 286   | $7.02 \times 10^3$ | 7359     | 5699 (22.6%)  | 6373 (13.4%)  |
| 476   | $1.66 \times 10^4$ | 73981    | 56387 (23.8%) | 59339 (19.8%) |

[Table 2.3](#) reflects the computational saving when the Cholesky decomposition is replaced by one of the alternative algorithms. The results indicate that the Chebyshev is more efficient than the Cholesky for the number of segments larger than 58 whereas the Lanczos is the best algorithm among the three for all of the studied cases. Moreover, one can achieve up to 25% computational saving by substituting highly efficient Cholesky decomposition with the the Lanczos algorithm when the chain consists of few hundred beads. We expect higher savings for  $N_b \propto \mathcal{O}(10^3)$  or higher. Clearly for these large scale systems, the decomposition has higher contribution to the overall timings and the difference between the time spent on decomposition part of the simulation when using the Lanczos instead of the Cholesky keeps increasing as  $N_b$  is increased (see [Figure 2.2\(a\)](#)).

### 2.1.5 Conclusions

We have considered a class of decomposition techniques, namely Cholesky factorization, Chebyshev polynomial, and Lanczos based techniques, for inclusion of HI and EV in BD simulations of bead-spring micro-mechanical models with the semi implicit predictor-corrector scheme. The Chebyshev polynomial and Lanczos algorithms are the most promising alternatives to Cholesky decomposition particularly when the chains contain a large number of segments. Both Chebyshev and Lanczos methods use polynomials to approximate the Brownian noise vector, and the latter requires a smaller degree of polynomial for achieving the same level of accuracy. Moreover, the Lanczos method does not need the estimation of extreme eigenvalues of  $\mathbf{D}$ , which is an expensive procedure involved in Chebyshev based techniques. We have further refined the aforementioned techniques towards increasing their computational efficiency.

The fidelity and efficiency of the algorithms were demonstrated by simulating the radius of gyration and the diffusivity of equilibrium and fractional extension as a function of Hencky strain in planar extensional flow. The results indicated that in order to achieve high computational efficiency and accurate prediction of material properties, the semi implicit predictor-corrector scheme can be employed with a relatively large  $dt$ . It was also shown that the selected  $\lambda_{\text{RPY}}$  should result in  $\lambda_{\text{RPY}}dt \leq 0.1$ .

Our studies in [section 2.2.6](#) indicated that the Chebyshev based techniques and the Lanczos method show the highest improvement in computational efficiency over the Cholesky algorithms when  $\lambda_{\text{RPY}}$  is set to 1. Hence, Lanczos based techniques are the most efficient algorithms for the range of  $N_b$  studied (10 to  $7 \times 10^3$ ). On the other hand, when larger  $\lambda_{\text{RPY}}$  is utilized there is a cross-over  $N_b$ , below which the Cholesky decomposition show the lowest computational time among the three. However, the Chebyshev and the Lanczos techniques become less expensive than the Cholesky after cross-over  $N_b$ . For the case of  $\lambda_{\text{RPY}} = 50$ , the asymptotic scaling exponents of computational time for Cholesky, Chebyshev and Lanczos algorithms approach to 3, 2.25 and 2, respectively.

## 2.2 Semidilute solutions (interacting multichain systems)

### 2.2.1 Introduction

The effect of concentration on equilibrium and dynamic properties of polymer solutions has been observed experimentally even at very low concentrations [37, 89, 62]. Accurate determination of the aforementioned properties of the polymer solutions near or above  $c^*$  (i.e., the semidilute regime) is of great importance to the polymer physics as well as polymer processing communities. To this end, development of hi-fidelity and computationally efficient simulation techniques for this class of fluids is important both from a scientific perspective and in industrial applications.

In semidilute polymeric solutions, HI is due to the movement of all segments of the same chain (intra-chain interaction) and the segments of other chains (inter-chain interaction). Because of the long-range nature of HI, simulations of large multi-chain systems are predominantly performed for homogeneous systems in unbounded domains which necessitates the application of periodic boundary condition. Moreover, EV is short-range, in the sense that the interaction is restricted to the entities involved in the cutoff radius.

In particular,  $N_c$  chains are considered in a periodic box, so the number of interacting beads is  $N = N_c N_b$ . Each bead interacts not only with the beads inside the primary simulation box, but also with particles in all periodic replicas (images) of the primary box. This sum is known to be slowly and/or conditionally convergent [10, 69]. Similar to Electrostatic interactions (which is an example of long-range interaction), Ewald summation can be employed to split the original sum into two exponentially decaying sums in real and reciprocal spaces [10, 149, 69]. In this approach, one can distribute the computational load between the real and reciprocal space sums by tuning a parameter  $\alpha$ , such that for instance one of the computations scales as  $\mathcal{O}(N)$  and the other scales as  $\mathcal{O}(N^2)$  [69]. Hence, in a straight forward implementation of the Ewald sum, the construction of the diffusion matrix requires  $\mathcal{O}(N^2)$  operations. This procedure followed by the decomposition which also scales

as  $\mathcal{O}(N^2)$  (if the Krylov subspace method is used) are the most cost prohibitive procedures in simulating the polymer solutions with concentrations well above  $c^*$ . Similar arguments apply for colloidal suspensions which contain  $N$  particles in the simulation box.

To mitigate the high computational cost of simulating long-range electrostatic interactions, approximation methods such as particle mesh Ewald (PME) [23, 36] and/or particle-particle particle-mesh (P<sup>3</sup>M) [56, 28] have been successfully introduced. Smooth particle mesh Ewald (SPME) is another variant of PME which has improved accuracy due to utilization of high-order B-splines instead of the Lagrange function in PME, in the grid value assignment and interpolation parts of the algorithm. In this approach, small subset of interacting particles is treated in the real space while the main load (large number of particles) is transferred to the reciprocal space sum where fast Fourier transform (FFT) is employed to accelerate the computations. Efficient implementation of this method leads to the scaling of  $\mathcal{O}(N \log N)$ .

Guckel [49] applied the idea of PME method developed for electrostatic interactions to hydrodynamic interactions of rigid particles in Stokes flow. Subsequently, Brady and co-workers introduced Accelerated Stokesian Dynamics (ASD) [140, 8] which benefits from PME algorithm in calculation of the far-field mobility matrix. Saintillan *et al.* [133] combined SPME and ASD algorithms to simulate long-range HI of sedimenting fibers. For polymer solution systems confined between two parallel walls, Hernández-Ortiz *et al.* [54, 53] introduced a “general geometry Ewald-like” BD method that scales as  $\mathcal{O}(N^{1.25} \log N)$ . In the context of BD simulations, Jain *et al.* [69] used another class of optimization which is based on the original Ewald summation but with an optimal value of  $\alpha$ , such that computational expense is evenly distributed between real and reciprocal space sums. Jain *et al.*, also used the Chebyshev polynomial approximation for calculating the decomposition of the diffusion tensor and were able to obtain the computational time which scales as  $\mathcal{O}(N^{1.8})$ .

Recently, Liu and Chow [98] introduced the “matrix-free” approach in the context of BD simulation of colloidal suspensions. In their approach, the computational burden of the real space sum is substantially reduced by considering the interaction of particles within a small cutoff radius. This causes the real part of the diffusion matrix to be highly sparse,



hence, it can be efficiently computed. To compute the decomposition of diffusion tensor, Liu and Chow used the Krylov subspace method (Note that in matrix-free algorithm, the direct decomposition of diffusion matrix, e.g., the Cholesky factorization, can not be used; see [section 2.2.4](#)). On the other hand, the reciprocal part is calculated using highly efficient FFT routines. The final implementation was capable of simulating systems with as many as 500,000 particles.

While the Ewald summation for HI in ASD is based on the Oseen-Burgers tensor [\[140\]](#), Beenakker’s Ewald sum [\[10\]](#) which is widely used in BD simulations is based on the Rotne-Prager-Yamakawa (RPY) tensor [\[149, 161, 69, 98\]](#). The RPY tensor, consists of two branches, namely far-field solution and the regularization of the singularity which occurs for inter-bead distances of less than the diameter of a bead (see [section 2.1.2](#)). The Beenakker’s solution only considers the far-field part of RPY. This solution works well only when the beads do not overlap, which is the case if a strong enough EV potential is utilized. However, there should be a correction to the original Beenakker’s formula for the simulation of the systems where the overlap of the beads is permitted, e.g.,  $\theta$ -solutions. Zhou and Chen [\[161\]](#) and Jain *et al.* [\[69\]](#) resolved this issue by appropriately taking into account the second branch of RPY in case of an overlap.

In [section 2.2.2](#), we start by formulating the stochastic differential equation (SDE) such that it can be used in both Euler-Murayama as well as semi implicit predictor-corrector schemes [\[112, 147, 130\]](#). Then, we adopt a matrix-free algorithm for simulating semidilute polymer solutions where an optimized version of the Krylov subspace approach recently developed for calculating Brownian displacements [\[5, 130\]](#) is implemented. Compared to the original implementation of matrix-free approach for colloidal suspensions [\[98\]](#), our implementation has the extended capability of correctly accounting for the overlap between the beads which is particularly important for polymer solutions in  $\theta$ -solvent or slightly better-than- $\theta$ -solvent. Also in this work, the EV potential is incorporated using the soft Gaussian potential which has been extensively used in predicting the behavior of macromolecules in slightly better than theta and good solvents [\[123, 151, 130\]](#). Overall, our algorithm has several improved features when compared to those of Stoltz *et al.* [\[149\]](#) and Jain *et al.* [\[69\]](#):

(i) it uses highly efficient libraries for sparse matrix vector multiplication (math kernel library or MKL) to calculate the real space contribution of diffusion tensor; (ii) FFT calculations are performed using the efficient MKL routines; (iii) fine-grained level parallelization for shared memory platforms using OpenMP has been added.

### 2.2.2 Governing equations

For simulation of semidilute polymer solution, the box is assumed to have sides with equal length  $L$ ; i.e.,  $V = L^3$  [149, 161, 69]. Therefore, the concentration of beads in the box is given by  $c = \frac{N}{V}$ , where  $N = N_c N_b$ . Here, we use the convention that  $\nu, \mu = 1, \dots, N$ ,  $\beta = 1, \dots, N_b$ ,  $\gamma = 1, \dots, N_b - 1$ ,  $i = 1, \dots, N_c$ , and  $q, s = 1, 2, 3$ . The configurational state of the system can be specified by the position vector of all beads  $\mathbf{r}_\nu$ , or equivalently using the connector vectors of all springs in the simulation box  $\mathbf{Q}_{i,\gamma}$  and the center of mass of all chains  $\mathbf{r}_{c,i}$ . The Itô SDE of bead-spring model (Equation (2.1)) is non-dimensionalized using the protocols mentioned in section 2.1.2. As we are dealing with the equilibrium properties of the semidilute polymeric solutions in this section, the terms regarding the flow is not present in the SDE,

$$d\tilde{\mathbf{Q}} = \tilde{\tilde{\mathbf{B}}} \cdot d\mathbf{r} = \tilde{\tilde{\mathbf{B}}} \cdot \left[ \frac{1}{4} \overbrace{\mathbf{D} \cdot \mathbf{F}^\phi}^u dt + \frac{1}{\sqrt{2}} \mathbf{C} \cdot d\mathbf{W} \right], \quad (2.32)$$

where  $\tilde{\mathbf{Q}}$  is a block column vector consisting of  $N_c$  block vectors  $\mathbf{Q}_i$ , each of which contains  $N_b - 1$  connector vectors between the adjacent beads of an individual chain  $i$ , i.e.,  $\mathbf{Q}_{i,\gamma} = \mathbf{r}_{\nu+1} - \mathbf{r}_\nu$  and  $\nu = (i - 1) N_b + \gamma$ .  $\tilde{\tilde{\mathbf{B}}}$  is a diagonal square block matrix with dimensions  $N_c$ , where each of its diagonal elements is  $\bar{\mathbf{B}}$ . The diffusion matrix  $\mathbf{D}$  is also a block matrix which contains  $N \times N$  blocks and due to long-range nature of HI, each block involves the sum of the corresponding RPY HI tensor  $\Upsilon_{\nu\mu}$  over infinite periodic images.

The excluded volume force for a bead  $\nu$  is calculated within an effective cutoff radius  $r_{c,F}$ :

$$\mathbf{F}_\nu^{\text{EV}} = \begin{cases} \sum_{\mu \neq \nu} \left( \frac{z^*}{d^{*5}} \right) \mathbf{r}_{\nu\mu} \exp \left( -\frac{r_{\nu\mu}^2}{2d^{*2}} \right) & r_{\nu\mu} \leq r_{c,F} \\ 0 & r_{\nu\mu} > r_{c,F}. \end{cases} \quad (2.33)$$

Note that the conservative spring force on the beads is obtained by using the relation  $\mathbf{F}^{\text{spr}} = -\tilde{\mathbf{B}}^T \cdot \mathbf{F}^c$ . Also, the term  $\mathbf{D} \cdot \mathbf{F}^\phi$  can be interpreted as a vector containing the velocity perturbation at the position of the beads  $\mathbf{u}$ .

The evolution equation for the position of center of mass of the chain  $i$ , i.e.,  $\mathbf{r}_{c,i} = (1/N_b) \sum_{\beta=1}^{N_b} \mathbf{r}_{i,\beta}$ , is written as,

$$r_{c,i;n+1}^q = r_{c,i;n}^q + \frac{1}{N_b} \left[ \frac{1}{4} \sum_{\beta=1}^{N_b} u_{\{i,\beta\};n}^q \Delta t + \frac{1}{\sqrt{2}} \sum_{\beta=1}^{N_b} \Delta S_{\{i,\beta\};n}^q \right], \quad (2.34)$$

where  $\{q = 1, 2, 3\}$  refers to the 3 Cartesian coordinates and  $\Delta \mathbf{S}_n = \mathbf{C}_n \cdot \Delta \mathbf{W}_n$  is the Brownian displacement after  $n$  time steps.

The numerical integration of the governing differential equation (Equation (2.32)) can be performed by either the Euler-Murayama or a semi implicit predictor-corrector scheme [130]. We have implemented both integration methods. In the predictor-corrector scheme, as  $\mathbf{F}^\phi$  gets updated in the corrector steps, it is necessary to calculate  $\mathbf{D} \cdot \mathbf{F}^\phi$ , which in the case of large  $N$  is a very expensive procedure. On the other hand, at equilibrium where  $10^{-3} \lesssim \Delta t \leq 10^{-2}$ , the Euler-Murayama method results in sufficient accuracy. Hence, this method is used in our computations reported in this paper. However, in non-equilibrium simulations, the difference between the appropriate time step for the Euler-Murayama and the semi implicit predictor-corrector can be around 3 orders of magnitude, particularly at high flow strengths [59]. The efficiency of the predictor-corrector versus the Euler-Murayama method for non-equilibrium simulations remains to be addressed in future communications.

It should also be noted that the positions of the beads are obtained from the conversion of  $\tilde{\mathbf{Q}}$  to  $\mathbf{R}$ , where  $\mathbf{R}_{i,\beta} = \mathbf{r}_{i,\beta} - \mathbf{r}_{c,i}$ , with the help of the equation  $\mathbf{R} = \tilde{\mathbf{B}} \cdot \tilde{\mathbf{Q}}$  and the matrix

$\tilde{\mathcal{B}}$  is  $N_c \times N_c$  matrix with only diagonal non-zero blocks  $\mathcal{B}$  which is defined as follows,

$$\mathcal{B}_{\beta\gamma} = \begin{cases} \frac{\gamma}{N_b} \delta & \gamma < \beta \\ -\left[1 - \frac{\gamma}{N_b}\right] \delta & \gamma \geq \beta. \end{cases} \quad (2.35)$$

### 2.2.3 Ewald representation of infinite sums

It was stated in [section 2.2.2](#) that  $\mathbf{D}_{\nu\mu}$  contains the hydrodynamic interaction of bead  $\nu$  with beads  $\mu$  not only in the simulation box (primary image) but also in all other replicas of primary image which span the entire space. It is known that HI is long range in nature, i.e., it scales with  $1/r$ . Therefore, to overcome the convergence issue of the infinite sum, Beenakker [\[10\]](#) used the idea of Ewald summation to split the sum into two exponentially decaying sums, one in the real space and the other in the reciprocal (or Fourier) space:

$$\mathbf{D}_{\nu\mu} = \mathbf{D}_{\nu\mu}^{\text{self}} + \mathbf{D}_{\nu\mu}^{\text{real}} + \mathbf{D}_{\nu\mu}^{\text{recip}}, \quad (2.36)$$

where the first term is the correction due to self interaction and the last two terms are the contribution of the real and the reciprocal space summation, respectively. Each term is written as,

$$\mathbf{D}_{\nu\mu}^{\text{self}} = \left(1 - \frac{6}{\sqrt{\pi}}\alpha a + \frac{40}{3\sqrt{\pi}}\alpha^3 a^3\right) \delta_{\nu\mu} \delta \quad (2.37a)$$

$$\mathbf{D}_{\nu\mu}^{\text{real}} = \sum'_{\mathbf{n} \in \mathbb{Z}^3} \mathbf{M}_{\alpha}^{(1)}(\mathbf{r}_{\nu\mu, \mathbf{n}}) \quad (2.37b)$$

$$\mathbf{D}_{\nu\mu}^{\text{recip}} = \frac{1}{V} \sum_{\mathbf{k}_{\lambda} \neq 0} \exp(-i\mathbf{k}_{\lambda} \cdot \mathbf{r}_{\mu\nu}) \mathbf{M}_{\alpha}^{(2)}(\mathbf{k}_{\lambda}). \quad (2.37c)$$

Here,  $a$  is the nondimensional bead radius, i.e.,  $a = a_b/l_H$ , and the parameter  $\alpha$  controls the relative computational load between the reciprocal and the real space and hence their convergence rate. If large values of  $\alpha$  are selected, the real space sum converges faster than its reciprocal counterpart.  $\delta_{\nu\mu}$  is the Kronecker delta. The vector  $\mathbf{n} = (n_x, n_y, n_z)$  with integer components specifies all images including the primary image ( $\mathbf{n} = 0$ ). However, as

indicated by the prime on the summation over  $\mathbf{n}$ ,  $\mathbf{n} = 0$  is omitted for  $\nu = \mu$ .  $\mathbf{M}_\alpha^{(1)}$  is a  $3 \times 3$  matrix which is a function of the vector connecting bead  $\mu$  to beads  $\nu$  in different images, i.e.,  $\mathbf{r}_{\nu\mu,\mathbf{n}} = \mathbf{r}_\nu - \mathbf{r}_\mu + \mathbf{n}L$ .  $\mathbf{M}_\alpha^{(1)}$  is written as,

$$\mathbf{M}_\alpha^{(1)}(\mathbf{r}) = \left[ C_1 \text{erfc}(\alpha r) + C_2 \frac{\exp(-\alpha^2 r^2)}{\sqrt{\pi}} \right] \boldsymbol{\delta} + \left[ C_3 \text{erfc}(\alpha r) + C_4 \frac{\exp(-\alpha^2 r^2)}{\sqrt{\pi}} \right] \frac{\mathbf{r}\mathbf{r}}{r^2}, \quad (2.38)$$

where  $r = |\mathbf{r}|$ ,  $\text{erfc}()$  denotes the complementary error function, and the  $C_i$  parameters are defined as follows,

$$\begin{cases} C_1 = \frac{3a}{4r} + \frac{a^3}{2r^3} \\ C_2 = 4\alpha^7 a^3 r^4 + 3\alpha^3 a r^2 - 20\alpha^5 a^3 r^2 - \frac{9}{2}\alpha a + 14\alpha^3 a^3 + \frac{\alpha a^3}{r^2} \\ C_3 = \frac{3a}{4r} - \frac{3a^3}{2r^3} \\ C_4 = -4\alpha^7 a^3 r^4 - 3\alpha^3 a r^2 + 16\alpha^5 a^3 r^2 + \frac{3}{2}\alpha a - 2\alpha^3 a^3 - \frac{3\alpha a^3}{r^2}. \end{cases} \quad (2.39)$$

In Equation (2.37c),  $\mathbf{k}_\lambda = \frac{2\pi}{L}\mathbf{l}$  where  $\mathbf{l} \in Z^3$  and  $\mathbf{M}_\alpha^{(2)}$  is written as,

$$\mathbf{M}_\alpha^{(2)} = m_\alpha^{(2)} \left( \boldsymbol{\delta} - \frac{\mathbf{k}_\lambda \mathbf{k}_\lambda}{k^2} \right), \quad (2.40)$$

where  $k = |\mathbf{k}_\lambda|$  and  $m_\alpha^{(2)}$  is defined as follows,

$$m_\alpha^{(2)} = \left( a - \frac{a^3 k^2}{3} \right) \left( 1 + \frac{k^2}{4\alpha^2} + \frac{k^4}{8\alpha^4} \right) \frac{6\pi}{k^2} \exp \left[ -\frac{k^2}{4\alpha^2} \right]. \quad (2.41)$$

Equation (2.37b) implicitly assumes no overlap between the beads, since Beenakker [10] exploited Equation (2.3b) to derive the Ewald sum of the RPY formulation for the HI tensor. To remove this assumption, Zhou and Chen [161] introduced a correction which is applied by adding Equation (2.3b) to the real part of the diffusion tensor for a pair of beads and subsequently subtracting Equation (2.3c) when there is an overlap between the two beads. This is particularly important for the primary image and all the images in its vicinity (27

replicas in total). This approach is equivalent to adding a  $3 \times 3$  matrix  $\mathbf{M}^*$  to the RHS of Equation (2.37b) in case of an overlap [69]:

$$\mathbf{D}_{\nu\mu}^{\text{real}} = \sum_{\mathbf{n} \in Z^3}^I \mathbf{M}_{\alpha}^{(1)}(\mathbf{r}_{\nu\mu, \mathbf{n}}) + \mathbf{M}^*(\mathbf{r}_{\nu\mu, \mathbf{n}})(1 - \delta_{\nu\mu}), \quad (2.42)$$

where  $\mathbf{M}^*$ , which is included only for  $\nu \neq \mu$ , is defined as,

$$\mathbf{M}^* = \begin{cases} 0 & r \geq 2a \\ \left[1 - \frac{9r}{32a} - \frac{3a}{4r} - \frac{a^3}{2r^3}\right] \boldsymbol{\delta} + \left[\frac{3r}{32a} - \frac{3a}{4r} + \frac{3a^3}{2r^3}\right] \frac{\mathbf{r}\mathbf{r}}{r^2} & r < 2a. \end{cases} \quad (2.43)$$

## 2.2.4 SPME representation of infinite sums

In this section, we present the matrix-free approach that is employed for the simulation of semidilute bead-spring polymer solutions. This approach uses smooth particle mesh Ewald for the calculation of reciprocal space based on the original SPME method for Electrostatic interactions by Essmann *et al.* [36]. PME based techniques for dealing with long range HI were also considered previously [140, 133, 98]. Our matrix-free approach is very similar to the one implemented by Liu and Chow [98] for simulation of suspension of Brownian particles and hence we try to follow similar nomenclatures and notations throughout this section.

Primarily, we are looking to obtain  $\mathbf{u}_{\nu} = (\mathbf{D} \cdot \mathbf{F}^{\phi})_{\nu} = \sum_{\mu} \mathbf{D}_{\nu\mu} \cdot \mathbf{F}_{\mu}^{\phi}$ . The RPY Ewald operator on the force  $\mathbf{F}^{\phi}$  can be expressed as:

$$\mathbf{D} \cdot \mathbf{F}^{\phi} = \overbrace{\mathbf{D}^{\text{real}} \cdot \mathbf{F}^{\phi}}^{\mathbf{u}^{\text{real}}} + \overbrace{\mathbf{D}^{\text{recip}} \cdot \mathbf{F}^{\phi}}^{\mathbf{u}^{\text{recip}}} + \overbrace{\mathbf{D}^{\text{self}} \cdot \mathbf{F}^{\phi}}^{\mathbf{u}^{\text{self}}}, \quad (2.44)$$

where the three terms on the RHS are related to the real, reciprocal, and self parts of the RPY interaction tensor. The reciprocal term can be written as:

$$\mathbf{u}_{\nu}^{\text{recip}} = \sum_{\mathbf{k}_{\lambda} \neq 0} \sum_{\mu=1} \exp(-i\mathbf{k}_{\lambda} \cdot \mathbf{r}_{\mu\nu}) \mathbf{M}_{\alpha}^{(2)}(\mathbf{k}_{\lambda}) \cdot \mathbf{F}_{\mu}^{\phi}. \quad (2.45)$$

After some minor manipulations, Equation (2.45) can be written as:

$$\mathbf{u}_\nu^{\text{recip}} = \sum_{\mathbf{m} \neq 0, \mu} \exp(2\pi i \mathbf{m} \cdot \mathbf{r}_\nu) \mathbf{M}_\alpha^{(2)}(2\pi \mathbf{m}') \cdot \exp(-2\pi i \mathbf{m} \cdot \mathbf{r}_\mu) \mathbf{F}_\mu^\phi, \quad (2.46)$$

where  $\mathbf{m}$ , the reciprocal lattice vector, is defined by  $\mathbf{m} = m_1 a_1^* + m_2 a_2^* + m_3 a_3^*$ , where  $a_q^*$  parameters are the conjugate reciprocal vectors defined based on  $a_s$  parameters which are the unit vectors that form the edges of the simulation box. The two aforementioned vectors are related as  $a_q^* \cdot a_s = \delta_{qs}$ . For a box with dimensions  $L \times L \times L$ ,  $\mathbf{m} = 1/L (m_1, m_2, m_3)$  where  $m_q$  range is  $0, \dots, K-1$ . Note that the periodic feature of complex exponentials were used to map the range of  $\mathbf{k}_\lambda$  to those of mesh grid points. Also,  $\mathbf{k}_\lambda = 2\pi \mathbf{m}'$  and  $\mathbf{m}' = m'_1 a_1^* + m'_2 a_2^* + m'_3 a_3^*$  where  $m'_i$  is defined as

$$m'_q = \begin{cases} m_q & 0 \leq m_i \leq K/2 \\ m_q - K & \text{otherwise.} \end{cases} \quad (2.47)$$

The term  $\sum_\mu \exp(-2\pi i \mathbf{m} \cdot \mathbf{r}_\mu) \mathbf{F}_\mu^\phi$  can be interpreted as the discrete Fourier transform of the forces  $\mathbf{F}_\mu^\phi$ , i.e.,  $\tilde{\mathbf{F}}(\mathbf{m})$ :

$$\mathbf{u}_\nu^{\text{recip}} = \sum_{\mathbf{m} \neq 0} \exp(2\pi i \mathbf{m} \cdot \mathbf{r}_\nu) \mathbf{M}_\alpha^{(2)}(2\pi \mathbf{m}') \cdot \tilde{\mathbf{F}}(\mathbf{m}); \quad (2.48)$$

here the summation over  $\mathbf{m}$  can be regarded as the inverse Fourier transform.

## Spreading the forces

As it was shown above,

$$\tilde{\mathbf{F}}(\mathbf{m}) = \sum_\mu \left\{ \prod_q \exp\left(-2\pi i \frac{m_q}{K} \xi_{\mu,q}\right) \right\} \mathbf{F}_\mu^\phi. \quad (2.49)$$

Here,  $\xi_{\mu,q} = K/L r_{\mu,q}$ . To take advantage of the fast Fourier transform (FFT), the force on the non-equally spaced particles can not be directly used. Instead, the forces have to be spread

onto a regular mesh which is the primary task of PME based methods. This can also be achieved by interpolating complex exponential on the regular grid defined earlier using the properties of Euler exponential splines [36]:

$$\exp\left(-2\pi i \frac{m_q}{K} \xi_{\mu,q}\right) \approx b_q^*(m_q) \sum_{k=-\infty}^{+\infty} M_p(\xi_{\mu,q} - k) \exp\left(-2\pi i \frac{m_q}{K} k\right). \quad (2.50)$$

The functions  $M_p$  are the cardinal B-splines of order  $p$  (piecewise polynomials of degree  $p-1$ ):

$$\begin{cases} M_2(x) = \begin{cases} 1 - |x - 1| & 0 \leq x \leq 2 \\ 0 & x < 0, x > 2 \end{cases} \\ M_p(x) = \frac{x}{p-1} M_{p-1}(x) + \frac{p-x}{p-1} M_{p-1}(x-1) & p > 2. \end{cases} \quad (2.51)$$

The  $M_p$  functions spread the forces for the particles near the boundaries based on the corresponding periodic grids inside the simulation box.  $b_q^*(m_q)$  is the complex conjugate of  $b_q(m_q)$  which is given by  $b_q(m_q) = \frac{\exp(2\pi i(p-1)m_q/K)}{\sum_{k=0}^{p-2} M_p(k+1) \exp(2\pi i m_q k/K)}$ . The distribution of the forces on the nearby grids is depicted in Figure 2.3.

### Forward Fourier Transform (3D FFT)

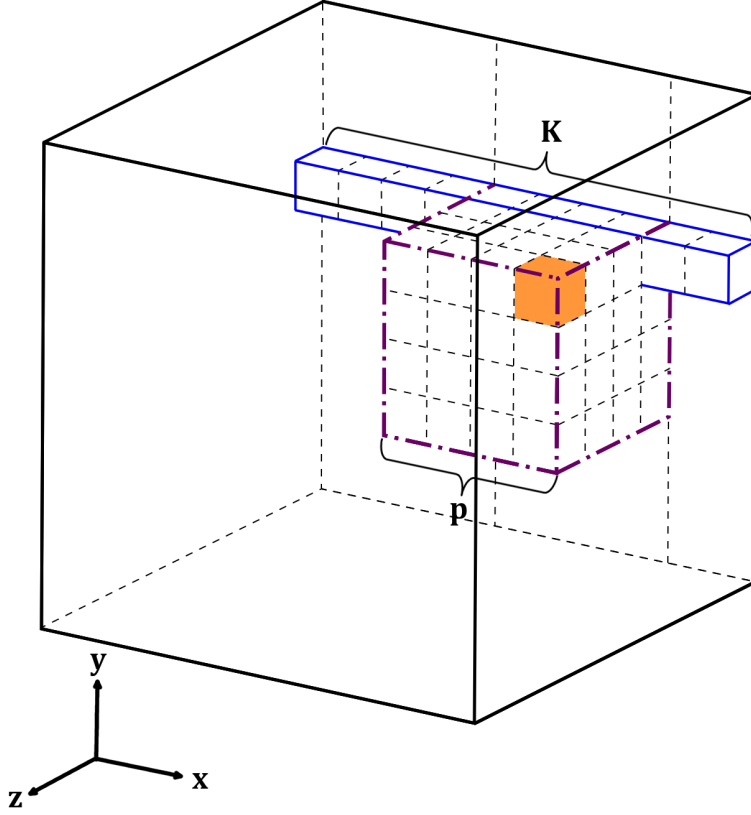
Now Equation (2.49) is approximated as,

$$\tilde{\mathbf{F}}(\mathbf{m}) \approx \hat{\mathbf{F}}(\mathbf{m}) = \left\{ \prod_q b_q^*(m_q) \right\} \mathcal{F}[\mathbf{F}^{\phi,g}](m_1, m_2, m_3), \quad (2.52)$$

where  $\mathbf{F}^{\phi,g}$  is the forces on the regular grid, i.e.,  $\mathbf{F}^{\phi,g} = \sum_{\mu} \left\{ \prod_q M_p(\xi_{\mu,q} - k_q) \right\} \mathbf{F}_{\mu}^{\phi}$ , and  $\mathcal{F}[\cdot]$  is the forward FFT operator which is defined as,

$$\begin{aligned} \mathcal{F}[\mathbf{F}^{\phi,g}](m_1, m_2, m_3) = \\ \sum_{k_1, k_2, k_3=0}^{K-1} \left\{ \prod_q \exp\left[-2\pi i \frac{m_q k_q}{K}\right] \right\} \mathbf{F}^{\phi,g}(k_1, k_2, k_3). \end{aligned} \quad (2.53)$$





**Figure 2.3:** Spreading the force on the regular mesh, where the cells represent the grid points. The filled cell is the nearest point to the particle and the cells bounded by the dash-dot line are  $p^3$  grid points at which the force on the particle is distributed.

### Backward Fourier Transform (3D IFFT)

Now back to Equation (2.48), again we use the properties of Euler exponentials but this time for  $\exp(2\pi i \mathbf{m} \cdot \mathbf{r}_\nu)$ :

$$\begin{aligned}
 \mathbf{u}_\nu^{\text{recip}} = & \sum_{k_1, k_2, k_3=0}^{K-1} \left\{ \prod_q M_p(\xi_{\nu, q} - k_q) \right\} \sum_{\mathbf{m} \neq 0} \left\{ \prod_q b_q(m_q) b_q^*(m_q) \right\} \\
 & \times M_\alpha^{(2)}(2\pi \mathbf{m}') \cdot \mathcal{F}[\mathbf{F}^{\phi, \mathbf{g}}](m_1, m_2, m_3) \left\{ \prod_q \exp\left[2\pi i \frac{m_q k_q}{K}\right] \right\}.
 \end{aligned} \tag{2.54}$$

If we define the influence function,  $\mathbf{I}(m_1, m_2, m_3)$  which is a  $3 \times 3$  matrix at each of  $K \times K \times K$  grid points, as  $\mathbf{I}(m_1, m_2, m_3) = \left\{ \prod_q |b_q(m_q)|^2 \right\} \mathbf{M}_\alpha^{(2)}(2\pi \mathbf{m}')$ , then,

$$\mathbf{u}_\nu^{\text{recip}} = \sum_{k_1, k_2, k_3=0}^{K-1} \left\{ \prod_q M_p(\xi_{\nu, q} - k_q) \right\} \mathcal{F}^{-1} [\mathbf{I} \cdot \mathcal{F} [\mathbf{F}^{\phi, \mathbf{g}}]], \quad (2.55)$$

where

$$\begin{aligned} \mathcal{F}^{-1} [\mathbf{I} \cdot \mathcal{F} [\mathbf{F}^{\phi, \mathbf{g}}]] (k_1, k_2, k_3) = \\ \sum_{\mathbf{m} \neq 0} (\mathbf{I} \cdot \mathcal{F} [\mathbf{F}^{\phi, \mathbf{g}}]) (m_1, m_2, m_3) \left\{ \prod_q \exp \left[ 2\pi i \frac{m_q k_q}{K} \right] \right\}. \end{aligned}$$

### Interpolation of the velocities to particle positions

The Equation (2.55) is interpreted as the back interpolation of the velocities on the grid, i.e.,  $\mathbf{u}^{\text{recip, g}}(k_1, k_2, k_3) = \mathcal{F}^{-1} [\mathbf{I} \cdot \mathcal{F} [\mathbf{F}^{\phi, \mathbf{g}}]] (k_1, k_2, k_3)$ , to the position of the particles which is done with the same functions used for spreading task.

### Accuracy of Ewald summation

The parameters which influence the accuracy of Ewald summation technique are identified as Ewald parameter  $\alpha$  which changes the distribution of load between the real and the reciprocal space sums, real space cutoff radius  $r_{c,D}$ , and  $k_{\text{max}}$ , a parameter which defines the accuracy in the reciprocal space summation. As shown below, these three parameters are related. In fact, only  $r_{c,D}$  and  $k_{\text{max}}$  are required to be optimized to ensure the accuracy of the Ewald summation.

Fincham [38] proposed a method to choose the optimal values of these parameters for electrostatic interactions. Similar discussions were made by Jain *et al.* [69] for the hydrodynamic interactions. Following the arguments made by Fincham [38] and Jain *et al.* [69] and based on Equation (2.38) and Equation (2.41), the convergence of the real and reciprocal space sums is determined by  $\exp(-\alpha^2 r_{c,D}^2)$  and  $\exp\left(-\frac{k^2}{4\alpha^2}\right)$ , respectively.  $M_{\text{exp}}$  is

defined such that  $\exp(-M_{\text{exp}}^2)$  becomes negligibly small, therefore,

$$\begin{cases} \alpha = \frac{M_{\text{exp}}}{r_{c,D}} \\ k_{\text{max}} = \frac{2M_{\text{exp}}^2}{r_{c,D}}. \end{cases} \quad (2.56)$$

Hence, the accuracy of the real and reciprocal space sums and therefore the Ewald summation are tuned using  $r_{c,D}$  and  $M_{\text{exp}}$ .

### 2.2.5 Optimal features of the matrix-free algorithm

This section, summarizes the main distinguishing features of matrix-free method when compared to the original Ewald summation as well as the straight forward implementations of PME based algorithms. As the term “matrix-free” implies, all instances of tensor variables are avoided in the numerical calculations. Specifically,  $\mathbf{D}^{\text{recip}} \cdot \mathbf{F}^\phi$  is directly calculated using the SPME technique without explicitly calculating  $\mathbf{D}^{\text{recip}}$ .  $\mathbf{D}^{\text{self}}$  is diagonal and therefore is calculated efficiently without storing the matrix.  $\mathbf{D}^{\text{real}}$  is, in general, a dense matrix which is made sparse in the matrix-free approach (as described in detail in [section 2.2.5](#)).  $\tilde{\mathbf{B}}$  and  $\tilde{\mathbf{B}}$  are both highly sparse and are treated efficiently using optimized MKL routines for sparse matrices.

#### Sparsification of $\mathbf{D}^{\text{real}}$

As pointed out earlier in the paper,  $\mathbf{D}^{\text{real}}$  has to be sparse in the matrix-free approach. To this end,  $r_{c,D}$  is made very small such that each bead interact with only a few surrounding beads. The sparse  $\mathbf{D}^{\text{real}}$  is then constructed using the combination of cell linked-list and the Verlet list [\[47, 3\]](#). As the elements  $\mathbf{D}_{\nu\mu}^{\text{real}}$  are  $3 \times 3$  tensors, the sparse variant of  $\mathbf{D}^{\text{real}}$  is stored based on the MKL’s block compressed sparse row format [\[98\]](#). Furthermore, as  $\mathbf{D}^{\text{real}}$  is symmetric, MKL’s sparse matrix vector operations (SpMV) for symmetric matrices are used in calculation of  $\mathbf{D}^{\text{real}} \cdot \mathbf{F}^\phi$  and SpMV operations which are involved in the Lanczos algorithm.

## Efficient implementation of SPME

Following the original matrix-free approach for HI [98], the  $N \times K^3$  transformation matrix  $P$  is defined as,

$$P(\mu, k_1 + k_2K + k_3K^2) = \left\{ \prod_{q=1}^3 M_p(\xi_{\mu,q} - k_q) \right\}; \quad (2.57)$$

note that  $P$  has only  $p^3$  non-zero terms at each row, which means that it is considerably sparse. It is stored according to the well-known compressed sparse row format. In addition,  $P$  only depends on the configuration of the system and hence can be computed *a priori* in each time step and reused for all the corresponding SpMV operations involved in the calculation of  $\mathbf{D} \cdot \mathbf{F}^\phi$  and the Lanczos decomposition.

Next, the forces on the particles are spread to the regular grid,

$$[F_x^{\phi,g}, F_y^{\phi,g}, F_z^{\phi,g}] = P^T \cdot [F_x^\phi, F_y^\phi, F_z^\phi].$$

Then, the forward 3D FFT at all grid points, i.e.,  $\mathcal{F}[\mathbf{F}^{\phi,g}]$ , is performed using efficient MKL discrete Fourier transform interfaces. In this regard, “in-place real-complex” storage scheme is used which is more efficient than “out-place complex-complex” variant from the memory transactions perspective.

Subsequently, the influence function is applied by calculating  $\mathbf{I} \cdot \mathcal{F}[\mathbf{F}^{\phi,g}]$  again at all grid points. It is obvious from the definition of  $\mathbf{I}$  in [section 2.2.4](#) that influence function is not dependent on configuration of the system. Hence, it can be stored once the number of mesh points are known. However, the memory efficient way of storing this function is to store only  $\left\{ \prod_q |b_q(m_q)|^2 \right\} m_\alpha^{(2)}$  and calculate  $(\delta - \frac{\mathbf{k}_\lambda \mathbf{k}_\lambda}{k^2})$  on-the-fly [98]. Furthermore, owing to the inversion symmetry of reciprocal space, the influence function is stored for about half of the grid points [69, 98]. This operation is followed by the inverse 3D FFT, where  $\mathcal{F}^{-1}[\mathbf{I} \cdot \mathcal{F}[\mathbf{F}^{\phi,g}]]$  is calculated at the regular grid points.

The last step in SPME is to interpolate the velocities at grid points to the location of the particles,

$$[u_x^{\text{recip}}, u_y^{\text{recip}}, u_z^{\text{recip}}] = P \cdot [u_x^{\text{recip,g}}, u_y^{\text{recip,g}}, u_z^{\text{recip,g}}].$$

## 2.2.6 Results and discussion

### Algorithm Verification

To validate the accurate implementation of the Ewald and matrix-free algorithms, the equilibrium properties of the dilute and semidilute polymer solutions are evaluated in both  $\theta$  and good solvents. To this end, the mean-square-displacement (MSD) as a function of time  $\tau$  and long time diffusivity of center of mass  $D_{cm}$  is used to track movement of the chains in a  $\theta$ -solvent:

$$D_{cm} = \lim_{\tau \rightarrow \infty} \frac{\text{MSD}(\tau)}{6\tau} = \lim_{\tau \rightarrow \infty} \frac{\langle (\mathbf{r}_c(t + \tau) - \mathbf{r}_c(t))^2 \rangle}{6\tau}. \quad (2.58)$$

In the case of theta or good solvent, the mean-square end-to-end distance and the mean-square radius of gyration are utilized to ascertain the accuracy of matrix-free algorithm,

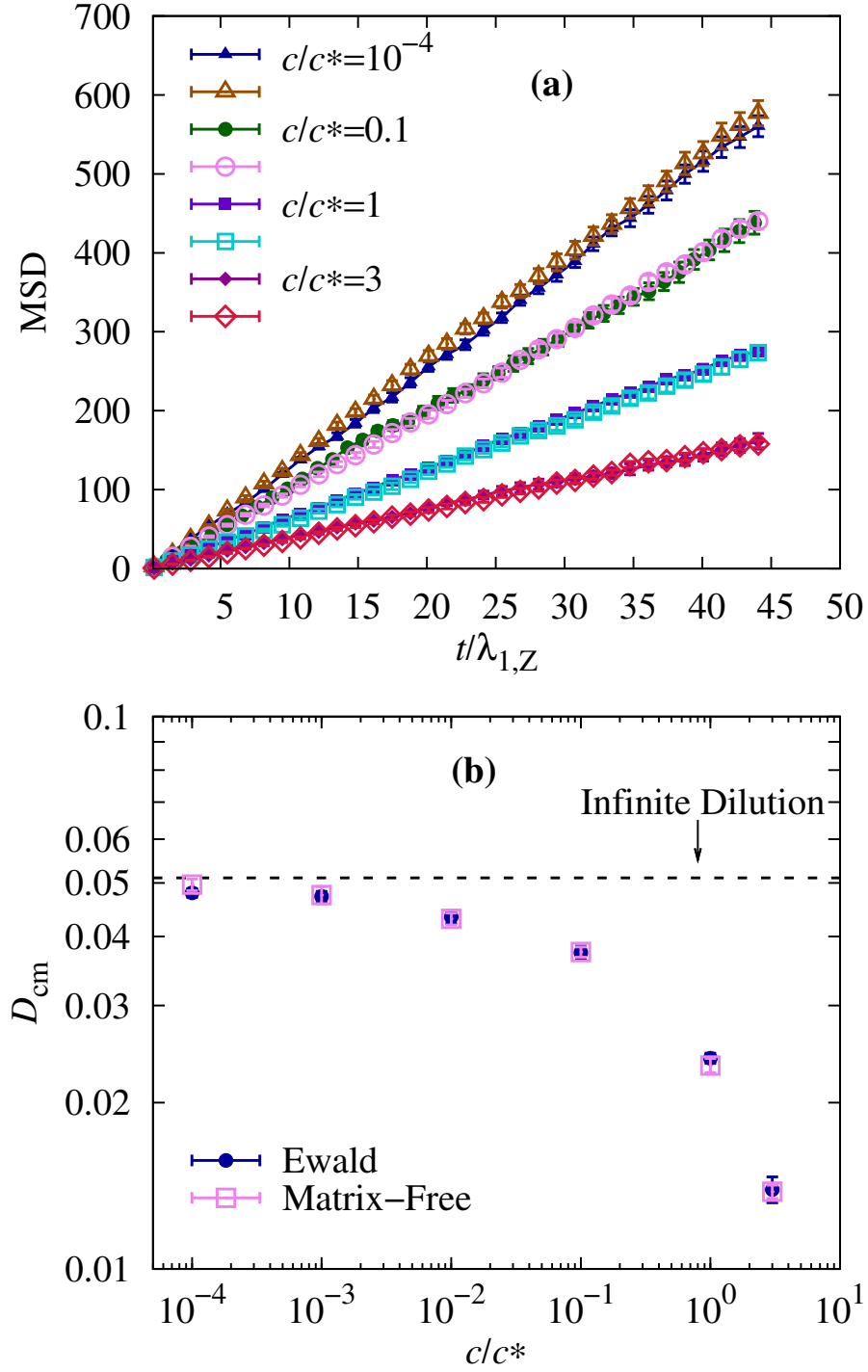
$$\langle R_{ee}^2 \rangle = \langle (\mathbf{r}_{N_b} - \mathbf{r}_1)^2 \rangle, \quad (2.59)$$

$$\langle R_g^2 \rangle = \frac{1}{N_b} \left\langle \sum_{\beta} (\mathbf{r}_{\beta} - \mathbf{r}_c)^2 \right\rangle. \quad (2.60)$$

### Diffusivity in $\theta$ -solvent

To validate the diffusivity of center of mass in semidilute regime, the values of MSD and  $D_{cm}$  for a system of multi-chains with  $N_b = 20$  at different  $c/c^*$  were computed (see [Figure 2.4](#)).

The overlap concentration is calculated using  $c^* = N/4/3\pi R_{g,0}^3$  where  $R_{g,0}$  is the radius of gyration at infinite dilution limit. It is known that in a  $\theta$ -solution (irrespective of concentration regime)  $\langle R_g^2 \rangle = \chi^2 \frac{N_b^2 - 1}{2N_b}$  and  $\langle R_{ee}^2 \rangle = 3\chi^2 (N_b - 1)$  [[11](#), [150](#)]. Our simulations for low concentrations, i.e.,  $c/c^* = 10^{-4} \sim 10^{-1}$ , typically consist of an equilibrium run of around 10 dimensionless longest relaxation times,  $\lambda_1$ , followed by a production run of from 25 to 50 relaxation times. As the macromolecules are in a  $\theta$ -solvent,  $\lambda_1$  is estimated using the Zimm formula,  $\lambda_{1,Z} \approx \frac{1.22 N_b^{3/2}}{h^* \pi^2}$ .  $N_c = 20$  was used in the simulations for low



**Figure 2.4:** (a) The mean-square-displacement and (b) the diffusivity of center of mass in  $\theta$ -solvent obtained using both Ewald and matrix-free techniques. The filled and open symbols represent the results for the Ewald and the matrix-free algorithms, respectively.

concentrations and hence the final results of MSD and  $D_{\text{cm}}$  are reported based on averaging over 20-50 independent runs. For higher concentrations, namely  $c/c^* = 1$  and 3,  $N_c = 50$  and equilibrium and production runs similar to lower concentration were used. The parameter  $h^*$  was chosen to be 0.25 and the time step size is 0.01. The springs are assumed Hookean. The parameters specifying the accuracy of Ewald and matrix-free algorithms are given in [Table 2.4](#). The  $r_{c,D}$  for SPME algorithm is chosen such that the diffusion tensor remain semi positive-definite throughout the course of simulation. Since there is a large degree of overlap between the beads in a  $\theta$ -solution, the minimum cut-off radius for very dilute cases were found to be on the order of box dimension. Subsequently, the real-space part of  $\mathbf{D} \cdot \mathbf{F}^\phi$  for the cases where  $r_c > 0.42L$  is obtained using dense matrix calculations. For matrix-free simulations, the degree of B-splines is equal to 4.

**Table 2.4:** The simulation parameters for multi-chain systems at different concentrations.  $L$  is obtained using the analytical radius of gyration of polymers in  $\theta$ -solvent. The simulation results of end-to-end distance and radius of gyration is given for both the Ewald and the matrix-free algorithms.

| $c/c^*$   | $L$    | $M_{\text{exp}}$ | Ewald     |                                   |                                  | Matrix-Free |                                   |                                  |
|-----------|--------|------------------|-----------|-----------------------------------|----------------------------------|-------------|-----------------------------------|----------------------------------|
|           |        |                  | $r_{c,D}$ | $\langle R_{\text{ee}}^2 \rangle$ | $\langle R_{\text{g}}^2 \rangle$ | $r_{c,D}$   | $\langle R_{\text{ee}}^2 \rangle$ | $\langle R_{\text{g}}^2 \rangle$ |
| $10^{-4}$ | 297.73 | 3.5              | 350       | $57.1 \pm 0.3$                    | $10.0 \pm 0.04$                  | 310         | $57.5 \pm 0.3$                    | $10.0 \pm 0.04$                  |
| $10^{-3}$ | 138.2  | 3.5              | 200       | $57.2 \pm 0.4$                    | $10.0 \pm 0.05$                  | 200         | $57.3 \pm 0.1$                    | $9.9 \pm 0.01$                   |
| $10^{-2}$ | 64.15  | 3.75             | 100       | $57.6 \pm 0.5$                    | $10.1 \pm 0.06$                  | 100         | $56.4 \pm 0.5$                    | $9.9 \pm 0.06$                   |
| 0.1       | 29.77  | 4.25             | 45        | $56.5 \pm 0.4$                    | $9.9 \pm 0.05$                   | 7           | $58.0 \pm 0.4$                    | $10.1 \pm 0.05$                  |
| 1         | 18.76  | 3.75             | 20        | $57.6 \pm 0.5$                    | $10.1 \pm 0.07$                  | 5           | $57.8 \pm 0.4$                    | $10.1 \pm 0.06$                  |
| 3         | 13     | 3.75             | 20        | $57.1 \pm 0.6$                    | $10.0 \pm 0.08$                  | 4           | $57.1 \pm 0.7$                    | $10.0 \pm 0.07$                  |

The asymptotic behavior of  $D_{\text{cm}}$  at low concentrations are further compared against the value of  $D_{\text{cm}}$  at infinite dilute solution at similar conditions. It is shown in [Figure 2.4\(b\)](#) that the value of  $D_{\text{cm}}$  at very low concentrations is correctly approaching the infinite dilute solution results. Furthermore, the differences between the Ewald and the matrix-free results for both MSD and  $D_{\text{cm}}$ , lie within the statistical error bars (see [Figure 2.4\(a\)](#) and [Figure 2.4\(b\)](#)). Note that the approach and the parameters are chosen closely correspond

to simulations by Jain *et al.* [69] and the results are in a very good agreement with their findings. Moreover, the radius of gyration and the end-to-end distance for all cases studied in this section were in excellent agreement with the theoretical values (see Table 2.4).

### Static dimension in good-solvent

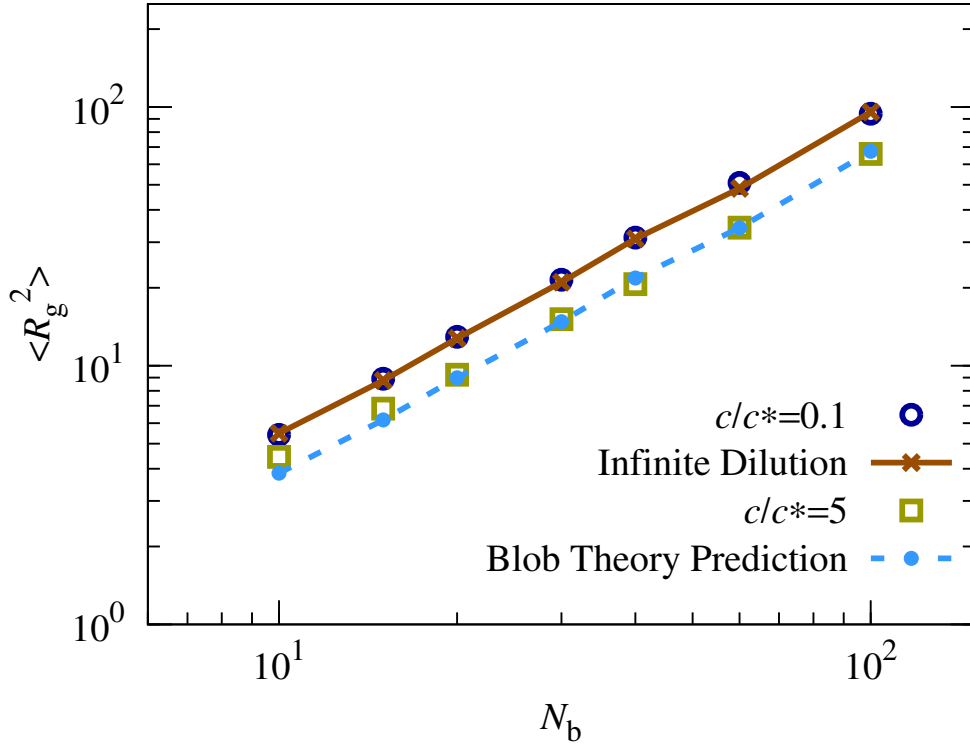
In this section, the behavior of multi-chain systems in good solvent is evaluated both in dilute as well as semidilute regimes. The static size of the chains for low concentrations ( $c/c^* < 0.1$ ) is expected to be equivalent to the dimensions of the chains in infinite dilution [149, 68]. Similar to an infinitely dilute solution, the dimensional scaling for multi-chain systems with low concentration is expected to follow  $\langle R_g^2 \rangle \propto N_b^{2\nu}$  where  $\nu$  is the effective EV exponent. It was found in section 2.2.6 that the effective excluded volume exponent based on center of mass diffusivity for the bead-spring system with FENE force-law and  $b = 20$  is  $\nu_{\text{cm}} = 0.581 \pm 0.01$ . Using the same parameter setting in the infinite dilute case,  $z\chi^3 = 1$  is selected for  $N_b = 10$  and is increased based on  $z\chi^3 \propto \sqrt{N_b}$  for higher number of beads. The broadness of the EV potential is determined based on  $d^* = z^{*1/5}$  [83]. The simulations in this section involve an equilibrium run of more than one chain relaxation time and a production run of between 5 to 15 relaxation times. The chain relaxation time here is approximated using  $\lambda \approx R_g^2/6D_{\text{cm}}$  (see Table 2.5). For the simulations of this section, the degree of B-splines is set as 6. It should be noted that the simulation box size is selected such that  $L \geq 2R_{\text{ee}}$  to prevent any unrealistic interaction of chain with itself.

At higher concentrations, however, one chain is surrounded by several other chains. Therefore, an individual macromolecule experiences the repulsion due to the other chains in its vicinity which results in the reduction in its dimensions. The blob theory takes this into consideration when determining the  $R_g$  scaling [128, 68],

$$R_g/R_{g,0} = (c/c^*)^{-(2\nu-1)/(6\nu-2)} \quad (2.61)$$

Here, we use this known theoretical fact to validate our matrix-free algorithm. To this end, the radius of gyration of the multi-chain systems with the relative concentration  $c/c^* = 5$





**Figure 2.5:** The mean-square radius of gyration as a function of number of beads in a multi-chain system with  $c/c^* = 0.1$  and 5. The error bars are smaller than the symbols.

is determined. It is clearly seen in Figure 2.5 that the results of our BD algorithm for multi-chain systems in a good solvent and dilute condition match the infinite dilution case. Although the theoretical scaling based on blob model holds true for long chains, the simulated static radius of gyration is consistent with the predictions from blob theory for  $N_b \gtrsim 20$ . Note that the relaxation time in semidilute regime is approximated based on the diffusivity obtained by  $D_{cm}/D_{cm,0} = (c/c^*)^{-(1-\nu)/(3\nu-1)}$  [68]. Moreover, as far as the calculation of box dimension is concerned, the  $R_{ee}/R_{ee,0}$  follows the same scaling as that of the radius of gyration.

### Computational time scaling

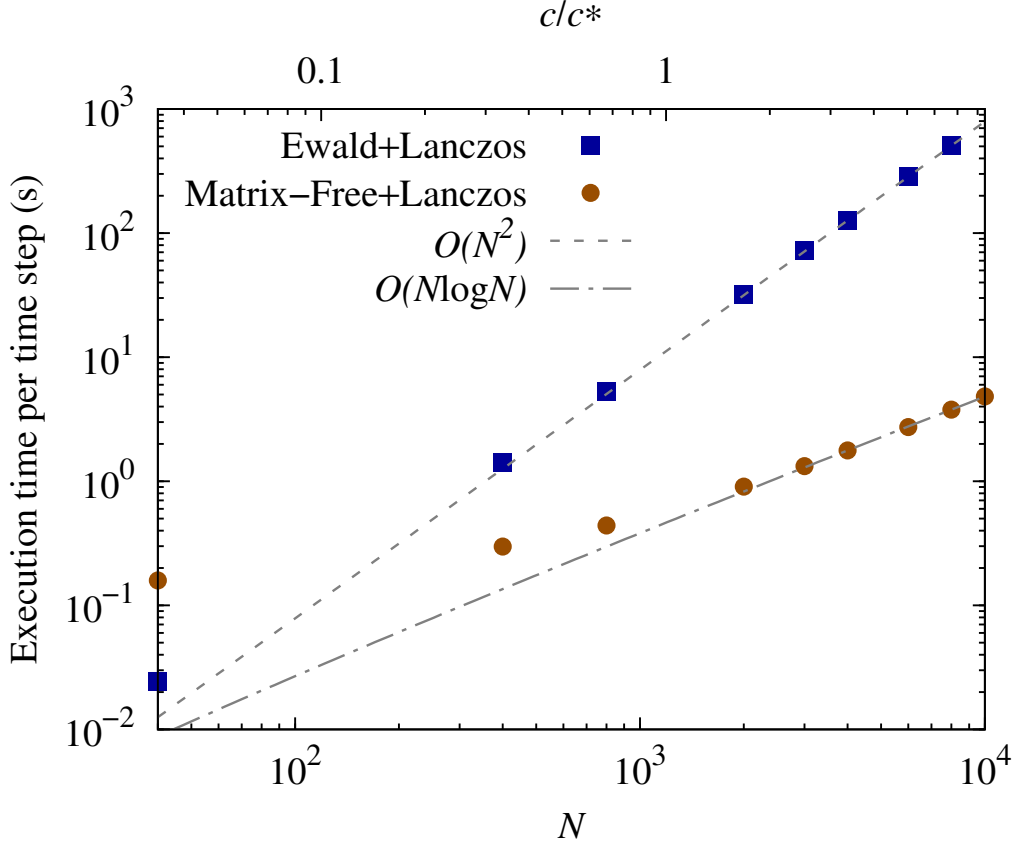
The recent comparison of the BD algorithm with the lattice Boltzmann molecular dynamics (LB/MD) by Jain *et al.* [69] indicated that BD with improved Ewald summation

**Table 2.5:** The parameters of the dilute and the semidilute multi-chain systems determined based on the diffusivity, the radius of gyration and the end-to-end distance of the chains in the infinitely dilute solution.

| $N_b$ | $D_{cm,0}$        | $\langle R_{g,0}^2 \rangle$ | $c/c^* = 0.1$ |                    |       | $c/c^* = 5$ |                    |       |
|-------|-------------------|-----------------------------|---------------|--------------------|-------|-------------|--------------------|-------|
|       |                   |                             | $\lambda$     | $L$ ( $L/R_{ee}$ ) | $N_c$ | $\lambda$   | $L$ ( $L/R_{ee}$ ) | $N_c$ |
| 10    | $0.074 \pm 0.005$ | $5.476 \pm 0.2$             | 12.35         | 28.23 (5)          | 42    | 21.55       | 14.21 (3)          | 267   |
| 20    | $0.048 \pm 0.003$ | $12.75 \pm 0.4$             | 44.27         | 44.04 (5)          | 45    | 77.25       | 22.17 (3)          | 286   |
| 40    | $0.031 \pm 0.002$ | $30.96 \pm 1.0$             | 166.45        | 69.55 (5)          | 47    | 290.44      | 23.34 (2)          | 88    |
| 60    | $0.026 \pm 0.002$ | $48.43 \pm 1.6$             | 310.45        | 87.83 (5)          | 48    | 541.70      | 29.48 (2)          | 91    |
| 100   | $0.018 \pm 0.001$ | $95.64 \pm 3.1$             | 871           | 127.1 (5)          | 52    | 1520        | 42.66 (2)          | 99    |

along with Chebyshev polynomial for decomposition is far more expensive than LB/MD. The matrix-free implementation for polymer solution developed in this chapter is expected to substantially reduce the difference between BD and other fast meso-scale simulation methods, such as dissipative particle dynamics (DPD) and LB/MD. Furthermore, total execution time versus number of beads in the simulation box is anticipated to scale as  $O(N \log N)$ . To this end, we test our code on a 16-core Intel Xeon E5-2670 by tracking the wall clock time spent in the simulation of a multi-chain system with  $N_b = 40$ . The chains are assumed to be in a good solvent, and hence there is EV interaction between each pair of particles and HI is considered with  $h^* = 0.25$ . A box with side length equal to 27.8 is considered to ensure that  $L \geq 2R_{ee}$ . The Ewald summation parameters are selected as  $M_{exp} = 4.25$  and  $r_{c,D} = 11$  and 5 for the Ewald and the matrix-free methods, respectively. The values of  $M_{exp}$  and  $r_{c,D}$  for the matrix-free approach imply  $K = 63$ . The degree of B-splines is chosen to be 6.

Using these parameters, the simulations are performed for about  $0.01\lambda$ , where  $\lambda$  is obtained using the same procedure outlined for static dimension in good solvent. This corresponds to more than 150 time steps with  $\Delta t = 10^{-2}$ . The execution time per time step is depicted in [Figure 2.6](#) as a function of  $N$ . It should be noted that the values of the relative error of the mean square radius of gyration at the end of  $0.01\lambda$ , calculated for the matrix-free approach compared to the corresponding results of the Ewald algorithm were less than  $5 \times 10^{-4}$  for all cases studied in this section.



**Figure 2.6:** Execution time per time step for Ewald as well as matrix-free algorithms.

Clearly the matrix-free implementation with proper choice of the Ewald parameters results in the total execution time which scales as  $\mathcal{O}(N \log N)$ . As expected, the scaling of the execution time for the original Ewald algorithm is as  $\mathcal{O}(N^2)$  as the algorithm uses a constant  $r_{c,D}$  [69].

### 2.2.7 Conclusions

A matrix-free approach has been developed to enhance the efficiency of BD simulations for a large system of macromolecules which are coupled through hydrodynamic interaction and excluded volume forces. The advantages of the matrix-free algorithm over the conventional BD is due to the fact that all matrices involved in BD are treated as sparse matrices, which in turn results in considerable computational speed-up. Moreover, the matrix-free

implementation benefits from using the SPME method in construction of diffusion tensor along with the block Lanczos method for computation of Brownian displacements.

The fidelity and computational efficiency of the matrix-free approach in equilibrium conditions was shown by evaluating the mean-square-displacement and the averaged diffusivity of the center of mass for a broad range of concentrations in a  $\theta$ -solvent as well as the mean-square end-to-end distance and the mean-square radius of gyration for chains with different degree of fine-graining in a theta or good solvent. The matrix-free results for center of mass diffusivity are found to be in excellent agreement with the ones obtained using the original Ewald summation technique. Moreover, the asymptotic values of diffusivity at very low concentrations correctly approach to the infinite dilution case. The radius of gyration of chains with different number of beads in dilute regime of concentration was predicted consistent to infinitely dilute system. At higher concentration, namely  $c/c^* = 5$ , the results of  $\langle R_g^2 \rangle$  are in a very good agreement with the values predicted by blob theory [128, 68].

Lastly, it is shown that the computational cost of the matrix-free technique is reduced by more than two orders of magnitude compared to conventional BDS for systems containing more than  $10^3$  beads. Furthermore, while the execution time for the method based on the Ewald summation and the Lanczos algorithm results in the computational cost scaling of  $\mathcal{O}(N^2)$ , the matrix-free technique improves the scaling to  $\mathcal{O}(N \log N)$ .

# Chapter 3

## BDpack project

This chapter is based on the manuscript:

- A. Saadat and B. Khomami. BDpack, an open source parallel Brownian dynamics simulation package. accepted to *J. Rheol.*

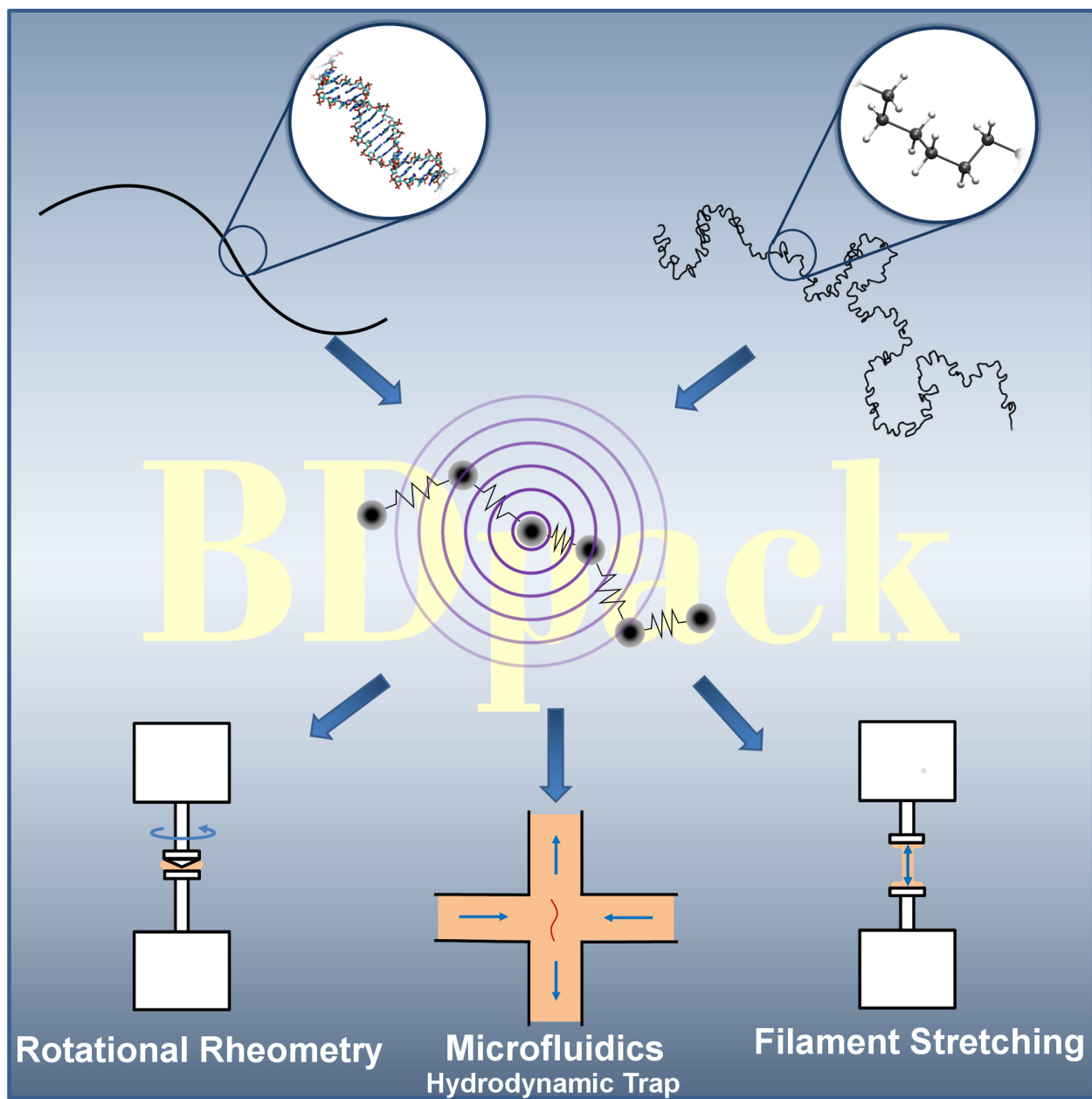
In this chapter, we report development of an open source Brownian dynamics package (BDpack) which incorporates all the known relevant physics in polymer solutions. To date, there have been numerous efforts to improve the physical models and numerical methods involved in BD simulations [39, 123, 147, 59, 156, 4, 130]. BDpack is based on the most computationally efficient algorithms that produce consistent results with theoretical models and experimental measurements [130, 131, 132]. In particular, the Krylov subspace based technique is implemented to enable fast calculations of Brownian displacements in single chain dynamics with computational expense scaling as  $\mathcal{O}(N_b^2)$ . For simulations of coupled multichain systems, a matrix-free approach for calculation of HI is implemented which leads to  $\mathcal{O}(N \log N)$  scaling of simulation time (see [chapter 2](#) for the details of the numerical techniques). Moreover, the package can be used to simulate polymers in quiescent solutions as well as in the presence of homogeneous flow. It should be mentioned that BDpack currently allows matrix-free calculation of HI for equilibrium condition as well as planar shear flow and the implementation for planar elongation is ongoing and will be provided in the next version of the package.

**Table 3.1:** The numerical algorithms implemented in BDpack.

| BD Formulation         | <i>Dilute</i>          | <i>Semidilute</i>                                                                                                      |
|------------------------|------------------------|------------------------------------------------------------------------------------------------------------------------|
| <b>SDE Integration</b> | Predictor-Corrector    | Euler                                                                                                                  |
| <b>HI</b>              | Mesh-free RPY          | Ewald, SPME                                                                                                            |
| <b>EV</b>              | Soft Gaussian, LJ      | Soft Gaussian (Short Range)                                                                                            |
| <b>Chain Stiffness</b> | Flexible, Semiflexible | Flexible, Semiflexible                                                                                                 |
| <b>Decomposition</b>   | Krylov (Lanczos)       | Krylov-SPME                                                                                                            |
| <b>Flow</b>            | Imposed Kinematics     | $\left\{ \begin{array}{l} \text{Shear: Lagrangian Rhomboid} \\ \text{Elongation: Kraynik Reinelt} \end{array} \right.$ |

There are several Brownian dynamics simulation packages available on-line [61, 43, 29, 26, 98]. To clearly distinguish BDpack from other available packages, the main features of BDpack are summarized in Figure 3.1 and Table 3.1. Among the aforementioned packages, only few of them are designed for multi-particle systems in a periodic box [43, 29, 98]. Brownmove [43] and BD\_BOX [29] use conventional algorithms for construction of diffusion matrix where the computational expense is typically orders of magnitude higher as compared to state-of-the-art techniques and algorithms implemented in BDpack [98, 131]. To the best of our knowledge, the only available BD package that uses a computationally efficient method for calculation of HI is the one by Chow and coworkers [98]. However, their current algorithm is for colloidal systems and does not account for non-equilibrium conditions which is essential for calculating material (rheological) functions.

It should also be mentioned that BD is not the only mesoscopic simulation technique for calculating hydrodynamic properties of polymers in solution. In particular, dissipative particle dynamics (DPD) [35, 48, 114, 108], hybrid lattice Boltzmann/molecular dynamics (LB-MD) [2, 117, 69], and hybrid multi-particle collision dynamics/molecular dynamics (MPCD) [46, 60] are examples of other mesoscopic techniques which have been developed rather recently. Although their computational expense roughly scales as  $\mathcal{O}(N)$ , they are known to be less efficient than BD in the limit of infinitely dilute solution due to the fact that unlike BD, the treatment of solvent is explicit in these methods [117, 69]. For multichain systems at finite concentration, LB-MD was found to be more efficient than BD



**Figure 3.1:** This figure shows a schematic of polymer types (flexible and semiflexible) which can be translated into the bead-spring micromechanical model for BD simulations with fluctuating hydrodynamic interaction and excluded volume forces. BDpack can be used to simulate the properties of polymeric solutions in different flow conditions such as elongational dynamics of single and multichain systems in microfluidic devices, planar shear in rotational rheometry and uniaxial extension in filament stretching device.

[69]. However, the comparisons regarding the computational efficiency as well as fidelity of these techniques should be revisited in the light of recent advances in Brownian dynamics techniques which are now available in BDpack.

As mentioned above, BDpack can be redistributed and/or modified under the terms of GNU General Public License (GPL). It is written in modular fashion using modern Fortran which facilitates understanding of the current codes and hence future developments. Moreover, message passing interface (MPI) is employed for large-scale parallelization while open multi-processing (OpenMP) and vectorization are used extensively for accelerating independent numerical operations. The package can be accessed through github repository at <http://amir-saadat.github.io/BDpack/>. A thorough instruction for installation, running, and user inputs are given in the website along with tutorials to clearly show the steps of the simulation using the package. The package currently has the BD algorithms for infinitely dilute solutions [130] and a beta version of multichain semidilute solutions [131].



# Chapter 4

## Extensional rheology of high $M_w$ polystyrene

This chapter is based on the published paper:

- A. Saadat and B. Khomami. Molecular based prediction of the extensional rheology of high molecular weight polystyrene dilute solutions: A hi-fidelity Brownian dynamics approach. *J. Rheol.*, 59:1507, 2015.

### 4.1 Introduction

Accurate measurement and prediction of elongational properties of macromolecules in extensional flows play a central role in many fields of science and engineering including polymer physics, rheology and polymer processing. Aside from the scientific interest in understanding polymer chain dynamics in strong flows, design and optimization of many polymer processing operations, such as blow molding and fiber spinning, require accurate knowledge of the fluid elongational properties.

The Filament Stretching Rheometer (FSR) is a reliable device to probe the transient extensional viscosity of polymer solutions and melts [152, 80, 50, 7, 105]. Specifically, in this device a well-controlled uniaxial extensional flow up to approximately 6 Hencky strains

is created that permits accurate measurement of the elongational properties of polymeric fluids.

In order to maximize the elastic effect in extensional rheometry while minimizing inertial effects, dilute solutions known as “Boger fluids” have been developed. These solutions contain nearly mono-disperse high molecular weight flexible macromolecules dissolved in a viscous solvent [145, 50, 7]. The solvent is usually composed of low molecular weight polymers dissolved in a low-viscosity medium. For high molecular weight polystyrene (HMWPS), the solvent can be either a low molecular weight polystyrene (LMWPS;  $M_w = 50,000$ ) dissolved in dioctylphthalate (DOP) (which is a  $\theta$ -solvent for polystyrene (PS) at 22°C) or oligomeric styrene which is commonly referred to as a picoelastic solvent [50, 7]. The LMWPS in DOP is thought to be roughly  $\theta$ -like for polystyrene, although some studies indicate that the polymer dimensions at rest might be slightly below their theta dimensions [145]. On the other hand, experiments on HMWPS in the oligomeric styrene show a slightly better than  $\theta$ -solvent properties of these systems [7].

There have been numerous efforts to simulate the extensional behavior of Boger fluids under FSR experimental conditions either using continuum level constitutive equations [111, 50, 7] or by exploiting mesoscopic level Brownian dynamics simulation with bead-spring and bead-rod micromechanical models [32, 95, 59, 122].

Gupta *et al.* [50] used the finitely extensible nonlinear elastic force-law proposed by Peterlin (FENE-P) and showed that although the steady shear and linear viscoelastic properties of the solutions are reasonably well described by the Zimm model under theta condition, this model is unable to correctly predict the stress growth and its steady state value in an ideal uniaxial extensional flow. They also reported an improvement in their predictions when using the Rouse relaxation spectrum along with an anisotropic drag coefficient. Li *et al.* [95] performed extensive Brownian dynamics simulations in the absence of HI and EV and compared their results with the experimental data for polystyrene solutions studied by Gupta *et al.* [50] and Orr and Sridhar [111]. They obtained nearly quantitative agreements for the lowest molecular weight polymer ( $1.95 \times 10^6$  PS); also consistent with the experiments, their predicted behavior at this molecular weight collapsed onto a single curve when the flow

strength was above a critical value, i.e.,  $Wi > 6$ . For higher molecular weight polystyrenes, the predicted strain value at which the upturn in elongational viscosity occurs shifts to higher values, while the experimental results show almost no change.

To explain the origin of the aforementioned discrepancy between experimental measurements and BD predictions, several attempts have been made, such as including HI which were neglected in the original simulations by Li *et al.* [95]. Hsieh *et al.* [59] and Prabhakar *et al.* [122] showed that inclusion of HI into the simulations allows closer agreement between experiment and BD simulations for  $1.95 \times 10^6$  molecular weight PS. These results also point to the acceleration of stress growth in elongational flow when HI is present. However, the agreement between the simulations and experiments deteriorates for higher molecular weights PS, i.e., 3.9, 10.2, and  $20 \times 10^6$  [86]. In particular, the slight over-prediction of steady state stress in the absence of HI, gets worsened in the presence of HI, while the delay in the strain value for which significant extension thickening is observed remains nearly unchanged.

There have been several reports on the effect of solvent quality on the stress growth both experimentally and using BD simulations [94, 150, 146]. It is generally believed that using a better-than- $\theta$  solvent system shows a more rapid upturn in elongational stress. This is mainly attributed to the static expansion of the polymer coil. In the aforementioned studies, the higher quality of the solvent is modeled by considering either the Weeks-Chandler-Anderson (WCA) potential [94] or the soft Gaussian potential [150, 146] EV potentials. In the paper by Li and Larson [94], the authors emphasize that the more rapid growth of stress in the good-solvent relative to the  $\theta$ -solvent suggests a possible explanation for the disagreement between theory and experiments for the case of larger molecular weight polystyrene in LMWPS/DOP solvent, because extensional flow is a sensitive “amplifier” of solvent quality effects.

The other aspect of BD using bead-spring chains is the level of fine-graining, i.e., the number of Kuhn steps per spring used in the micromechanical model. This is particularly important due to the high molecular weight of the PS used in the experiment. This effect was first considered by Li *et al.* [95] where the sensitivity of the rheological behavior was evaluated for 12, 20, and 60 beads for the  $10.2 \times 10^6$  molecular weight PS solution. Specifically, they

found identical results for the three cases studied. It will be shown later in this article that closer agreement with experiment is seen with successive fine-graining [122, 151, 150].

In this chapter, a highly efficient Brownian dynamics algorithm that uses the semi implicit predictor-corrector scheme in the presence of HI and EV along with Krylov subspace for calculation of Brownian noise is utilized to predict the measured material properties of high molecular weight dilute polystyrene solutions under uniaxial extensional flow [50, 95]. The effect of key parameters, namely HI and EV interactions, level of fine-graining, and flow strength is carefully evaluated to shed light on the origin of the aforementioned discrepancies between BD simulations and the reported experimental data.

## 4.2 Parameter selection

### 4.2.1 Free-draining condition

The molecular parameters for different molecular weights  $M_w$  in the free-draining condition, i.e., the number of Kuhn steps and the number density of polymers  $n$  were chosen according to Table I of the paper by Li *et al.* [95]. A 3-parameter exponential fit to the decay of the mean square end-to-end distance is used to obtain the longest dimensionless relaxation time [146].

In order to non-dimensionalize  $\eta_s$ , one has to specify  $\lambda_H$ . For this purpose,  $\lambda_1^*$  is calculated via BD. The longest relaxation time  $\lambda_1$  reported by Li *et al.* [95] is used for the free-draining simulations. Li *et al.* [95] related the longest relaxation time to the characteristic relaxation time  $\lambda_\eta$ ,

$$\lambda_\eta = \frac{[\eta_0] M_w \eta_s}{N_A k_B T}, \quad (4.1)$$

where  $[\eta_0]$  is the polymer intrinsic viscosity and  $N_A$  is the Avogadro's number. Based on the Zimm spectrum,  $\lambda_\eta = \sum_{i=1}^{N_b-1} \lambda_i = 2.369 \lambda_1$ . To compare the results with the predictions of Li *et al.* [95], the same values of  $\lambda_1$  calculated by Li *et al.* [95] are chosen for the free-draining cases which is denoted as  $\lambda_1^Z$ . It is important to note that the values of  $\lambda_1^Z$  are close in magnitude to the relaxation time  $\lambda_1^{\text{ext}}$  obtained by Prabhakar *et al.* [122] in the limit

$N_b \rightarrow N_K + 1$  for the polymer solutions in a  $\theta$ -solvent,

$$\lambda_1^{\text{ext}} = U_{1R}^{\infty} \frac{\eta_s b_K^3 N_K^{3/2}}{k_B T}, \quad (4.2)$$

where  $U_{1R}^{\infty}$  is a universal constant obtained when  $N_b, N_K \rightarrow \infty$ , and its value is reported by Prabhakar *et al.* [122] to be  $0.21 \pm 0.01$ . Hence, for the cases where HI is ignored,  $\lambda_1^Z$  is utilized to calculate  $Wi$  and  $\eta_s^*$ .

**Table 4.1:** Molecular parameters calculated by Li *et al.* [95] to simulate free-draining bead-spring chains with 19 segments.  $\lambda_1^{\text{ext}}$  is the longest relaxation time obtained for macromolecules in  $\theta$ -solvent and assuming  $N_b, N_K \rightarrow \infty$ .  $\lambda_1^{\text{exp}}$  is the experimental relaxation time measured by Gupta *et al.* [50].

| solution | $M_w$<br>million | $n$<br>(molecules/ $\mu\text{m}^3$ ) | $N_K$ | $b_K$<br>( $\mu\text{m}$ ) | $\lambda_1^Z$ (s) | $\lambda_1^{\text{ext}}$ (s) | $\lambda_1^{\text{exp}}$ (s) | $\eta_s$<br>(Pa.s) |
|----------|------------------|--------------------------------------|-------|----------------------------|-------------------|------------------------------|------------------------------|--------------------|
| 1        | 1.95             | 239.8                                | 2626  | 0.001803                   | 1.12              | 1.23                         | 0.8                          | 30.13              |
| 2        | 3.9              | 71.3                                 | 5253  | 0.001803                   | 3.16              | 3.54                         | 2.4                          | 30.67              |
| 3        | 10.2             | 5.51                                 | 13740 | 0.001803                   | 13.32             | 14.53                        | 9.48                         | 30.66              |
| 4        | 20               | 2.16                                 | 26938 | 0.001803                   | 36.71             | 41.96                        | 26                           | 31.30              |

It should be emphasized that the exact experimental value of relaxation time for the polymer solutions studied by Gupta *et al.* [50] is not known. However, Table 4.1 depicts the values of  $\lambda_1^{\text{exp}}$  which are the relaxation times obtained by Gupta *et al.* [50] by fitting the Zimm spectrum to the results of linear viscoelastic measurements. In turn, in comparing BD results obtained using SFG in the presence of HI with experimental data given in section 4.3.3,  $\lambda_1^{\text{exp}}$  is utilized to calculate  $Wi$ .

Selecting a single time step size which work for all cases in BD simulations is not a straight forward task. It is critical to ensure that the results are not dependent on the time step size.  $\Delta t$  is not similar for cases with different bead-spring parameters. One of the main reason of this behavior is the rapid coil-stretch transition of the molecules. In other words, the contribution of configurations near the maximum extension dominates the behavior of the system, particularly for  $\epsilon \gtrsim 4$ . To confirm this, we tested the effect of linearizing the force extension behavior near the singular point (maximum extension). It was found that

when one linearizes the force after 0.995 of maximum extension, the behavior of the system with no linearization can be recovered. Thus, the results are strongly dependent on accuracy of the numerical algorithm {e.g.,  $\Delta t$  and the accuracy of the predictor-corrector scheme, i.e.,  $\epsilon_{\text{pc}}$ } and numerical precision, i.e., single or double precision arithmetics and compiler related optimizations. Nevertheless,  $\Delta t = 10^{-2}$  and  $\epsilon_{\text{pc}} = 10^{-5}$  were found to be sufficiently small for more coarse-grained systems, e.g.,  $N_{\text{b}}$  up to 191 for  $M_w = 10.2 \times 10^6$  and  $M_w = 20 \times 10^6$ . For more fine-grained systems, we employed an adaptive time step size, where a sequence of time steps are used starting from  $\Delta t = 5 \times 10^{-3}$  for  $\epsilon < 2$ , then  $\Delta t = 5 \times 10^{-4}$  for  $2 \leq \epsilon < 4.5$  and finally  $\Delta t = 2.5 \times 10^{-4}$  for  $\epsilon > 4.5$ . For the case of  $M_w = 10.2 \times 10^6$  and  $N_{\text{b}} = 761$  we used the first two  $\Delta t$  values. Also,  $\epsilon_{\text{pc}} = 2.5 \times 10^{-6}$  for the cases where the multi time step algorithm was used.

#### 4.2.2 Successive fine-graining (SFG) in the presence of HI and EV

In order to minimize the dependency of the results on model parameters, such as  $N_{\text{b}}$  and  $d^*$ , one can implement the SFG algorithm introduced by Prabhakar *et al.* [122] and Sunthar and Prakash [151]. A relevant discussion in the context of progressive fine-graining of bead-spring micromechanical model is also given by Venkataramani *et al.* [158].

Using the SFG method, the main inputs to the model for performing BD simulations in the presence of HI and EV reduces to the solvent quality  $z$ , the equilibrium radius of gyration under  $\theta$ -solvent condition  $R_{\text{g,eq}}^\theta$  and the contour length of the polymer (or equivalently number of Kuhn steps  $N_{\text{K}}$  and Kuhn length  $b_{\text{K}}$ ). The parameter  $b$  can then be determined for any choice of  $N_{\text{b}}$  as,

$$b/\chi(b)^2 = \frac{3N_{\text{K}}}{(N_{\text{b}} - 1)}.$$

The HI parameter  $\tilde{h}^*$  is fixed at a value which is assumed to be  $\tilde{h}_{\text{K}}^*$ . In other words,  $a^*$  is chosen such that  $a^*/Q_{\text{eq}}^*$ , with  $Q_{\text{eq}}^*$  being the dimensionless equilibrium length of a spring, has the same value as  $a_{\text{K}}/b_{\text{K}}$ , where  $a_{\text{K}}$  is the radius of the bead in the limit  $N_{\text{b}} \rightarrow (N_{\text{K}} + 1)$ . The EV interaction parameter  $d^*$  is first chosen arbitrarily, but it is shown that the computed results are insensitive to this initial choice. For each value of  $N_{\text{b}}$ , the HI parameter  $h^*$  is

obtained using  $h^* = \chi \tilde{h}_K^*$  and the EV interaction parameters are calculated using  $z^* = z\chi^3/\sqrt{N_b}$  along with  $d^* = z^{*1/5}$  [83]. Using the aforementioned choice of parameters, the non-dimensional longest relaxation time  $\lambda_1^*$  is obtained using a 3-parameter exponential fit to the decay of the mean square end-to-end distance [146]. Also, the averaged dimensionless mean-square end-to-end distance at equilibrium  $\langle R_{ee}^{*2} \rangle_{eq}$ , is determined and used in the calculation of a universal ratio as described below. The number of beads in the system is then progressively increased while having  $z$ ,  $N_K$ , and  $b_K$  fixed. Next, a non-dimensional variable is chosen similar to the equilibrium universal ratios which can be suitably defined in uniaxial extensional flow [122, 151]. In this work, this non-dimensional ratio was defined as

$$U_{\bar{\eta}R}^+ = \frac{\eta_p}{\eta_s n R_{ee,eq}^3}, \quad (4.3)$$

where  $R_{ee,eq}$  is the dimensional equilibrium end-to-end distance of macromolecules in a dilute solution. This ratio is related to the simulation variables as follows,

$$U_{\bar{\eta}R}^+ = {}^{3/2} \frac{\pi^{3/2} h^* \eta_p^*}{R_{ee,eq}^3} \quad (4.4)$$

In turn, at several values of the strain  $\epsilon$ , the results of  $U_{\bar{\eta}R}^+$  for different values of  $N_b$  are accumulated and extrapolated to the limit  $N_b \rightarrow N_K + 1$ .

Although the equilibrium results have been shown to be insensitive to the value of  $\tilde{h}^*$ , it will be shown in [section 4.3.2](#) that as the strain is increased in uniaxial extensional deformation of polymer solutions, the systems demonstrate higher sensitivity to the value of  $\tilde{h}^*$ . In turn, a set of  $h^*$  value for different  $N_b$  are utilized as calculated by Hsieh *et al.* [59]. That is the drag force from a fully extended bead-spring model in extensional flow is matched with that of Batchelor's theory for a cylindrical rod. The value of  $\tilde{h}^*$  in the limit of  $N_b \rightarrow (N_K + 1)$ , i.e.,  $\tilde{h}_K^*$ , is then calculated by proper extrapolation of the appropriate  $\tilde{h}^*$  at different  $N_b$  values.

In addition to the parameters listed above, the flow strength  $Wi = \lambda_1 \dot{\epsilon}$  should also be incorporated as the input to the simulation which will be remained fixed in the course of SFG. To evaluate the effect of adding HI for comparison with free-draining results ([section 4.3.2](#)),

$\lambda_1^Z$  is used to calculate  $Wi$ . For all the cases thereafter, the experimental value of  $Wi$  is used,  $Wi = \lambda_1^{\text{exp}}\dot{\epsilon}$  to provide a one to one comparison of BD results and experimental measurements.

For all cases where SFG is employed,  $\epsilon_{\text{pc}} = 2.5 \times 10^{-6}$ . Moreover, in order to ensure that BD predictions are independent of time-step size, simulations were performed using successively smaller time steps and the results were extrapolated to the limit of zero time-step discretization [112, 121].

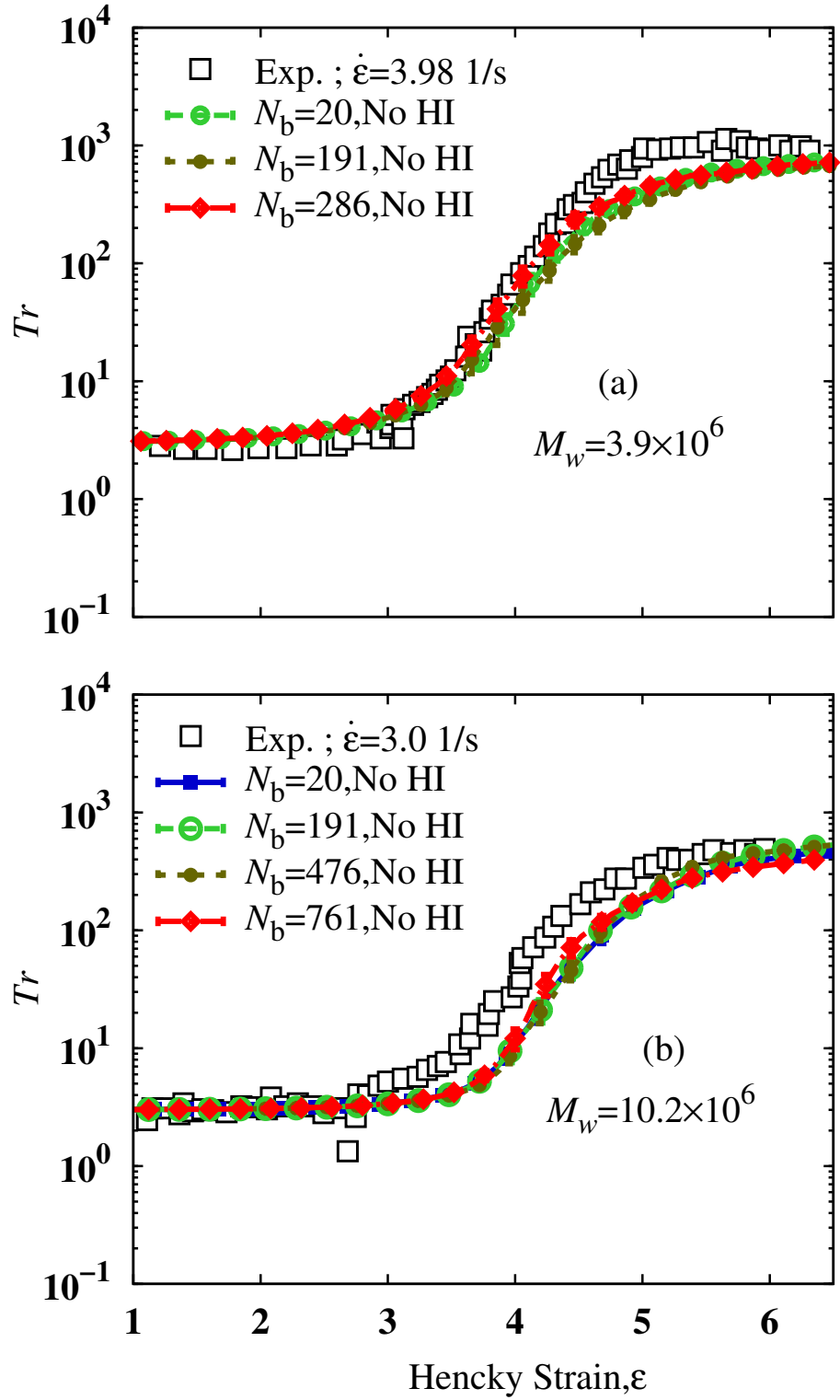
## 4.3 Results and discussion

### 4.3.1 Effect of fine-graining

In the original work by Li *et al.* [95],  $N_b = 20$  was used in the simulations. Using the  $N_K$  shown in Table 4.1, this translated into 276, 723, and 1418 Kuhn steps in each spring for molecules with 3.9, 10.2, and  $20 \times 10^6$  molecular weights, respectively. Thus, the systems are highly coarse-grained. Li *et al.* [95] also examined the results for  $M_w = 10.2 \times 10^6$  and  $N_b$  ranging from 12 to 60 and they observed minor changes to the behavior of  $Tr$  as a function of time. However,  $N_{K,s}$  for  $N_b = 60$  is still well beyond the minimum number of Kuhn steps per spring for ILCCP force law, i.e.,  $N_{K,s} \approx 10$ . To this end, we have examined the importance of fine-graining by reducing  $N_{K,s}$  to approximately 18.

Figure 4.1 illustrates the effect of changing  $N_b$  in an ensemble of 100 chains on the  $Tr$  vs.  $\epsilon$  for  $M_w = 3.9 \times 10^6$  and  $10.2 \times 10^6$ . An improvement in the prediction of strain at the stress upturn, i.e.,  $\epsilon_c$ , with an increase in the number of beads from 20 to 286 which corresponds to  $N_{K,s} \approx 18$  is obtained for  $M_w = 3.9 \times 10^6$ . However, the steady state plateau  $Tr_\infty$ , differs from that of experiment. As will be shown in section 4.3.2, incorporating HI will remedy this discrepancy between BD results and experimental behavior. Motivated by this success, we examined the influence of increased fine-graining on the delayed stress hardening predicted using BD simulations compared to the experimental results for  $M_w = 10.2 \times 10^6$  (see Figure 4.1(b)). In spite of a gradual improvement in the BD predictions, a noticeable





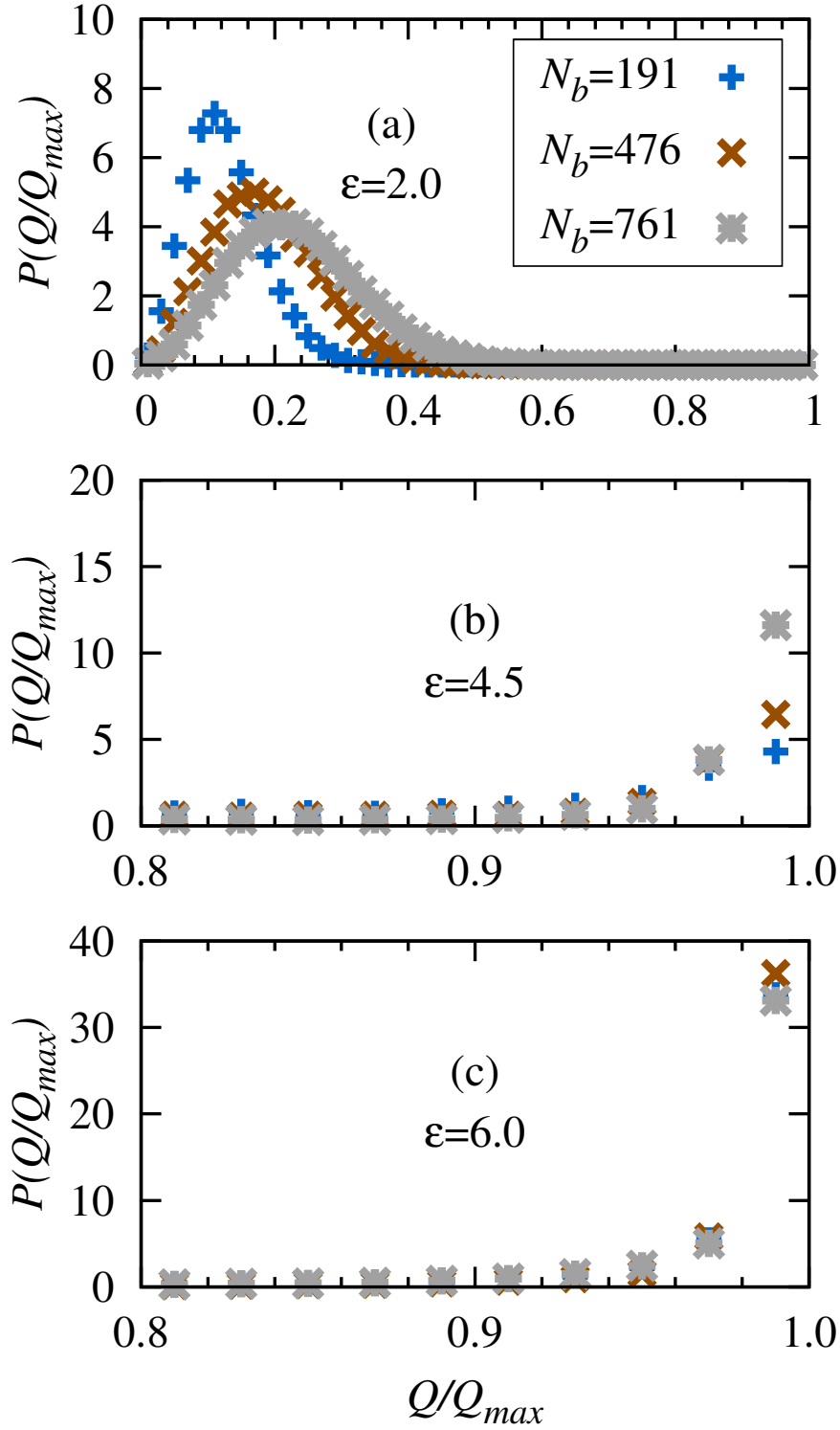
**Figure 4.1:** Effect of  $N_b$  on  $Tr$  vs.  $\epsilon$  of chains with (a)  $M_w = 3.9 \times 10^6$  and (b)  $M_w = 10.2 \times 10^6$  using BD simulations in the absence of HI and at  $Wi = 12.58$  for the former and  $Wi = 39.96$  for the latter.

gap still exists between the BD results with  $N_{K,s} \approx 18$  and the experimental data. It is not clear if a more fine-grained description ( $N_{K,s} < 18$ ) can shift the curves any further. The probability distribution function (PDF), which is denoted by  $P$ , was utilized to examine any configurational differences between the cases with different number of beads. It was found that the PDF of end-to-end shows minor changes (data not shown), whereas the segmental PDF demonstrates a clear transition to higher fractional extensions as  $N_b$  is increased (see Figure 4.2). This difference is more pronounced for smaller fractional extensions and gradually fades away as one approaches the maximum extension, i.e.,  $Q/Q_{max} \rightarrow 1$ . This behavior is consistent with the improved predictions observed in Figure 4.2, where a faster linear to nonlinear transition in the force extension behavior is expected.

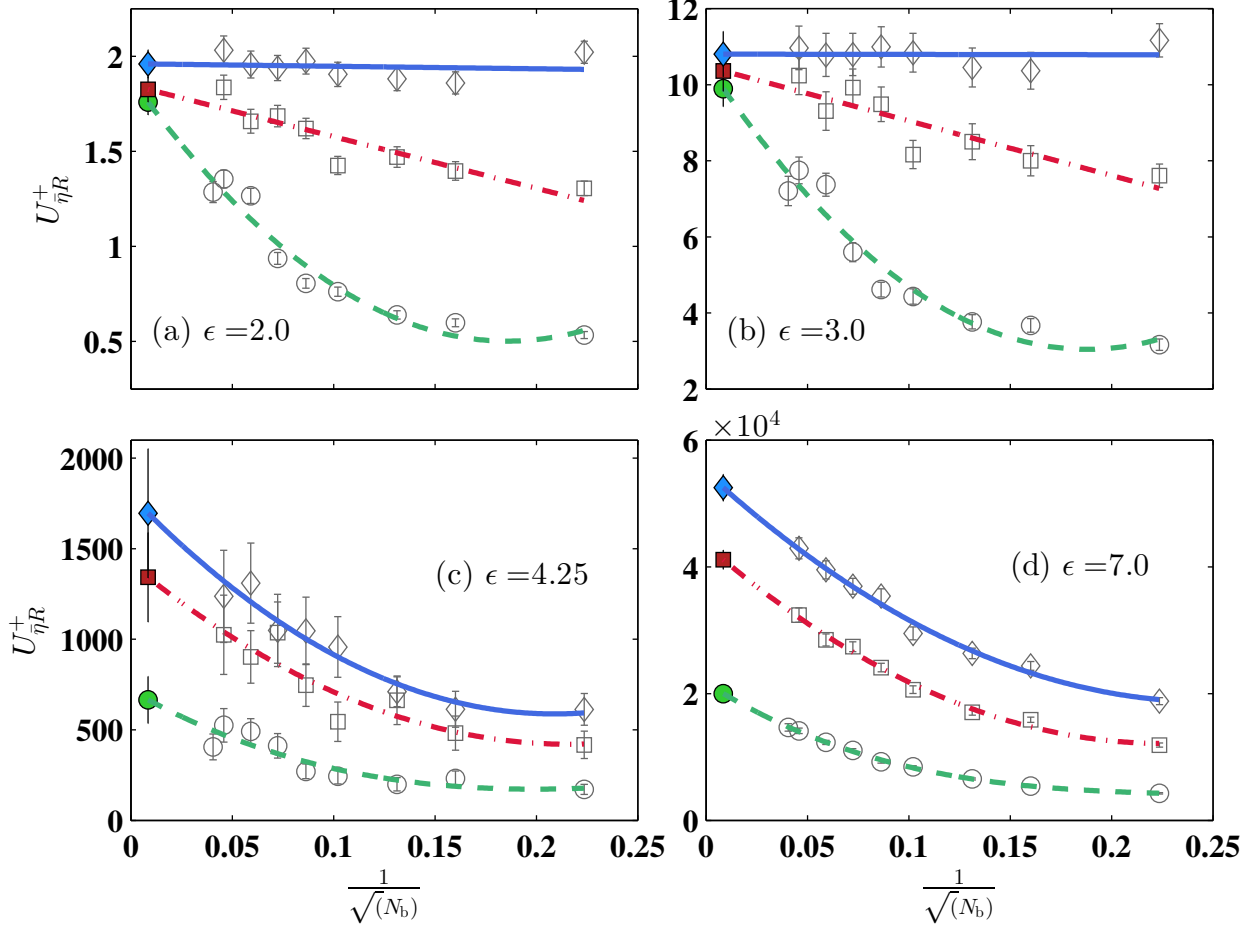
### 4.3.2 SFG in the presence of HI

Previous attempts of simulating the extensional behavior of high molecular weight polystyrene highlighted the importance of incorporating HI into the model [122, 59, 58]. In order to properly account for the presence of HI, here the results are evaluated in the limit of a bead-rod chain that for the high molecular weight polymers considered in this study is close to the non-draining limit, i.e.,  $h \rightarrow \infty$ , where  $h = h^* \sqrt{N_b}$ . To this end,  $\tilde{h}_K^*$  values of 0.05, 0.15, and 0.25 were considered to ascertain the sensitivity of the predictions to the choice of  $\tilde{h}_K^*$  for the polymer solution with  $M_w = 10.2 \times 10^6$ . The results of  $U_{\eta R}^+$  vs  $1/\sqrt{N_b}$  at four different strains are shown in Figure 4.3 (the values of  $U_{\eta R}^+$  at different  $N_b$  are represented by open symbols). An ensemble of 200-300 chains with  $N_b$  ranging from 20 to 609 were considered for the simulations and the data accumulated for this range of number of beads is extrapolated to the limit  $N_b \rightarrow N_K + 1$  which is shown by filled symbols.

For  $\epsilon \lesssim 3.5$ , the results of  $\tilde{h}_K^* = 0.15$  and 0.25 vary linearly with  $1/\sqrt{N_b}$  and becomes nonlinear afterwards, while the ones for  $\tilde{h}_K^* = 0.05$  are nonlinear in the entire strain regime. For  $\epsilon \lesssim 3$ , the extrapolated  $U_{\eta R}^+$  at  $N_b = N_K + 1$  (which is presumably close to the non-draining limit for such high molecular weight dilute solutions) collapses into a single value. This is consistent with the previous findings that the macroscopic properties under



**Figure 4.2:** Effect of  $N_b$  on non-equilibrium segmental PDF for chains with  $M_w = 10.2 \times 10^6$  in the absence of HI at  $Wi = 39.96$ .



**Figure 4.3:** Extrapolation of  $U_{\eta R}^+$  obtained for different levels of fine-graining to the limit  $N_b \rightarrow N_K + 1$  for  $\tilde{h}_K^* = 0.05$  (circles),  $\tilde{h}_K^* = 0.15$  (squares), and  $\tilde{h}_K^* = 0.25$  (diamonds). The data shown have been obtained for  $M_w = 10.2 \times 10^6$  and  $Wi = 39.96$  at different strains.

equilibrium condition do not depend on the choice of  $\tilde{h}_K^*$  [82, 122]. The other important observation under near equilibrium conditions is the weak dependency of  $U_{\eta R}^+$  with respect to  $N_b$  for  $\tilde{h}_K^* = 0.25$  (see Figure 4.3(a) and Figure 4.3(b)). This is consistent with the existence of a  $\tilde{h}^*$ , i.e., fixed  $\tilde{h}^*$  or  $\tilde{h}_f^*$ , close to 0.25 where the corresponding simulation results show the least dependence on the level of fine-graining.

At strains greater than 3, the value of  $U_{\eta R}^+$  at  $N_b = N_K + 1$  does not approach a single value. At such high values of strain, a chain with sufficiently large number of beads under an external force  $f$  can be subdivided into a sequence of tension blobs of size  $\xi \approx \frac{k_B T}{f}$  [128],

where each blob contains  $g$  segments. The chain conformation is extended for length scales larger than  $\xi$  while it remains almost unperturbed for smaller length scales. In the context of the bead-spring micromechanical model, the length scale of the blobs can be estimated as  $\xi \approx l_H g^{\nu_{\text{eff}}}$ , where  $\nu_{\text{eff}}$  is the effective EV exponent. If  $\xi$  is much larger than the size of the beads, the drag on the polymer chain and consequently the polymer viscosity are expected to be independent of individual bead dimension and  $\tilde{h}_K^*$ .

For large values of  $Wi$  and strains, the blob size shrinks down to the level of individual beads. Similar to what was observed in [Figure 4.2\(c\)](#), the segmental PDF for bead-spring chains in the presence of HI at  $Wi = 39.96$  and  $N_b$  values up to 609 revealed a dominant contribution of segments with near maximum extension (data not shown). This implicitly indicates that the length scale of unperturbed blobs is smaller than the individual springs which leads to the dependency of the chain friction on the value of  $\tilde{h}_K^*$ . Evidently, higher value of  $\tilde{h}_K^*$  implies larger bead radius, greater drag on the chain, and consequently higher extensional viscosity.

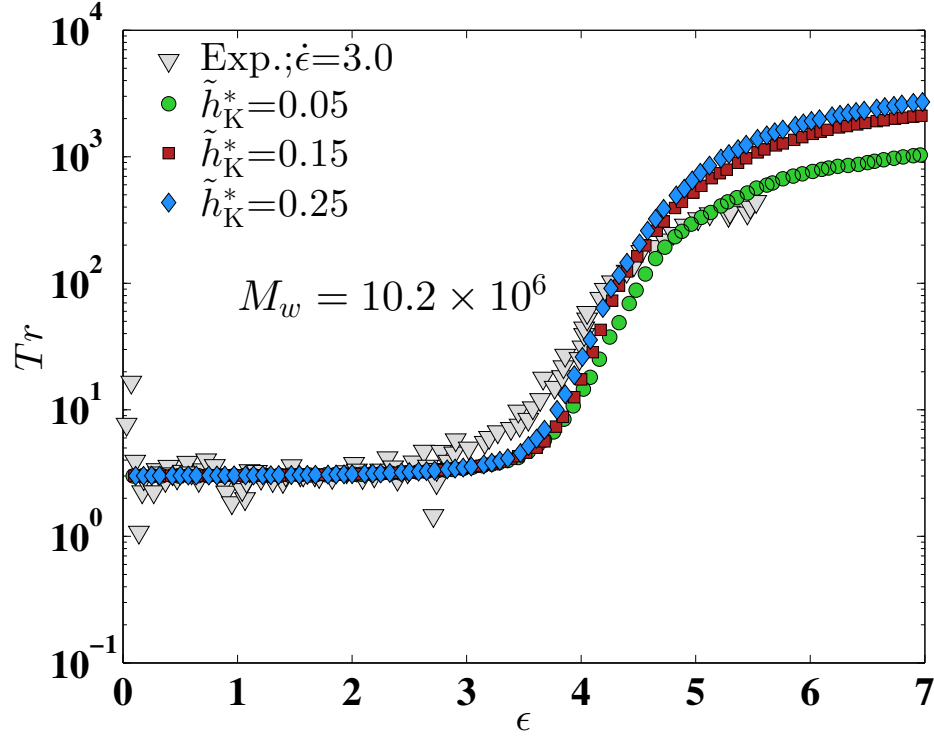
However, it should be noted that in spite of an accurate polynomial fit presented in [Figure 4.3\(a\)](#)-[Figure 4.3\(d\)](#), the shape of the curve may change if the results of more fine-grained chains are included in the plot (see for instance Fig. 3 of the paper by Prabhakar *et al.* [122]). However, the dependency of  $U_{\bar{\eta}R}^+$  in the limit  $N_b \rightarrow N_K + 1$  on  $\tilde{h}_K^*$  at large strains as shown in [Figure 4.3\(c\)](#)-[Figure 4.3\(d\)](#) is expected since the chains approach their maximum extension.

Using the extrapolated  $U_{\bar{\eta}R}^+$  at  $N_b = N_K + 1$ ,  $Tr$  is calculated as

$$Tr(\epsilon) \approx \frac{\bar{\eta}_u}{\eta_s} = 3 + nR_{\text{ee,eq}}^3 U_{\bar{\eta}R}^+. \quad (4.5)$$

The corresponding  $Tr$  vs.  $\epsilon$  at different  $\tilde{h}_K^*$  are depicted in [Figure 4.4](#) (note that in a  $\theta$ -solution,  $\langle R_{\text{ee}}^2 \rangle_{\text{eq}} = N_K b_K^2$ ).

Increasing  $\tilde{h}_K^*$  improves the predictions of the onset of stress growth compared to the free-draining case. Simultaneously, however, higher values of  $\tilde{h}_K^*$  result in a pronounced over-estimation of  $Tr_\infty$ . These observations are consistent with previous reports by Hsieh



**Figure 4.4:** Effect of SFG in the presence of HI with various  $\tilde{h}_K^*$  values at  $Wi = 39.96$  on the results of  $Tr$  vs.  $\epsilon$  for  $M_w = 10.2 \times 10^6$ . The error bars are approximately equal or smaller than the symbols.

and Larson [58]. Nevertheless, the correct value of  $\tilde{h}_K^*$  is essential in predicting the correct  $Tr_\infty$ . Hsieh and Larson [58] reported  $h^*$  for different choices of  $N_b$  based on matching the drag on a fully extended chain to the drag from Batchelor's theory for a cylindrical rod. Their reported values are utilized here and extrapolated to the limit at  $N_K + 1$  to find  $\tilde{h}_K^*$  (see Table 4.2). Irrespective of the molecular weight, the  $\tilde{h}_K^*$  is found to be around 0.1. These values of  $\tilde{h}_K^*$  is used in the next section to compare BD predictions with experimental measurements of extensional viscosity.

**Table 4.2:**  $h^*$  as a function of  $N_b$  reported by Hsieh and Larson [58]. In this table,  $\tilde{h}_K^*$  is calculated by fitting the values of  $h^*$  vs.  $N_b$  to a power function and extrapolating to  $N_K + 1$ .

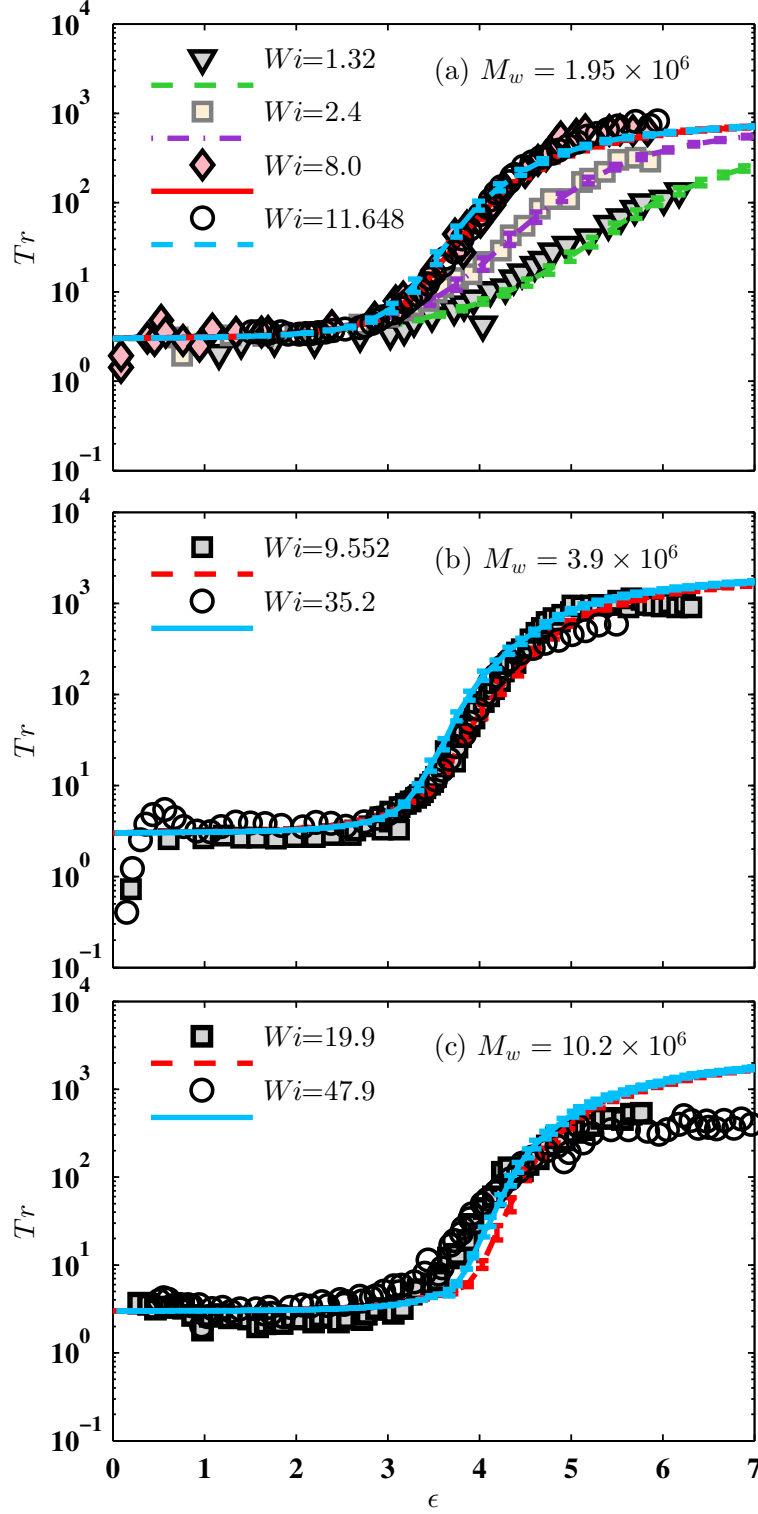
| $M_w = 1.95 \times 10^6$ |       |               | $M_w = 3.9 \times 10^6$ |       |               | $M_w = 10.2 \times 10^6$ |       |               | $M_w = 20 \times 10^6$ |       |               |
|--------------------------|-------|---------------|-------------------------|-------|---------------|--------------------------|-------|---------------|------------------------|-------|---------------|
| $N_b$                    | $h^*$ | $\tilde{h}^*$ | $N_b$                   | $h^*$ | $\tilde{h}^*$ | $N_b$                    | $h^*$ | $\tilde{h}^*$ | $N_b$                  | $h^*$ | $\tilde{h}^*$ |
| 10                       | 0.568 | 0.569         | 10                      | 0.739 | 0.74          | 10                       | 1.075 | 1.075         | 10                     | 1.41  | 1.41          |
| 20                       | 0.475 | 0.477         | 20                      | 0.613 | 0.614         | 20                       | 0.884 | 0.885         | 20                     | 1.15  | 1.15          |
| 40                       | 0.386 | 0.389         | 40                      | 0.494 | 0.496         | 40                       | 0.706 | 0.707         | 40                     | 0.913 | 0.914         |
| 60                       | 0.341 | 0.345         | 60                      | 0.433 | 0.436         | 80                       | 0.557 | 0.559         | 60                     | 0.792 | 0.793         |
| 100                      | 0.291 | 0.298         | 100                     | 0.367 | 0.371         | -                        | -     | -             | 100                    | 0.661 | 0.662         |
| $N_K + 1$                | -     | 0.118         | $N_K + 1$               | -     | 0.113         | $N_K + 1$                | -     | 0.111         | $N_K + 1$              | -     | 0.106         |

### 4.3.3 Comparison of BD predictions using SFG in the presence of HI with experiment

In this section, the SFG procedure in the presence of HI outlined in [section 4.2.2](#) and [section 4.3.2](#) is used to provide a comprehensive picture of how well BD can predict the extensional rheology of dilute solutions of HMWPS under uniaxial extensional flow [50].

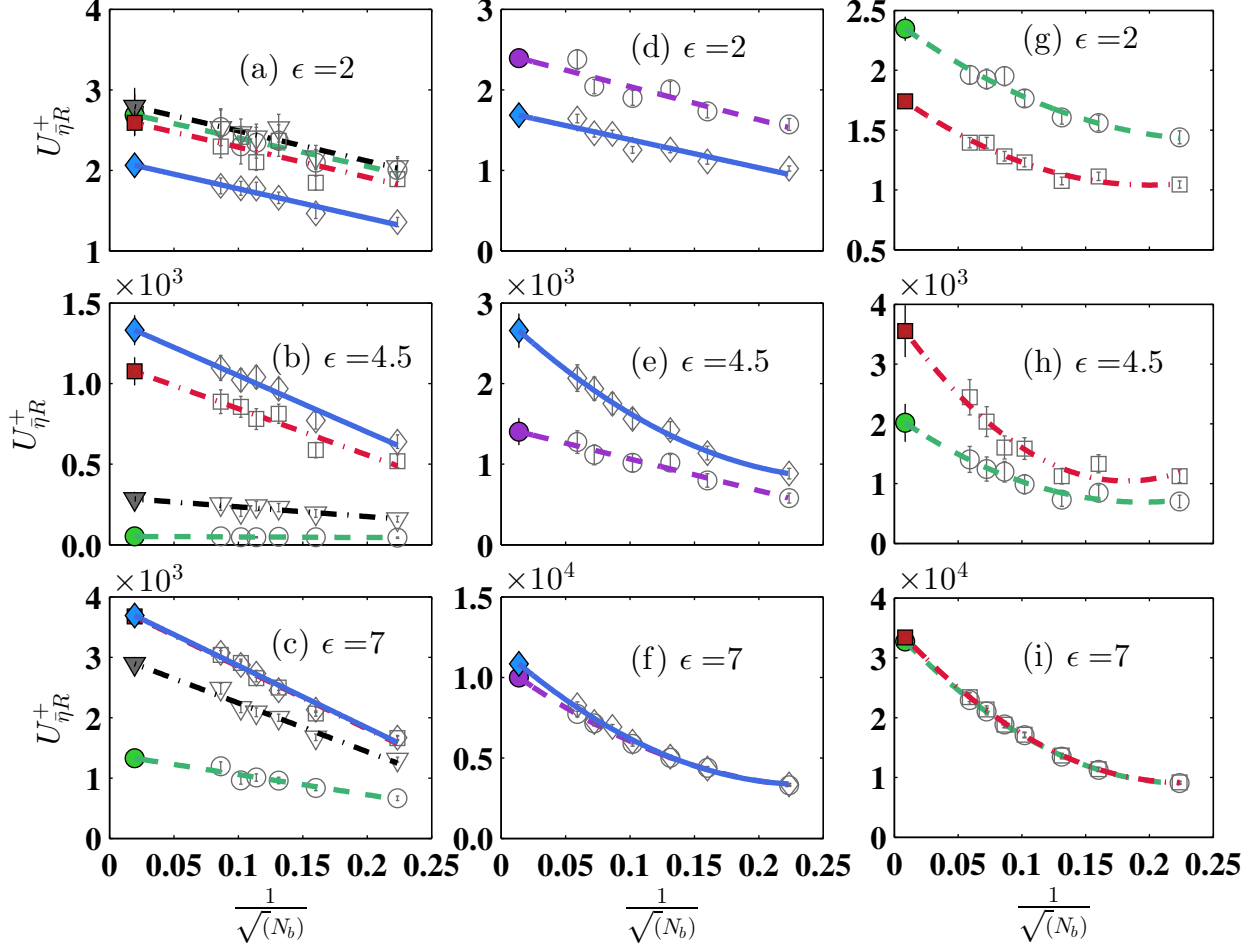
The comparison for the three lower values of molecular weight, namely  $1.95 \times 10^6$ ,  $3.9 \times 10^6$ , and  $10.2 \times 10^6$  are shown in [Figure 4.5](#). The agreement between BD and experiment for these molecular weights at different  $Wi$  is remarkable. Furthermore, the over-prediction of  $Tr_\infty$  reported in previous investigations of these systems [122, 58] are not seen, presumably due to the proper choice of  $\tilde{h}_K^*$ . The  $Wi$  after which  $Tr$  vs.  $\epsilon$  remains approximately unchanged is also predicted correctly. The details of SFG procedure used for the three lower molecular weight chains are presented in [Figure 4.6](#).

The comparison for the highest molecular weight, namely  $20 \times 10^6$ , is shown in [Figure 4.7](#). Although a considerable improvement in predicting  $\epsilon_c$  compared to the free-draining case is achieved when SFG is applied in the presence of HI, a small lag in the growth of simulated  $Tr$  relative to the experimental data still remains. Experimental data in [Figure 4.5](#) and [Figure 4.7](#) shows a extension thinning phenomena where  $Tr_\infty$  decays as  $Wi$  or  $\dot{\epsilon}$  is increased, particularly for the highest molecular weight PS (for detailed illustration of the problem see the papers by Gupta *et al.* [50] and Anna *et al.* [7]). However, BD simulations for dilute



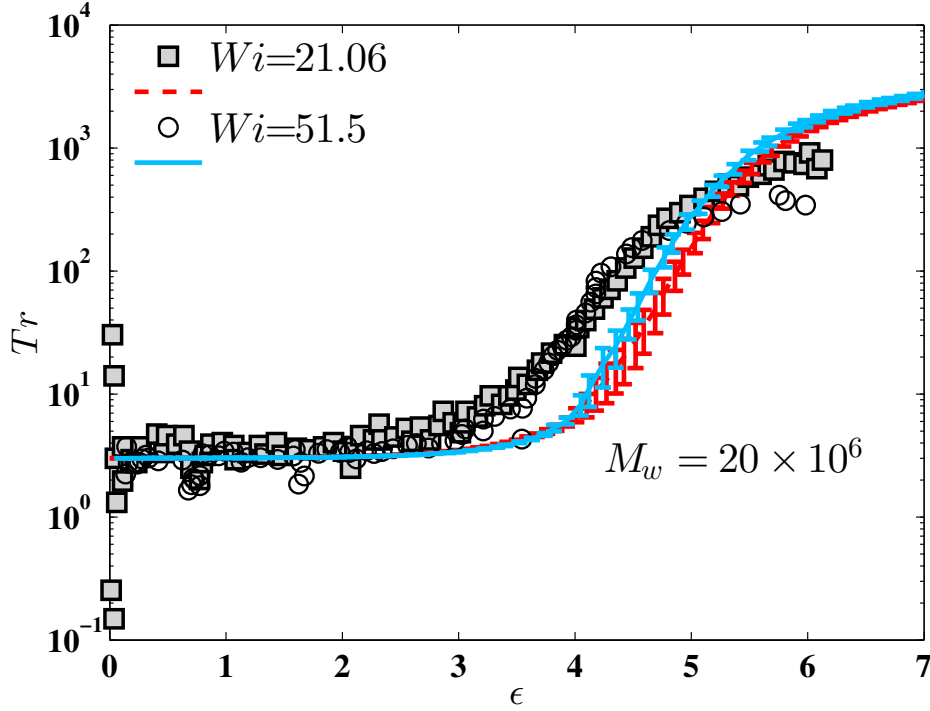
**Figure 4.5:** Effect of SFG in the presence of HI with  $\tilde{h}_K^*$  chosen based on Table 4.2 at different  $Wi$  on the results of  $Tr$  vs.  $\epsilon$  for (a)  $M_w = 1.95 \times 10^6$ , (b)  $M_w = 3.9 \times 10^6$ , and (c)  $M_w = 10.2 \times 10^6$ .





**Figure 4.6:** The SFG procedure for  $M_w = 1.95 \times 10^6$  [from (a) to (c)],  $M_w = 3.9 \times 10^6$  [from (d) to (f)], and  $M_w = 10.2 \times 10^6$  [from (g) to (i)] at different strains. The SFG data for  $M_w = 1.95 \times 10^6$  are provided at  $Wi = 1.32$  (circles), 2.4 (inverted triangles), 8 (squares), and 11.65 (diamonds), while the ones for  $M = 3.9 \times 10^6$  are obtained at  $Wi = 9.55$  (circles) and 35.2 (diamonds). The SFG data for  $M_w = 10.2 \times 10^6$  are determined at  $Wi = 19.9$  (circles) and 47.9 (squares).

polymer solutions does not show any change in  $Tr_{\infty}$  as  $\dot{\epsilon}$  is increased. Moreover, the extension thinning can not be explained by physical arguments for dilute solutions in a uniaxial flow as all molecules eventually become fully extended. This can be an indication of error in the experimental data at large strains for  $10.2 \times 10^6$  and  $20 \times 10^6$  molecular weights. Hsieh and Larson [58] and Larson [86] mentioned several possible scenarios including inter-chain interactions as a result of deviation from infinite dilution assumption and chain scission for



**Figure 4.7:** Effect of SFG in the presence of HI with  $\tilde{h}_K^*$  chosen based on [Table 4.2](#) at different  $Wi$  on the results of  $Tr$  vs.  $\epsilon$  for (a)  $M_w = 10.2 \times 10^6$  and (b)  $M_w = 20 \times 10^6$ .

the discrepancy between the experimental and simulated plateau Trouton ratio. In addition, end-plate instabilities observed by McKinley *et al.* [104] can result in failure of experiment to correctly capture the large strain extensional hardening of polymer solutions.

Molecular theory also predicts a higher minimum average Hencky strain for a polymer molecule to extend from its equilibrium state to its fully extended state as the molecular weight is increased [58]. This phenomena is clearly consistent with the results shown in [Figure 4.5](#) and [Figure 4.7](#) where the polymer molecules were assumed to be mono-disperse and dissolved in a  $\theta$ -solvent. As far as the consistency with experimental data is concerned, it has been shown by Li *et al.* [95] that poly-dispersity may slightly shifts the  $Tr$  vs.  $\epsilon$  curves towards lower strains. Moreover, the EV interaction (or deviation from  $\theta$ -solvent) has a similar influence. This will be discussed in more detail in the next section.

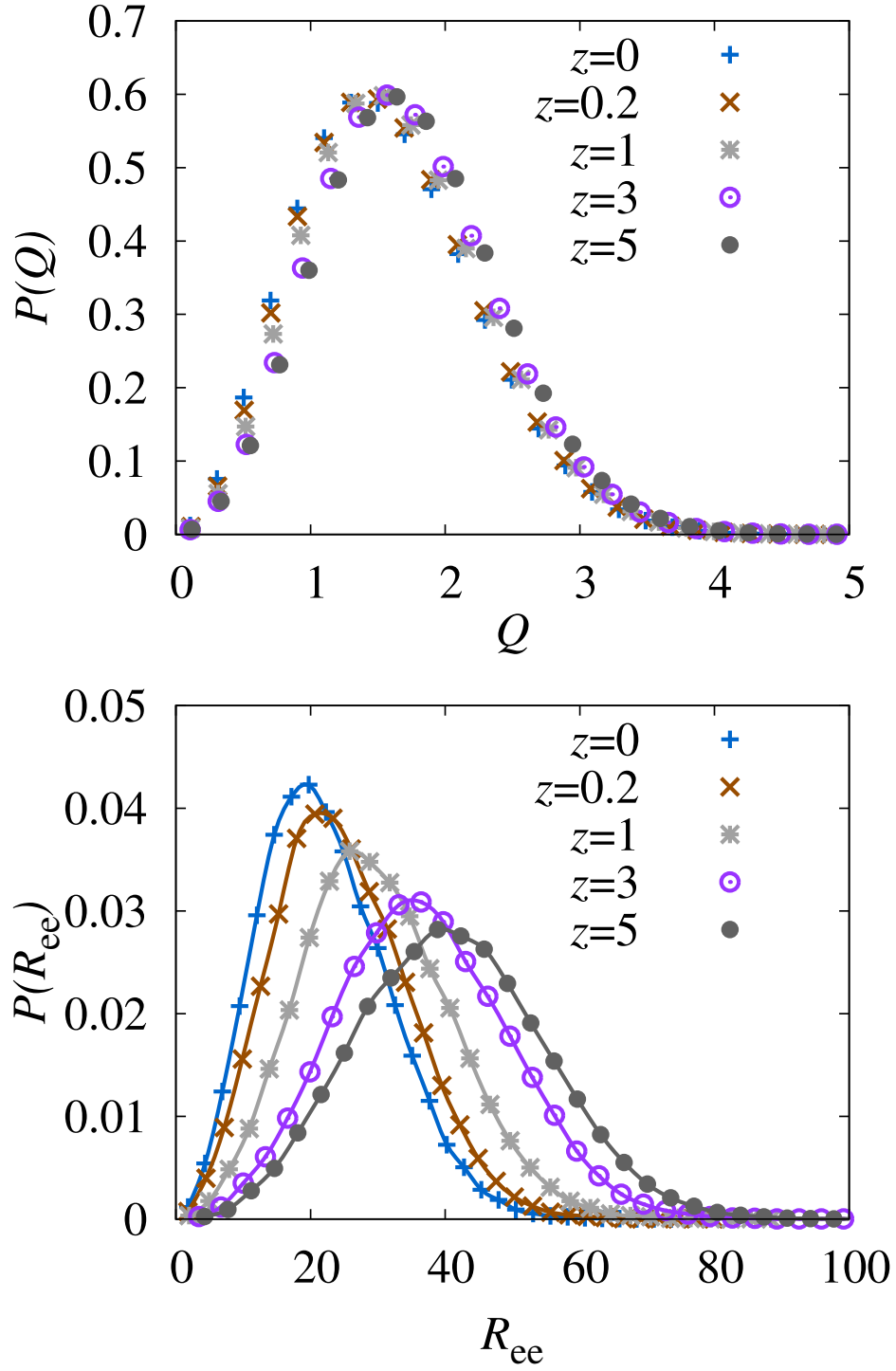
#### 4.3.4 Effect of EV with soft Gaussian potential

Although the solvents are assumed to be roughly  $\theta$ -like, the repulsive forces due to the overlap between different parts of the chain is still present. Moreover, a small deviation from  $\theta$ -solvent for lower molecular weight systems, means more significant EV effect for higher ones as  $z \propto \sqrt{M_w}$ . Therefore, it is worthwhile to assess the influence of EV interaction on the stress growth of the HMWPS solutions. For this purpose, the equilibrium segmental and end-to-end distribution function is plotted in [Figure 4.8](#) as a function of segmental length and end-to-end distance, respectively, for the cases with no EV and in the presence of a soft Gaussian EV potential with different  $z$  values.

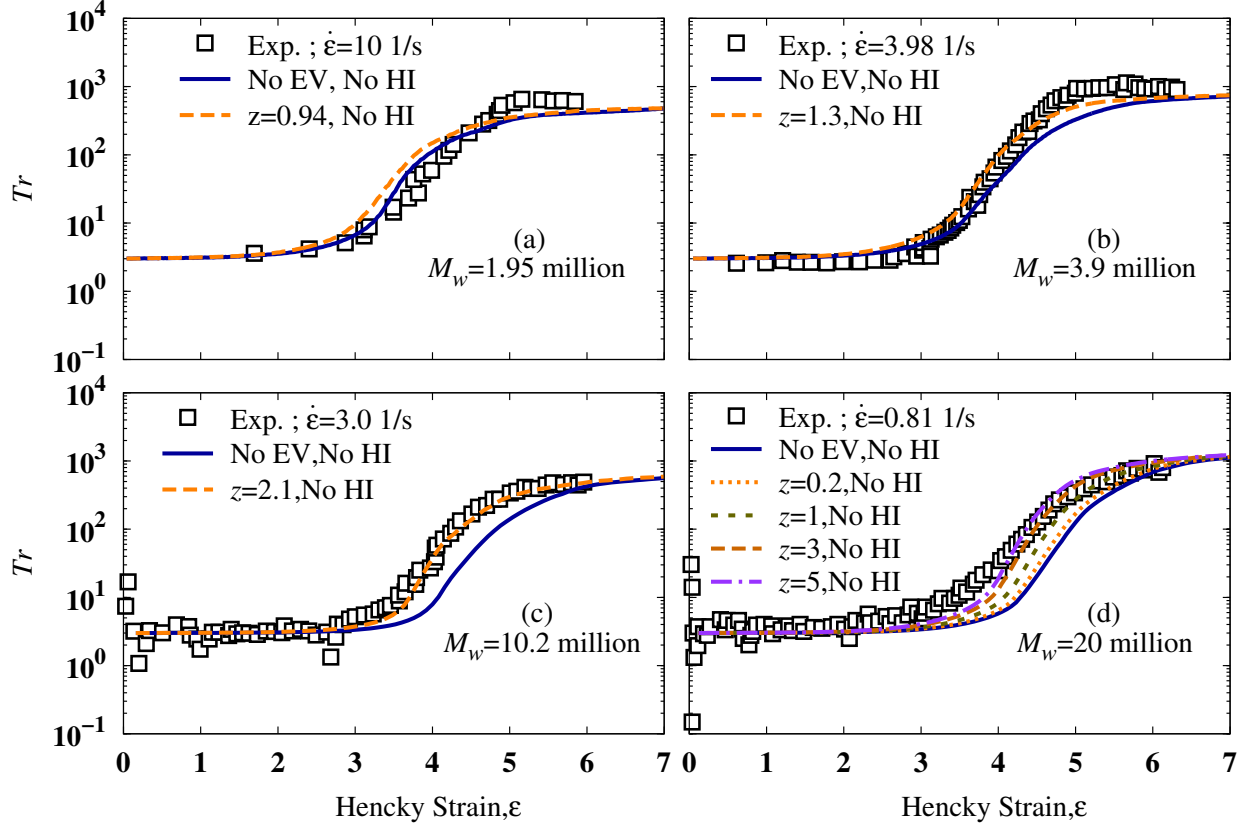
Although the segmental PDF shows a slight shift to larger  $Q$  in the presence of EV, the increase in the average end-to-end distance due to coil expansion, particularly for the highest  $z$ , is much more pronounced. This static swelling of the chains in the presence of EV is the main reason for the shift of the onset of stress upturn to smaller strains. To further illustrate this point, an ensemble of 100 chains with  $N_b = 191$  under free-draining condition and in the presence of EV interactions with different values of  $z$  were simulated (see [Figure 4.9](#)).

In the absence of HI, the minimum solvent quality to have a close agreement between simulations and experiment was found to be  $z = 3$  for  $M_w = 20 \times 10^6$ . Selecting this value of  $z$  for  $M_w = 20 \times 10^6$  and decreasing it based on the  $z \propto \sqrt{M_w}$  scaling results in very good agreement between BD predictions of  $\epsilon_c$  with the corresponding experimental measurements for  $M_w = 3.9 \times 10^6$  and  $10.2 \times 10^6$  (see [Figure 4.9\(b\)](#)-[Figure 4.9\(c\)](#)). However, the presence of EV in simulations for  $M_w = 1.95 \times 10^6$  leads to the over-prediction of  $\epsilon_c$  (see [Figure 4.9\(a\)](#)). Note that the chemistry of the solvent is assumed to remain the same as the molecular weight of the macromolecule is reduced in the polymer solution. Therefore, Equation (2.31) simply implies that the solvent quality should be decreased proportional to the square root of molecular weight. Hence, the corresponding lag between BD results and experimental data in the presence of EV becomes smaller as the molecular weights is decreased.

Furthermore, the probability distribution at different strains shown in [Figure 4.10](#) demonstrates a trend toward larger fractional end-to-end distance when EV is included in the



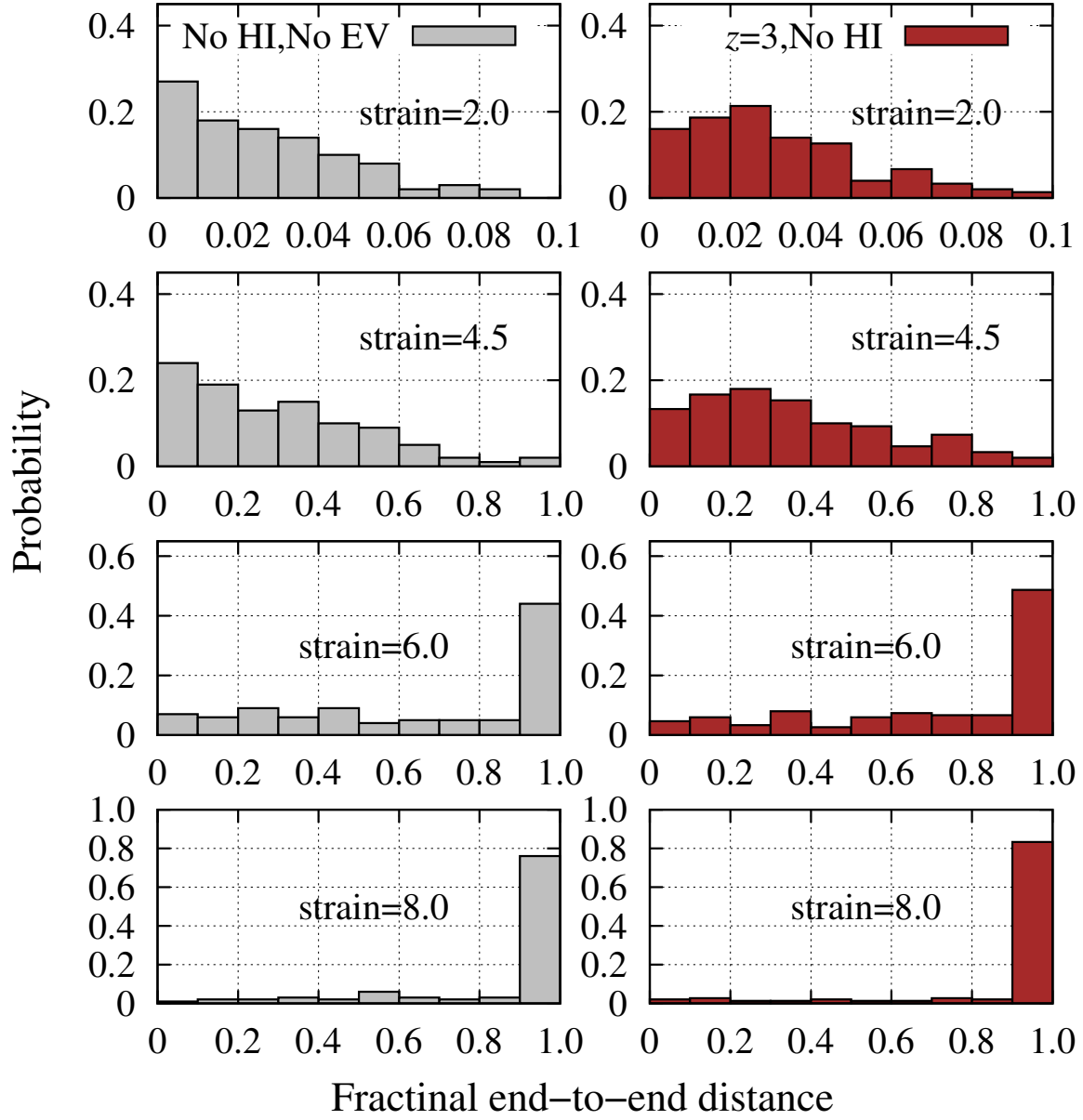
**Figure 4.8:** Effect of soft Gaussian potential EV on equilibrium PDF of segmental connector vector and end-to-end distance of chains with  $M_w = 20 \times 10^6$  and  $N_b = 191$ .



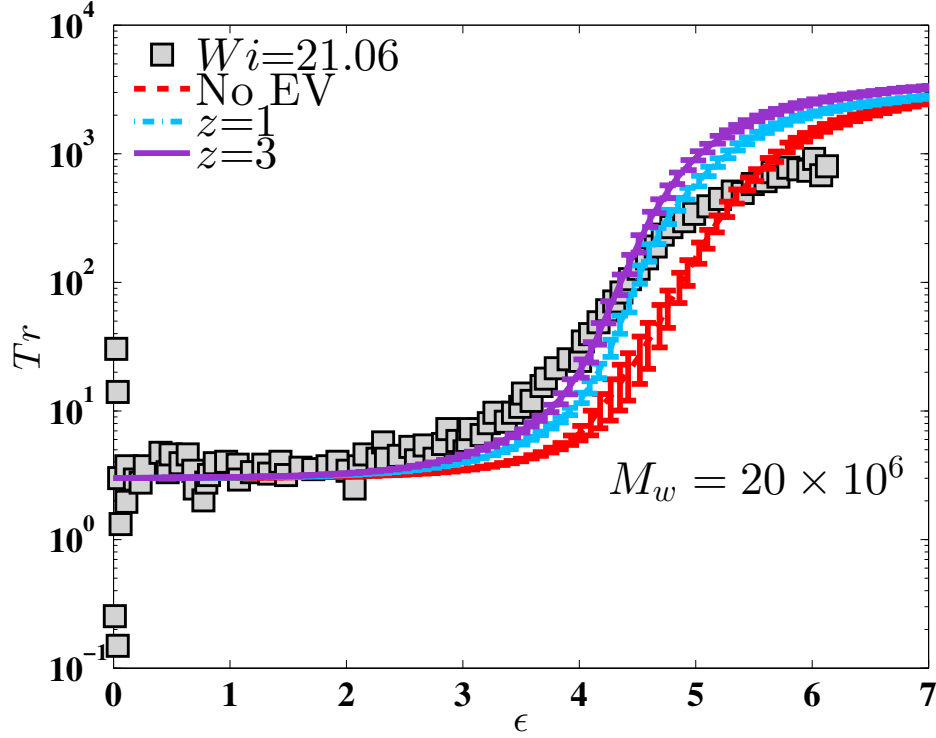
**Figure 4.9:** Effect of soft Gaussian EV on  $Tr$  vs.  $\epsilon$  of chains with  $N_b = 191$  and different molecular weights in the absence of HI with and without inclusion of EV at  $Wi = 11.2, 12.58, 39.96$ , and  $29.74$  for  $M_w = 1.95 \times 10^6, 3.9 \times 10^6, 10.2 \times 10^6$ , and  $20 \times 10^6$ , respectively.

simulations. The results shown in [Figure 4.9](#) and [Figure 4.10](#) highlight the relative influence of EV interaction on the BD predictions and the importance of increased molecular weight in better-than-theta solvents.

In order to accurately examine the effect of having EV interaction in the presence of HI, SFG is employed with  $z = 1$  and  $3$  for  $M_w = 20 \times 10^6$  as shown in . Note that  $R_{ee,eq}$  in Equation (4.5) is calculated using the swelling ratio  $\alpha = R_{ee,eq}/R_{ee,eq}^\theta$  as suggested by Kumar and Prakash [83] where  $\alpha(z = 1) = 1.3116$  and  $\alpha(z = 3) = 1.5926$ . A behavior similar to what was shown in [Figure 4.9](#) is observed where closer agreement between experiment and BD results is achieved when EV interaction is included in the simulations.



**Figure 4.10:** Effect of soft Gaussian EV on probability distribution at different strains for chains with  $M_w = 20 \times 10^6$  and  $N_b = 191$  at  $Wi = 29.74$  in the absence of HI.



**Figure 4.11:** Effect of soft Gaussian EV with  $z = 1$  and  $3$  on  $Tr$  vs.  $\epsilon$  of chains with  $M_w = 20 \times 10^6$ . The SFG is employed in the presence of HI with and without EV.

## 4.4 Conclusions

This chapter presents a comprehensive study on how key parameters (HI and EV interactions, level of fine-graining, and  $Wi$ ) alter the results of  $Tr$  vs.  $\epsilon$  in BD simulations of uniaxial extensional flow using the bead-spring micromechanical model description. In particular, it has been shown that:

- In absence of HI and EV, progressive fine-graining provides a closer agreement between experimental data and simulation results. Specifically, for polystyrene with  $3.9$  and  $10.2 \times 10^6$  molecular weight, increasing the number of beads in the chain results in shifting the onset of stress growth  $\epsilon_c$  to lower values. This trend is attributed to the segmental connectivity probability distribution function, where a clear transition towards larger fractional extension is observed as one adds more segments to the bead-spring chain model.

- The SFG method in the presence of HI affects the steady state plateau of Trouton ratio, where increasing  $\tilde{h}_K^*$  results in higher  $Tr_\infty$ . This is mostly attributed to the enhanced drag on the chain as  $\tilde{h}_K^*$  is increased in the simulations.
- The SFG method in presence of HI, was shown to be very successful in predicting the extensional hardening of polymer solutions with  $M_w = 1.95 \times 10^6$ ,  $3.9 \times 10^6$ , and  $10.2 \times 10^6$  at different  $Wi$ . The consistency of simulated plateau Trouton ratio with that of experimental data is attributed to the proper choice of  $\tilde{h}_K^*$  which was calculated based on the strategies outlined in [section 4.3.2](#). In spite of considerable improvement in simulated  $Tr$  vs.  $\epsilon$  for  $20 \times 10^6$  as compared to the free-draining case, a small difference between the simulated and experimental strain at the stress upturn still remains.

The delayed stress hardening observed in BD results for the highest molecular weight polymer solution, namely  $20 \times 10^6$ , can be overcome when EV interaction using the soft Gaussian potential is incorporated into the simulations. It was also demonstrated that increasing  $z$  in the soft Gaussian potential decreases the strain at which the stress upturn is observed. This is attributed to the static expansion of the polymer molecules at equilibrium.



# Chapter 5

## Improved bead-spring model for semiflexible chains

This chapter is based on the manuscript:

- A. Saadat and B. Khomami. A new bead-spring model for simulation of semiflexible macromolecules. accepted to *J. Chem. Phys.*.

### 5.1 Introduction

A broad range of semiflexible macromolecules, particularly biological polymers such as double-stranded DNA, worm-like micelles, and actin filaments, are modeled using the worm-like chain (WLC) model [17, 66, 102, 21]. Based on the physics of the problem, models should incorporate certain level of details to correctly evaluate the chain properties. For instance, DNA in microfluidic devices can be studied at different length scales ranging from the persistence length [106, 97, 81] to the end-to-end distance of the macromolecule [116, 106, 97, 160, 81]. A wide variety of applications such as genome and sequence analysis involves confinement of biopolymers in micro and nanochannels [153, 81, 31, 25]. For simulating this class of experiments, the resolution of the model is critical to describing polymer dynamics under confinement.

In this chapter, a new bead-spring model (denoted as WLC-SK) is introduced for simulating semiflexible chains that builds upon the real WLC model. The model is capable of accurately predicting the correlations along the backbone of the chain. Moreover, WLC-SK is designed to provide sufficient resolution regardless of the characteristic length scale of the problem of interest. This is an improvement over previous coarse-grained bead-spring models where the force-extension relations were developed with no bending potential [102, 156]. In order to evaluate the fidelity of the WLC-SK bead-spring model in describing the properties of semi-flexible macromolecules at different length and time scales, the BD technique is employed to obtain the average mean-square spring length and the force-extension behavior of the macromolecule using a constant force ensemble of linear semiflexible molecules. It will be shown that the properties of the real WLC are accurately reproduced using this new model.

We further evaluate the dynamics of different length scales of the chain in the light of the relaxation time of the Rouse modes. It is important to note that the application of the Rouse normal coordinates is not restricted to linear flexible chains (the Rouse model) [51, 148, 85, 71]. Under equilibrium conditions, the nonlinear springs and the introduction of the bending force can be thought as a small and local perturbation to the system [51, 148]. Under these circumstances, one may assume a Gaussian distribution for each segment length and use Rouse coordinates as the independent normal coordinates of the chain.

In [section 5.2](#) below, a brief review of BD scheme used for evaluating the new model is provided. Next, the model derivation and parametrization are explained in detail. Finally, the force-extension relation and different relaxation modes for the new bead-spring model are explored to ensure the consistency of the proposed model in comparison with the real WLC.

## 5.2 BD scheme for bead-spring models

In BD simulations considered in this article, the segments of WLC are modeled via micromechanical springs which contain at least 1 Kuhn step per spring. The Itô SDE is,

$$d\mathbf{Q}_s = \bar{\mathbf{B}} \cdot \left\{ \frac{1}{\zeta} \mathbf{F}^\phi dt + \sqrt{\frac{2k_B T}{\zeta}} d\mathbf{W} \right\}, \quad (5.1)$$

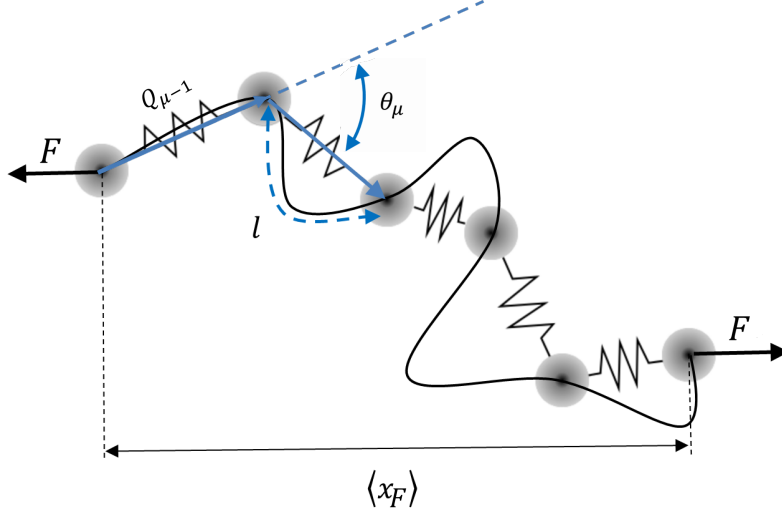
$$d\mathbf{r}_c = \sqrt{\frac{2k_B T}{\zeta}} \frac{1}{N_b} \sum_{\mu=1}^{N_b} d\mathbf{W}_\mu, \quad (5.2)$$

where  $\mathbf{F}^\phi = \mathbf{F}^{\text{spr}} + \mathbf{F}^{\text{b}} + \mathbf{F}^{\text{ext}}$  is the block force vector which consists of  $\mathbf{F}_\nu^{\text{spr}}$ , the net spring force,  $\mathbf{F}_\nu^{\text{b}}$ , the bending force, and  $\mathbf{F}_\nu^{\text{ext}}$ , the external force applied on the beads.  $\mathbf{F}_\nu^{\text{spr}}$  is obtained from the tension in the neighboring springs  $\mathbf{F}_{s,\nu}^c$  and  $\mathbf{F}_{s,\nu-1}^c$  with  $\mathbf{F}_{s,\nu}^c$  defined based on the spring connectivity vector between the adjacent beads,  $\mathbf{Q}_{s,\nu}$ , and their corresponding force law. The derivation of the  $\mathbf{F}_\nu^{\text{b}}$  for a bead-spring chain with bending potential is given in Appendix C. For the case of chains in the constant extension ensemble, only the first three and the last three components of  $\mathbf{F}^{\text{ext}}$  are non-zero.  $\mathbf{W}$  is a  $3N_b$  dimensional Wiener process [112].

The semi implicit predictor-corrector scheme described in chapter 2 is used to integrate Equation (5.1) to compare the segmental connectivity vector of the chains at each time step.

### 5.3 Mesoscopic bead-spring chain with bending potential

Consider a coarse-grained segment of the continuous WLC with contour length  $L_c$  shown in Figure 5.1. The segment has contour length  $l$  and contains  $N_{K,s}$  Kuhn steps (or  $2N_{K,s}$  persistence lengths). The vector that describes the connectivity of  $i^{\text{th}}$  segment is denoted by  $\mathbf{Q}_i$ . The mean square value of segmental length normalized by contour length, i.e.,  $\langle \hat{Q}_i^2 \rangle_{\text{eq}} = \langle Q_i^2 \rangle_{\text{eq}} / l^2$ , and the normalized mean value of correlation of nearest neighboring segments, i.e.,  $\langle \hat{\mathbf{Q}}_i \cdot \hat{\mathbf{Q}}_{i+1} \rangle_{\text{eq}}$ , can be obtained exactly at equilibrium based on the average correlation of the tangent vector in the continuous WLC (the derivation of the equations are



**Figure 5.1:** Schematic representation of a constant force ensemble of bead-spring chains with bending rigidity.

given in Appendix D):

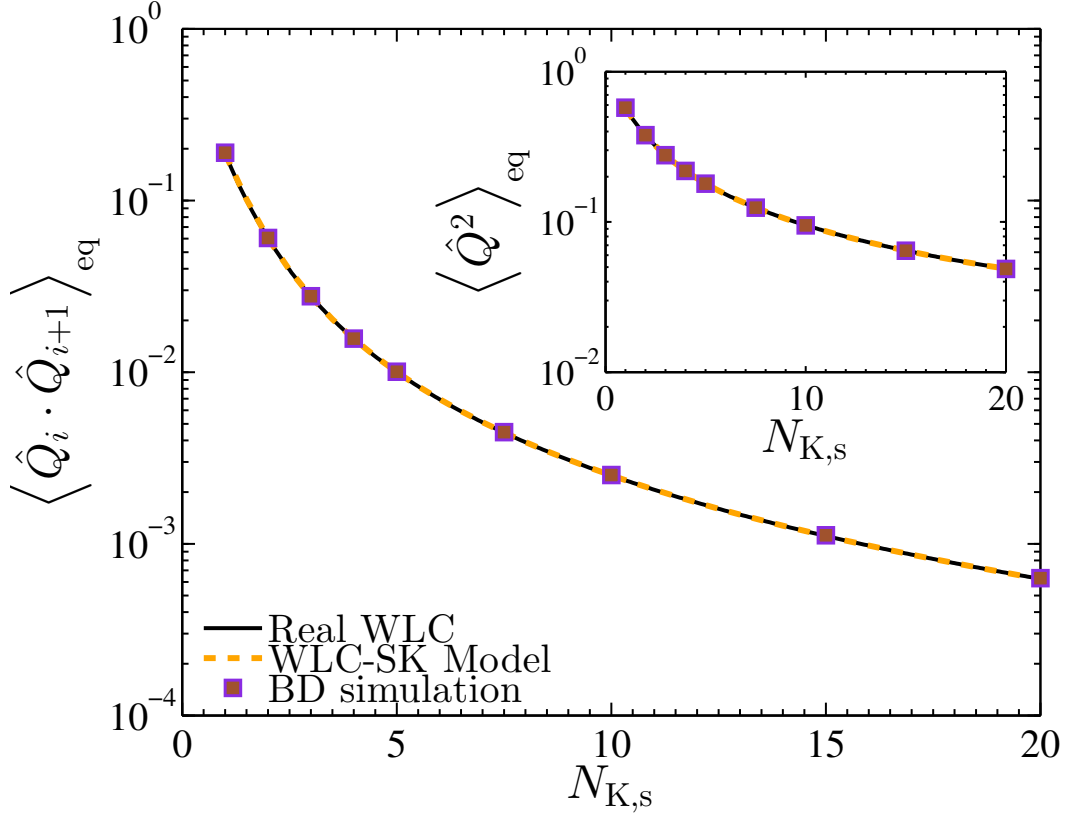
$$\left\langle \hat{Q}_{\text{wlc},i}^2 \right\rangle_{\text{eq}} = \frac{1}{N_{\text{K},s}} \left( 1 + \frac{1}{2N_{\text{K},s}} \{ \exp(-2N_{\text{K},s}) - 1 \} \right), \quad (5.3)$$

$$\left\langle \hat{Q}_{\text{wlc},i} \cdot \hat{Q}_{\text{wlc},i+1} \right\rangle_{\text{eq}} = \frac{1}{4N_{\text{K},s}^2} (1 - \exp(-2N_{\text{K},s}))^2. \quad (5.4)$$

The equivalence between the mesoscopic bead-spring model and the real continuous WLC is satisfied by reproducing the properties defined in Equation (5.3), and Equation (5.4). Note that next-nearest neighbor correlations, i.e.,

$$\left\langle \hat{Q}_{\text{wlc},i} \cdot \hat{Q}_{\text{wlc},j} \right\rangle_{\text{eq}} = \frac{1}{4N_{\text{K},s}^2} \exp(-2\{j-i-1\}N_{\text{K},s}) (1 - \exp(-2N_{\text{K},s}))^2, \quad (5.5)$$

where  $j > i + 1$ , exhibit exponential decay. Therefore, they are only important for over-discretized bead-spring models ( $N_{\text{K},s} < 1$ ) and are assumed negligible in this work. The present coarse-grained bead-spring models such as the one proposed by Marko and Siggia [102] (WLC-MS) or the model by Underhill and Doyle [156] (WLC-UD) do not take into account the bending potential between the springs and hence assume negligible correlation



**Figure 5.2:** The comparison of the theoretical correlation of nearest neighbors for the real long WLC and WLC-SK models with the results of BD simulations. Inset: the comparison of the squared segmental connectivity vector for the real WLC and WLC-SK models with the results of Brownian dynamics. Note that the WLC-MS and WLC-UD models assume  $\langle \hat{Q}_{s,i} \cdot \hat{Q}_{s,i+1} \rangle_{\text{eq}} = 0$  at all coarse-graining levels.

between nearest neighboring segments, i.e.,  $\langle \hat{Q}_{s,i} \cdot \hat{Q}_{s,i+1} \rangle_{\text{eq}} = 0$ . Although this assumption is reasonable when the springs contain several Kuhn steps, the deviation from the real WLC becomes significant as the limit of 1 Kuhn step per spring is approached (see Figure 5.2).

For models with no bending potential, the most important feature of an accurate spring force-law is matching of the force-extension behavior of bead-spring chain and the continuous WLC [102, 155, 101]. Unlike flexible chains, the form of force-extension relation for short worm-like chains ( $N_K \sim \mathcal{O}(1)$ ) is different than that of very long chains. However, one can show that for large enough values of  $N_K$ , the relative error between force at different

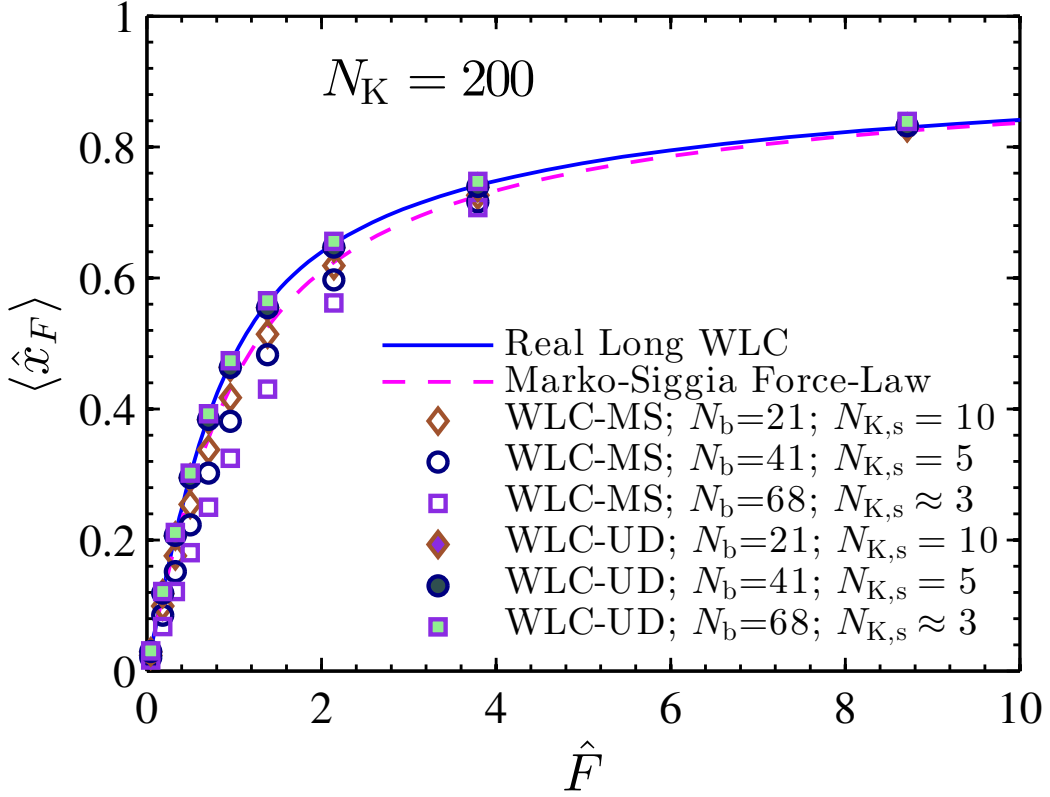
extensions for finite  $N_K$  compared to  $N_K \gg 1$  decays as  $1/N_K$  [156]. Hence in this chapter, it is assumed that the simulated chains are sufficiently long, such that the force-extension relation is no longer a function of the chain length. Note that the exact analytic force-extension relation for the real WLC is not known. However, approximate formulations are often employed to fit the numerical force-extension calculations for the real long WLC [14, 156]. We use the one proposed by Underhill and Doyle [156] which has a maximum error of 0.04% over the entire extension range:

$$\hat{F} = \frac{\hat{R}_{ee}}{(1 - \hat{R}_{ee}^2)^2} + \frac{3}{32}\hat{R}_{ee} + \frac{5}{64}\hat{R}_{ee}(1 - \hat{R}_{ee}^2) + \frac{21}{64}\hat{R}_{ee}G(\hat{R}_{ee})(1 - \hat{R}_{ee}^2)^2, \quad (5.6)$$

where  $\hat{R}_{ee}$  is the end-to-end distance normalized by  $L_c$ ,  $\hat{F} = \frac{Fb_K}{2k_B T}$  is the dimensionless force and  $G(\hat{R}_{ee}) = 1 + \frac{41}{35}\hat{R}_{ee}^2 + 0.627\hat{R}_{ee}^4 - 11.71\hat{R}_{ee}^6 + 10.26\hat{R}_{ee}^8$ .  $k_B$  is the Boltzmann constant, and  $T$  is the absolute temperature.

The force-extension relations (interpolation formulas) for the WLC-MS and WLC-UD models are developed such that the asymptotic behavior at small and large forces are reproduced accurately. Due to the form of the Marko-Siggia force-extension relation, it is necessary to introduce a correction factor to recover the behavior of the real long WLC from bead-spring simulations. This correction is made either at small forces or at large ones. A single choice of this correction factor is not sufficient to accurately predict the force-extension relation at the two extremes. The low-force criterion is commonly chosen [151, 156] in simulations of the WLC-MS model. We have also used this criterion in this article (see Figure 5.3). If this correction is not incorporated in the model, the equilibrium segmental length and end-to-end distance of the bead-spring chain does not match the real long WLC. The correction factor is commonly referred to as either ratio of effective to true persistence lengths  $\lambda$  [155, 156] or finite extensibility parameter  $\chi$  [151, 118]. Since the low force criterion is chosen, the relative extension in Figure 5.3 shows significant deviation from the real long WLC at medium forces.

A different interpolation formula is used in the WLC-UD bead-spring model:



**Figure 5.3:** Average fractional extension as a function of the applied force for the WLC-MS and WLC-UD bead-spring models using BD simulations. The results are shown at different coarse-graining levels and compared with the real long WLC.

$$\hat{\mathbf{F}}_{s,i}^c = \left[ a_1 \left( 1 - \hat{Q}_{s,i}^2 \right)^{-2} + a_2 \left( 1 - \hat{Q}_{s,i}^2 \right) + a_3 + a_4 \left( 1 - \hat{Q}_{s,i}^2 \right) \right] \hat{\mathbf{Q}}_{s,i}, \quad (5.7)$$

where  $\hat{\mathbf{F}}_{s,i}^c = \frac{\mathbf{F}_{s,i}^c b_K}{2k_B T}$  is the nondimensional conservative force on the spring  $i$ . Also,  $\hat{Q}_{s,i} = \left| \hat{\mathbf{Q}}_{s,i} \right|$  is the spring length normalized by contour length.  $a_i$  values are generally functions of the coarse-graining level.  $a_1 = 1$ ,  $a_2 = -\frac{7}{2N_{K,s}}$ , and  $a_3 = \frac{3}{32} - \frac{3}{8N_{K,s}} - \frac{6}{4N_{K,s}^2}$  are found based on the asymptotic expansion of  $\hat{x}_F$ , the extension in the direction of applied force  $F$ , for the real long WLC at large forces (see [Figure 5.1](#)),

$$\langle \hat{x}_F \rangle \sim 1 - \frac{1}{2\hat{F}^{1/2}} - \frac{1}{128\hat{F}^{3/2}} + \mathcal{O}\left(\frac{1}{\hat{F}^2}\right). \quad (5.8)$$

On the other hand,  $a_4$  is assumed to have a Padé functional form,

$$a_4 = P_2^2 (1/2N_{K,s}) = \frac{p_{s,0} + p_{s,1} (2N_{K,s})^{-1} + p_{s,2} (2N_{K,s})^{-2}}{1 + p_{s,3} (2N_{K,s})^{-1} + p_{s,4} (2N_{K,s})^{-2}}, \quad (5.9)$$

where  $p_{s,i}$  values are found according to the behavior of bead-spring chain at small forces. WLC-UD with  $p_{s,i} = \{13/32, 0.8172, -14.79, -4.225, 4.87\}$  was developed for a bead-spring chain without a bending potential to reproduce the behavior of infinitely long worm-like chains ( $N_K \gg 1$ ) with a maximum error of about 1% if each spring contains more than two Kuhn steps. This force-law represents a significant improvement since the force-extension relation in WLC-MS deviates more than 10% at intermediate forces as fine-graining is performed beyond the common value of  $N_{K,s} \approx 10$  (see [Figure 5.3](#)). Moreover, the calculation of finite extensibility parameter  $\chi$ , which is critical for the correct evaluation of excluded volume and hydrodynamic interaction parameters present in WLC-MS [\[151\]](#), is not required since irrespective of the level of fine-graining, the spring end-to-end distance at equilibrium is  $\langle \hat{Q}_s^2 \rangle_{\text{eq}}^{1/2} \approx \sqrt{N_{K,s} b_K} / l$  by construct and hence,  $\chi \approx 1$ . This choice of  $\langle \hat{Q}_s^2 \rangle_{\text{eq}}^{1/2}$  for the WLC-UD model guarantees the correct force-extension behavior at small forces. In this regard, Underhill and Doyle [\[156\]](#) made a compromise when using the bead-spring model without a bending potential. Specifically, in order to correctly describe the force-extension of the chain in the absence of a bending repulsion, the average squared length of a spring under equilibrium condition should be set to  $1/N_{K,s}$ . The error associated with this approximation becomes more significant as one continues to fine-grain the springs as shown in [Figure 5.4](#).

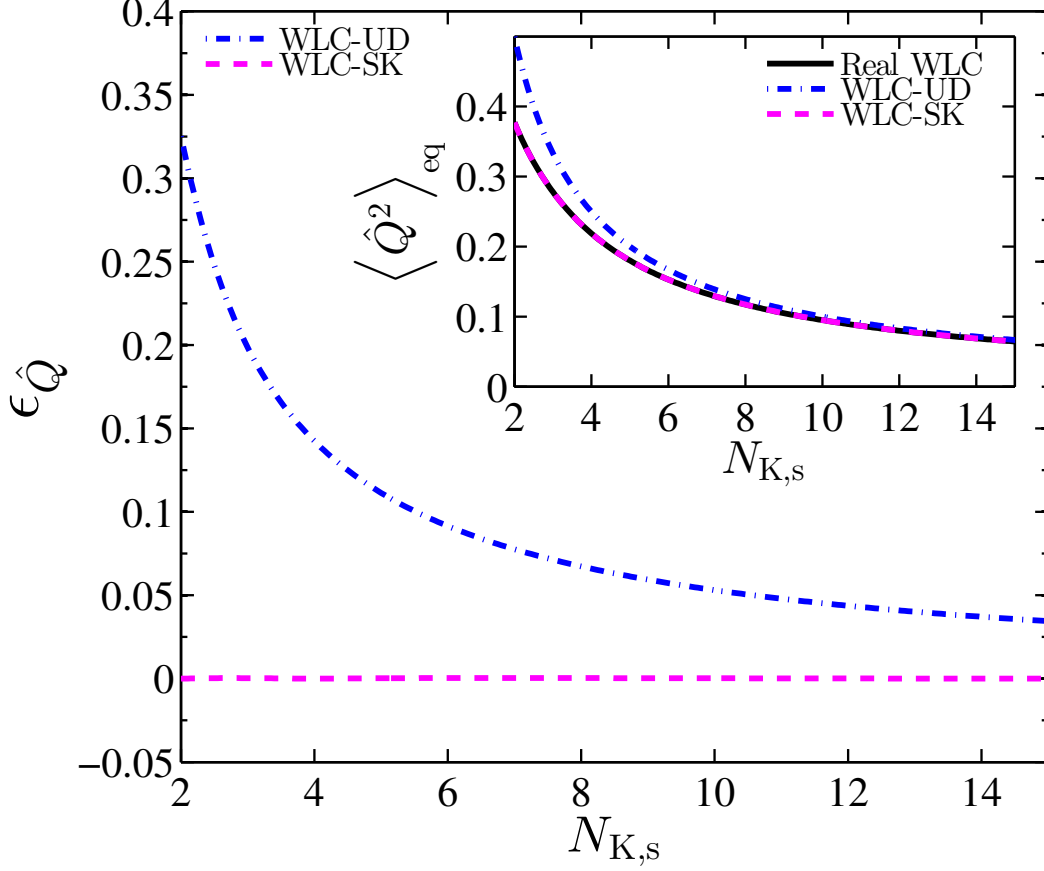
In the WLC-SK model, the mean-square end-to-end distance normalized by  $L_c$  is matched to the corresponding value of this property for the real WLC, i.e.,

$$\langle \hat{R}_{\text{wlc,ee}}^2 \rangle_{\text{eq}} = \frac{1}{N_K} \left( 1 + \frac{1}{2N_K} \{ \exp(-2N_K) - 1 \} \right), \quad (5.10)$$

to recover the correct force-extension at small forces. It is straight forward to show that, [\[128\]](#)

$$\langle R_{\text{ee}}^2 \rangle = \sum_{i=1}^{N_b} \left( \sum_{j=1}^{i-1} \langle \mathbf{Q}_i \cdot \mathbf{Q}_j \rangle + \langle Q_i^2 \rangle + \sum_{j=i+1}^{N_b} \langle \mathbf{Q}_i \cdot \mathbf{Q}_j \rangle \right). \quad (5.11)$$





**Figure 5.4:** The relative error  $\epsilon_{\hat{Q}} = \frac{|\langle \hat{Q}_s^2 \rangle_{\text{eq}} - \langle \hat{Q}_{\text{wlc}}^2 \rangle_{\text{eq}}|}{\langle \hat{Q}_{\text{wlc}}^2 \rangle_{\text{eq}}}$  of segmental dimension at equilibrium for WLC-UD and WLC-SK compared to the real WLC model as a function of the number of Kuhn steps per spring. Inset: squared segmental connectivity vector for the real WLC, WLC-UD, and WLC-SK models.

Since next-nearest neighbor correlations are assumed negligible for the case of  $N_{K,s} \geq 1$ , matching Equation (5.3) and Equation (5.4) is sufficient to satisfy the correct equilibrium end-to-end mean-square distance of the real worm-like chain. In Figure 5.4, the relative error of the value of squared spring end-to-end distance considered in the WLC-UD and WLC-SK models relative to the real WLC model is depicted as a function of the coarse-graining level.

## 5.4 Determination of WLC-SK parameters

The WLC-SK model is also designed to correctly take into account the correlation along the chain by introducing a bending potential between neighboring springs. Hence, inaccuracies as a result of neglecting bending potential are avoided. The force-extension relationship is assumed to follow the same form as WLC-UD but with revised parameters. At asymptotically large forces, the meso-scopic springs ( $N_{K,s} \gtrsim 1$ ) orient along the direction of the force and they stretch close to their maximum extension. In such an extreme condition, it is assumed that the spring force-extension relation in the WLC-SK model takes the same form as that of the WLC-UD model and hence their  $a_1$ ,  $a_2$ , and  $a_3$  are similar. It will be shown later that this assumption works well even when  $N_{K,s} = 1$ .

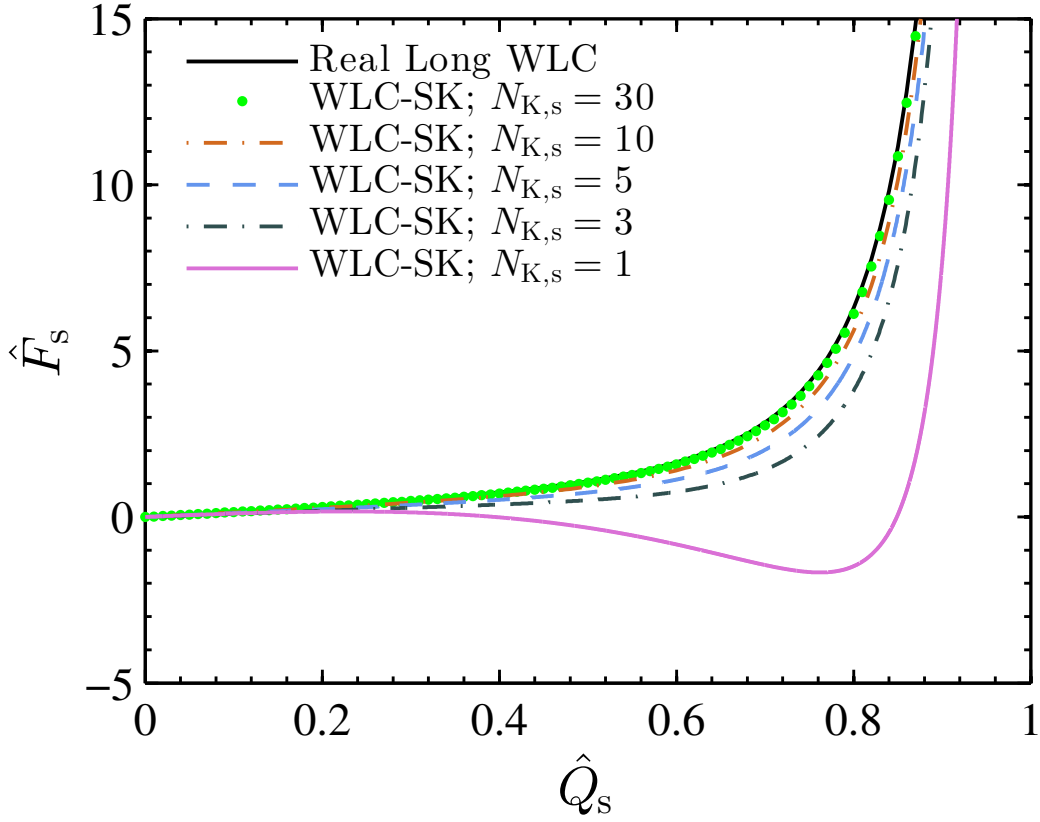
$a_4$  has the same Padé functional form as Equation (5.9), where  $p_{s,i}$  values are found by imposing the condition that  $\langle \hat{Q}_s^2 \rangle_{\text{eq}}$  is equal to the right-hand-side of the Equation (5.3). For a spring with a particular spring potential,  $\langle \hat{Q}_s^2 \rangle_{\text{eq}}$  is found by performing an integration over all possible configurations in spherical coordinates as follows,[155, 151, 132]

$$\langle \hat{Q}_s^2 \rangle_{\text{eq}} = \frac{\int_0^1 d\hat{Q}_s \hat{Q}_s^4 \exp(-\hat{\phi}_s)}{\int_0^1 d\hat{Q}_s \hat{Q}_s^2 \exp(-\hat{\phi}_s)}. \quad (5.12)$$

where  $\phi_s$  is the spring potential which for the WLC-SK model is obtained based on Equation (5.7) and the relation  $\hat{\mathbf{F}}_s = \frac{\partial \hat{\phi}_s}{\partial \hat{\mathbf{Q}}_s}$  (Note that the additive constant does not affect the final result and is dropped):

$$\hat{\phi}_s = \frac{\phi_s}{k_B T} = 2N_{K,s} \left\{ \frac{a_1}{2(1 - \hat{Q}_s^2)} + \frac{a_2}{2} \ln(1 - \hat{Q}_s^2) + \frac{a_3}{2} \hat{Q}_s^2 - \frac{a_4}{4} \hat{Q}_s^2 (\hat{Q}_s^2 - 2) \right\} \quad (5.13)$$

Using this equation and  $a_4$  with  $p_{s,i} = \{^{13/32}, 3.4719, 2.5064, -1.2906, 0.6482\}$  results in the exact second moment of spring length at  $N_{K,s} = 1, 2, 4, 15, \infty$  and the relative error for all other  $N_{K,s}$  values is less than 0.08%. As expected, the form of spring force-extension at



**Figure 5.5:** Spring force as a function of fractional extension at different coarse-graining level for the WLC-SK bead-spring model.

small values of  $N_{K,s}$  is very different than the real long WLC (see Figure 5.5). For  $N_{K,s} \lesssim 2$ , the minimum force is not at zero extension. For the limiting case of 1 Kuhn step per spring, the minimum occurs at fractional extension equal to 0.76.

The correlation of any two consecutive springs  $i$  and  $i+1$  can be written as  $\langle \hat{\mathbf{Q}}_{s,i} \cdot \hat{\mathbf{Q}}_{s,i+1} \rangle_{\text{eq}} = \langle \hat{Q}_s \rangle_{\text{eq}}^2 \langle \cos \theta_i \rangle$ , since the spring length and the bending angle between the springs  $\theta_i$  independently contribute to the potential energy. Again,  $\langle \cos \theta \rangle$  can be found from integration of the following equation in spherical coordinates, i.e.,

$$\langle \cos \theta \rangle = \frac{\int_0^\pi d\theta \sin \theta \cos \theta \exp(-C \{1 - \cos \theta\})}{\int_0^\pi d\theta \sin \theta \exp(-C \{1 - \cos \theta\})}. \quad (5.14)$$

The bending constraint is assumed between adjacent segments through a potential of the form [6, 76, 67],

$$\phi_{b,i}/k_B T = \mathcal{C}(N_{K,s}) \{1 - \cos \theta_i\} \quad (5.15)$$

where  $\mathcal{C}$  is a measure of the bending stiffness of WLC and is a function of  $N_{K,s}$ . We propose a  $P_3^2(2N_{K,s})$  Padé expansion for  $\mathcal{C}$ , since it results in the correct asymptotic behavior at  $N_{K,s} \rightarrow 0$  and  $\infty$ . Namely,  $\mathcal{C} = \frac{1+p_{b,1}(2N_{K,s})+p_{b,2}(2N_{K,s})^2}{2N_{K,s}+p_{b,3}(2N_{K,s})^2+p_{b,4}(2N_{K,s})^3}$  is considered which implies  $\mathcal{C}(N_{K,s} \rightarrow 0) = 1/2N_{K,s}$  and  $\mathcal{C}(N_{K,s} \rightarrow \infty) \approx 0$ .  $p_{b,i}$  values are determined in correspondence with the values of  $p_{s,i}$  in the WLC-SK model and by satisfying the correct correlation along the chain (Equation (5.4)).  $p_{b,i} = \{-1.237, 0.8105, -1.0243, 0.4595\}$  results in the exact nearest neighbor correlation at  $N_{K,s} = 0, 1, 2, 4, 15, \infty$  when the spring force parameters of the WLC-SK model are  $p_{s,i} = \{13/32, 3.4719, 2.5064, -1.2906, 0.6482\}$ . The mean square segmental length and nearest neighbor correlation for this bead-spring model is shown in Figure 5.2.

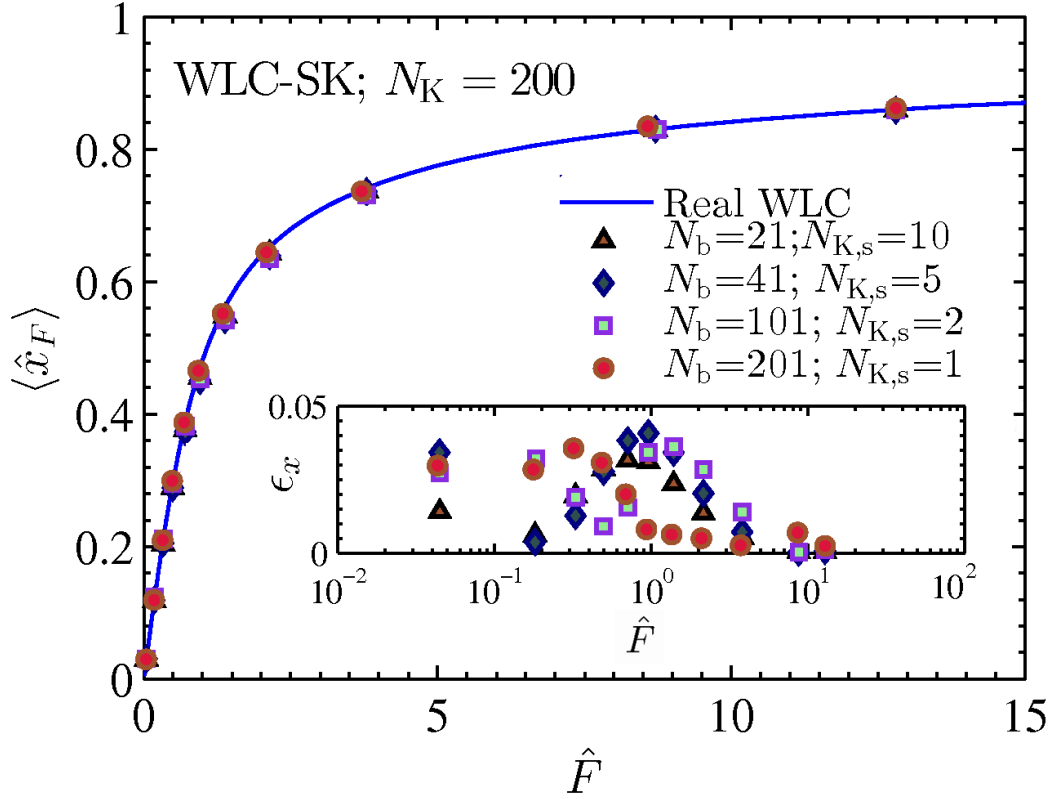
Based on the results shown in Figure 5.2, this new model is consistent with the theoretical predictions of the real long WLC. Likewise, the results of Brownian dynamics simulations with the proposed WLC-SK bead-spring model results in the desired segmental length and correlation along the backbone of the chain. The largest relative error in the force-extension relation of the entire chain occurs in the interpolation regime, i.e., at intermediate forces and it is approximately 4% (see Figure 5.6).

## 5.5 Relaxation modes of WLC-SK

The normal (Rouse) coordinates are defined based on the configuration of the chains as:

$$\mathbf{X}_p(t) = \frac{1}{N_b} \sum_{i=1}^{N_b} \mathbf{r}_i(t) \cos \left\{ \frac{\pi p}{N_b} (i - 1/2) \right\}, \quad p = 1, 2, \dots, N_b \quad (5.16)$$

where  $p$  values are the modes. It is assumed that the normalized correlation function of the  $p$ th mode  $C_p(t) = \frac{\langle \mathbf{X}_p(t) \cdot \mathbf{X}_p(0) \rangle}{\langle \mathbf{X}_p(0) \cdot \mathbf{X}_p(0) \rangle}$ , decays exponentially according to the relaxation time of the

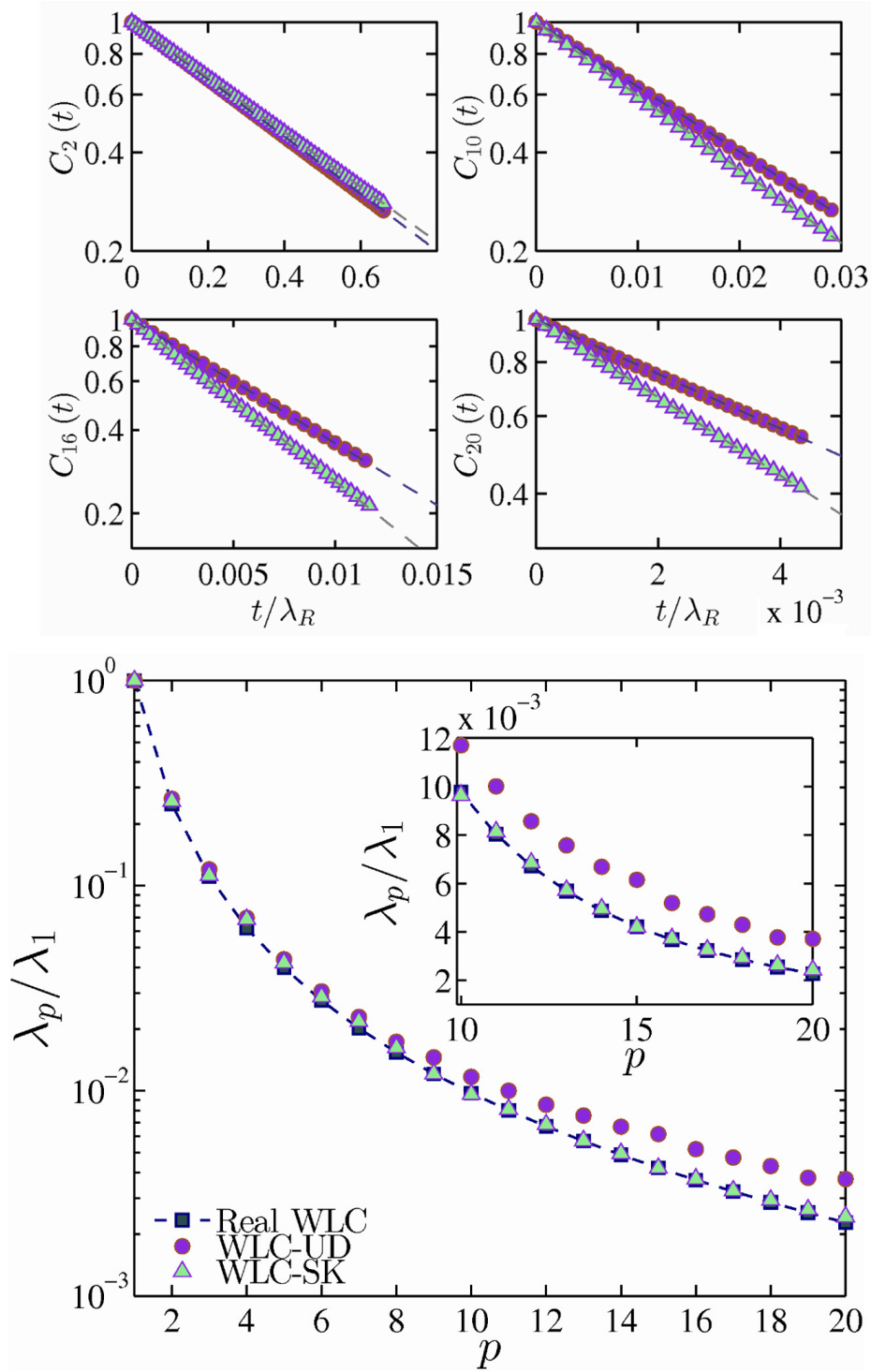


**Figure 5.6:** Average fractional extension as a function of the applied force for the WLC-SK bead-spring model compared via BD simulation. The results are shown at different coarse-graining levels and compared with the real long WLC. Inset: relative error associated with BD simulations using the WLC-SK model with respect to the results of the real long WLC.

same mode  $\lambda_p$ , i.e.,  $C_p(t) = \exp(-t/\lambda_p)$ . Note that  $\lambda_p$  represents the motion of a section of the chain with  $N_b/p$  segments. Steinhauser[148] solved the equation of motion for semiflexible chains under equilibrium condition and derived the relaxation of different modes,

$$\frac{\lambda_p}{\lambda_1} = \left( \frac{2N_K p^2 + \frac{\pi^2 p^4}{2N_K}}{2N_K + \frac{\pi^2}{2N_K}} \right)^{-1}. \quad (5.17)$$

Note that the relaxation time has two terms with  $p^2$  and  $p^4$  scaling which are attributed to the entropic tension and the mechanical bending forces, respectively. In the absence of the bending rigidity, the  $p^2$ -scaling of flexible chains is recovered.



**Figure 5.7:** The top 4 figures demonstrate the correlation function of four selected modes, namely, 2, 10, 16, and 20, as a function of normalized time  $t/\lambda_R$ , where  $\lambda_R$  is the Rouse relaxation time. The bottom figure shows the Relaxation time of all modes for the real WLC, WLC-UD, and WLC-SK models.

The relaxation time of WLC-UD and WLC-SK models for a chain with 100 Kuhn steps and 40 springs ( $\nu_K = 2.5$ ) are compared with the results of the real WLC model in [Figure 5.7](#).

For Rouse modes up to 8, the relaxation time values are consistent. This is expected, since the WLC-UD model aims to reproduce the behavior of the real WLC in the length scale of the end-to-end distance. For Rouse modes higher than 10, the deviation of WLC-UD relative to real WLC is larger than 10%, while the results of WLC-SK is almost identical for all values of normal mode. Hence, inaccurate segmental lengths and neglecting bending potential influences the local dynamics of polymer fragments with up to 4 springs with  $\nu_K = 2.5$ .

## 5.6 Conclusions

In conclusion, we have developed a mesoscopic bead-spring model which provides a better physical picture of real WLC model compared to the currently available models in the literature. This has been achieved through incorporation of a bending potential which is parametrized using the properties of real WLC model. The accuracy of the theoretical model was further investigated using Brownian dynamics simulation. All evaluated properties at different length scales ranging from the length scale of a single spring to the end-to-end distance of the macromolecule was found to be in excellent agreement with the real WLC model.

# Chapter 6

## Dynamics of comb DNA molecules

This chapter is based on the manuscript:

- A. Saadat, D. J. Mai, C. M. Schroeder, and B. Khomami. Brownian dynamics simulation of single comb DNA molecules. In preparation.

### 6.1 Introduction

Comb polymers are an important subcategory of architecturally complex macromolecules, which are composed of a main backbone with several side branches (arms). Natural and synthetic comb-like polymers have drawn much attention, due to their important biological aspects and versatile applications. For instance, the configurational properties, folding, and self assembly of proteins are substantially influenced due to the presence of side chains [16]. Moreover, synthetic comb polymers are used in drug delivery [136, 33], renewable energy devices [18], supra-molecular nano-composites [72], high performance membranes for desalination [19], and antifouling coatings [27]. These versatile applications stem from the fact that the structural and dynamical properties of comb-shaped polymers are fundamentally different than their linear counterparts.

For polymeric melts, rheological measurements clearly highlight the distinct properties of comb polymers with respect to linear chains in the linear viscoelastic regime [22, 73, 64],



stress overshoot in the startup of shear flow [144, 143], relaxation after cessation of a step strain [77] and steady shear and extensional flow [126, 75, 92]. Remarkably, the start of shear thinning of branched polymers appears at lower shear rates compared to linear polymers with similar molecular weights and identical molecular weight distribution. This has an important effect on the polymer processing of these materials. On the other hand, comb polymers exhibit strain hardening in transient extensional flow (deviation of transient elongational viscosity with respect to the linear response in the limit of low strain rates) [75, 92]. This effect becomes more pronounced as the length of the branches is increased and hence has an implication in the stabilization of film and fiber processing [75, 92].

There have been numerous studies on the conformation and the scaling of static dimension of comb polymers as a function of molecular weight and branching geometries since the pioneering work by Zimm and Stockmayer [163, 13, 127, 120, 103, 41]. The intent of these studies have been to relate the dimensional properties, such as radius of gyration, to the detailed geometrical characteristics of the branched polymers, e.g., length, grafting density, and solvent quality.

To the best of our knowledge, few studies have been devoted to assess the changes in dynamical properties of comb-like polymeric solutions [162, 125, 42, 65, 20, 90, 45, 74]. In addition, assumptions such as Rouse model for entropic forces [74, 45] and negligible hydrodynamic interaction effects [90], are used to simplify the problem. Over the past two decades, single molecule visualizations have provided new insights into the molecular origin of the rheological properties of polymeric solutions [116, 142, 141, 137, 99, 96, 100]. With the advent of novel synthesis techniques, Mai *et al.* [99] have been able to create well controlled comb topologies with chemically identical backbone and arms and in turn perform single molecule visualization. The aim of the present work is to combine high fidelity Brownian dynamics simulation of comb polymers with single-molecule measurements of Schroeder and coworkers [99] to gain a molecular-level understanding of topology-property relationships of comb-shaped polymers in planar extensional flow.

## 6.2 Methodology

In BD simulations considered in this chapter, the segments of worm-like chains are modeled via bead-spring model, where each spring represent 1 Kuhn step [11, 112, 147, 130] (the highest level of mesoscopic detail). The bead-spring chain contains  $N_{b,t}$  total beads which resemble the centers of hydrodynamic resistance, connected by  $N_{b,t} - 1$  massless springs which account for the entropic force between the adjacent beads. For chains with comb architecture, the number of arms, the number of beads in the backbone, and the number of beads in each arm are denoted by  $N_a$ ,  $N_{b,bb}$ , and  $N_{b,ar}$ .

The configurational state of the system can be specified by the position vector of all beads  $\{\mathbf{r}_\mu | \mu = 1, \dots, N_{b,t}\}$ , or equivalently using the connector vectors of all springs  $\{\mathbf{Q}_k | k = 1, \dots, N_{b,t} - 1\}$  and the center of mass of the chain  $\mathbf{r}_c$ . The configurational evolution equation using the Itô SDE is,

$$d\mathbf{Q} = \left\{ \mathbf{K} \cdot \mathbf{Q} + \frac{1}{\zeta} \bar{\mathbf{B}} \cdot \mathbf{D} \cdot \mathbf{F}^\phi \right\} dt + \sqrt{\frac{2k_B T}{\zeta}} \bar{\mathbf{B}} \cdot \mathbf{C} \cdot d\mathbf{W} \quad (6.1)$$

$$d\mathbf{r}_c = \left\{ \boldsymbol{\kappa} \cdot \mathbf{r}_c + \frac{1}{\zeta} \frac{1}{N_b} \sum_{\mu=1}^{N_b} \mathbf{u}_\mu \right\} dt + \sqrt{\frac{2k_B T}{\zeta}} \frac{1}{N_b} \sum_{\mu=1}^{N_b} d\mathbf{S}_\mu, \quad (6.2)$$

$\mathbf{Q}$  is a block column vector consisting of  $N_{b,t} - 1$  spring connector vectors between adjacent beads. The block diagonal matrix  $\mathbf{K}$  contains  $(N_{b,t} - 1) \times (N_{b,t} - 1)$  blocks of  $3 \times 3$  matrices and the diagonal blocks are equal to tensor  $\boldsymbol{\kappa}$  and the rest of the blocks are equal to  $\mathbf{0}$ . In planar elongational flow,  $\boldsymbol{\kappa}$  is defined as

$$\boldsymbol{\kappa} = \dot{\epsilon} \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (6.3)$$

where  $\dot{\epsilon}$  is the extension rate.  $\bar{\mathbf{B}}$  is a  $(N_{b,t} - 1) \times N_{b,t}$  block matrix to convert position vectors to connector vectors and its definition depends on the molecular architecture [11, 90]. For

linear chains  $\bar{\mathbf{B}}_{k,\nu} = \{\delta_{k+1,\nu} - \delta_{k,\nu}\} \boldsymbol{\delta}$ , with  $\delta_{k,\nu}$  being the Kronecker delta and  $\boldsymbol{\delta}$  the  $3 \times 3$  unit tensor. For comb polymers, the form of  $\bar{\mathbf{B}}$  depends on the indexing of the springs. Assuming that the first  $N_b - 1$  springs belong to the backbone and the rest of  $N_{b,t} - N_{b,bb}$  segments belong to the branches,  $\bar{\mathbf{B}}$  takes the following form

$$\bar{\mathbf{B}}_{k,\nu} = \begin{cases} (\delta_{k+1,\nu} - \delta_{I_a(i+1),\nu}) \boldsymbol{\delta} & k = N_{b,bb} + (i-1)[N_{b,ar} - 1] \\ (\delta_{k+1,\nu} - \delta_{k,\nu}) \boldsymbol{\delta} & \text{otherwise.} \end{cases} \quad (6.4)$$

Here,  $I_a$  is an array which specifies the index of the beads at the grafting positions. The first element of  $I_a$  is always one followed by the index of the beads attached to the arms, and  $i \in [1, N_a]$ . For instance,  $I_a = [1, 2, 5]$  is for a comb polymer with branches grafted at second and fifth beads.  $\mathbf{F}^\phi = \mathbf{F}^{\text{spr}} + \mathbf{F}^{\text{EV}} + \mathbf{F}^b$  is the block force vector which consists of  $\mathbf{F}_\nu^{\text{spr}}$ , the net spring force,  $\mathbf{F}_\nu^{\text{EV}}$ , the non neighboring excluded volume interactions, and  $\mathbf{F}_\nu^b$ , the bending force.  $\mathbf{F}_\nu^{\text{spr}}$  is obtained from the tension in the neighboring springs  $\mathbf{F}_\nu^c$  using the relation  $\mathbf{F}^{\text{spr}} = -\bar{\mathbf{B}}^T \cdot \mathbf{F}^c$ , with  $\mathbf{F}_\nu^c$  defined based on the spring connectivity vector between the adjacent beads,  $\mathbf{Q}_\nu$ , and the WLC-SK force law. Note that the form of the transformation tensor  $\mathbf{B}$  for the comb topology is significantly different than linear polymers (Equation (2.35)). However,  $\mathbf{B}$  can be easily obtained from a formulation that relates position vectors to connectivity vectors. One such relation is,

$$\mathbf{r}_\nu = \begin{cases} \mathbf{r}_1 + \sum_{k=1}^{\nu-1} \mathbf{Q}_k & \nu \leq N_{b,bb} \\ \mathbf{r}_1 + \sum_{k=1}^{I_a(i+1)-1} \mathbf{Q}_k + \sum_{k=1}^{\nu-1} \mathbf{Q}_{g(k)} & \nu > N_{b,bb}; i = \left\lfloor \frac{\nu - N_{b,bb} - 1}{N_{b,ar} - 1} \right\rfloor + 1. \end{cases} \quad (6.5)$$

where  $g(k) = \{N_{b,bb} - 1 + (i-1)[N_{b,ar} - 1] + k\}$ . The position of the first bead  $\mathbf{r}_1$  is related to the center of mass position of the chain using the relation,

$$\mathbf{r}_c = \mathbf{r}_1 + \sum_{k=1}^{N_{b,bb}-1} \frac{(N_{b,bb} - k)}{N_{b,t}} \mathbf{Q}_k + \sum_{i=1}^{N_a} \left\{ \sum_{k=1}^{N_{b,ar}-1} \frac{(N_{b,ar} - k)}{N_{b,t}} \mathbf{Q}_{g(k)} + \frac{(N_a - i + 1)(N_{b,ar} - 1)}{N_{b,t}} \sum_{k=I_a(i)}^{I_a(i+1)-1} \mathbf{Q}_k \right\}, \quad (6.6)$$

The semi implicit predictor-corrector scheme described in our earlier papers[147, 130] is used to integrate Equation (6.1) and obtain the internal configurations of the chains at each time step. Note that the form of the WLC-SK force-law necessitates solving a septic equations in corrector steps [112, 130].

## 6.3 Result and discussions

### 6.3.1 Parameter Selection

Table 6.1 summarizes the molecular parameters for DNA fragments which build the backbone and arms of the comb polymer (the contour length, the number of Kuhn steps and the end-to-end distance at  $\theta$ -temperature). The contour length of the bare DNA can be estimated using the equation  $n_{\text{bp}} \times 0.34 \text{ nm}$  [115]. The intercalating dye, namely, YOYO-1 iodide, which is added for imaging purposes is known to extend the contour length by 25-30%. Subsequently, the number of Kuhn steps  $N_K$  are approximated by assuming Kuhn length  $b_K = 114 \text{ nm}$ , which is attained if electrostatic interactions are fully screened by adding sufficient amount of salt to the solutions [84]. It has been shown by Kundukad *et al.* [84] that the persistence length is not sensitive to the addition of YOYO-1. Note that the dimension of sufficiently long backbone and arms of a comb polymer under  $\theta$  condition can be approximated using  $R_{\text{ee}}^\theta \approx \sqrt{N_K} b_K$ , where  $N_K$  is the total number of Kuhn steps in DNA fragments.

**Table 6.1:** Molecular properties of DNA fragments which comprise the backbone and branches of comb macromolecules.

| size (bp)               | $L_c$ ( $\mu\text{m}$ ) | $N_K$ | $R_{\text{ee}}^\theta$ ( $\mu\text{m}$ ) |
|-------------------------|-------------------------|-------|------------------------------------------|
| 48502 ( $\lambda$ -DNA) | 21.1                    | 185   | 1.551                                    |
| 40051                   | 17.4                    | 153   | 1.41                                     |
| 10051                   | 3.42                    | 30    | 0.62                                     |
| 2200                    | 0.75                    | 7     | -                                        |
| 951                     | 0.32                    | 3     | -                                        |

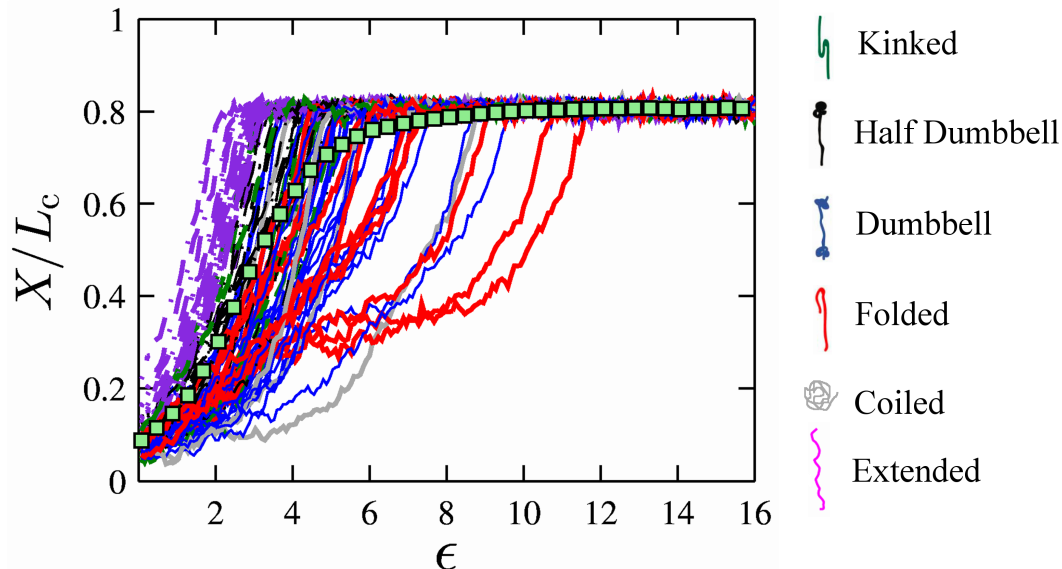
The HI parameter is the measure of the hydrodynamic radius of the bead to the equilibrium root-mean-square length of the finitely extensible spring, i.e.  $h^* = \sqrt{\frac{3}{\pi}} \frac{a}{Q_{\text{eq}}}$ . We follow a procedure which was initially adapted by Hsieh and Larson [58] and applied successfully by Saadat and Khomami [132]. In this approach, the drag on the fully extended linear chain is matched to the drag for a cylindrical rod based on Batchelor’s theory. Assuming a diameter of 3 nm for double-stranded DNA and the molecular parameters reported in Table 6.1,  $h^* = 0.061$  is obtained.

The EV parameters are determined based on the solvent quality. The solvent quality in BD simulations is related to EV strength  $z^*$  as  $z = z^* \sqrt{N_b}$  [123, 83]. Prakash and coworkers showed that  $z = 1$  results in the best agreement between experiment and simulation for  $\lambda$ -DNA at 22°C. This value is also consistent with the experimental evaluations by Pan *et al.* [115]. They estimated the solvent quality for DNA solutions by defining  $z$  as  $z = k \left(1 - \frac{T_g}{T}\right) \sqrt{M_w}$ , where the empirical parameter  $k$  is measured by finding a value of  $z$  that produces the same amount of the hydrodynamic swelling ratio  $\alpha_H = R_H/R_H^0$  in BD simulations as observed experimentally. Pan *et al.* [115] reported a value of  $k = 0.0047 \pm 0.0003$  (g/mol) $^{-1/2}$  for linear DNA molecules with different molecular weights. Subsequently,  $z^*$  can be obtained for a given level of fine-graining (1 Kuhn step per spring for the simulations in this paper), based on the corresponding number of beads of DNA backbone. Here, the same value of  $z^* = 0.073$  is used for both the backbone and the arms, since their chemistry and  $N_{K,s}$  are similar.

### 6.3.2 Stretching dynamics: A comparison with experimental data

To evaluate the strength of the flow in stretching of DNA in elongational settings, it is necessary to determine the longest relaxation time  $\lambda_1$  of the polymer backbone. Consistent with experiment, the relaxation time values are obtained based on the decay of ensemble averaged maximum projected extension of a polymer,  $X = \langle \max_{\mu,\nu} (r_{\mu,x} - r_{\nu,x}) \rangle$ , as a function of time,

$$X^2 = A \exp(-t/\lambda_1) + B, \quad (6.7)$$

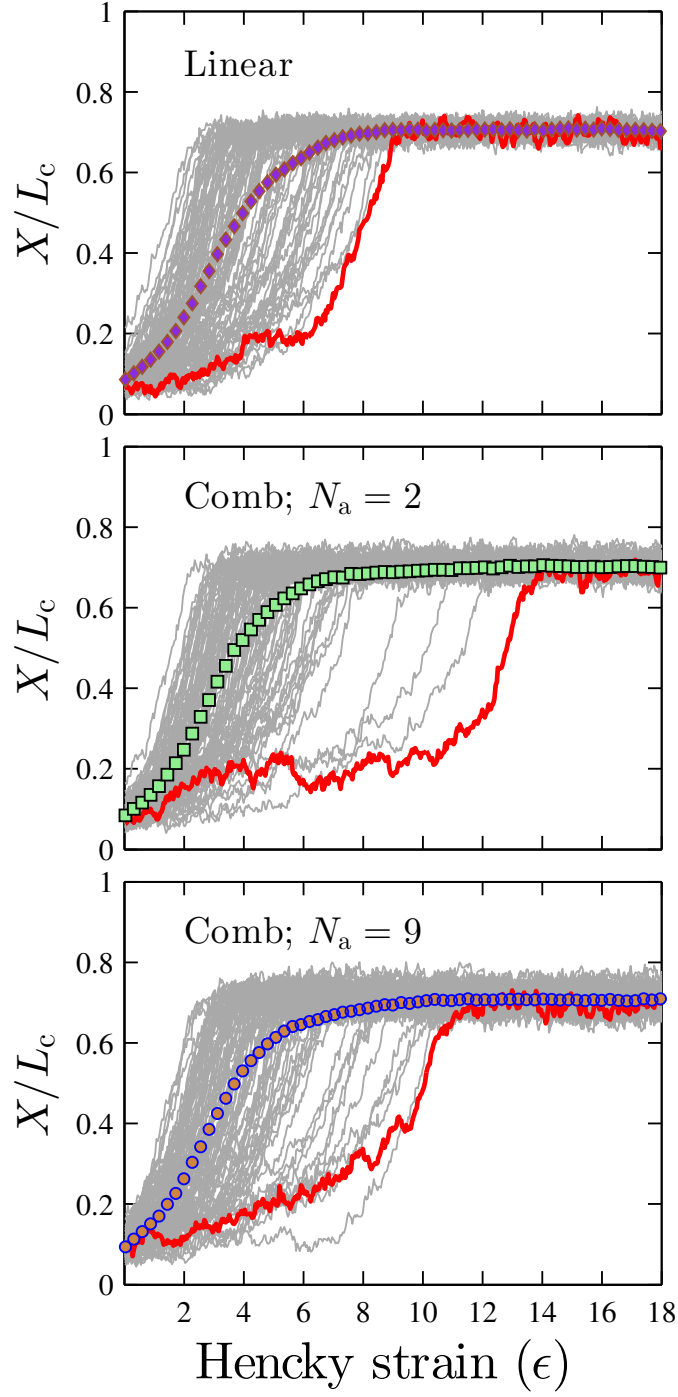


**Figure 6.1:** The normalized fractional extension of linear DNA with 40 kbp backbone as a function of Hencky strain at  $Wi = 4$ . Different conformation types, i.e., kinked (dashed green), half dumbbell (dash-dot black), dumbbell (thin solid blue), folded (thick solid red), coiled (thick solid gray), and extended (dash-dot purple) are formed during the transient coil-stretch transition. The classification in this figure is based on the automatic conformation sorting algorithm [87, 157] at  $\epsilon = 3$ .

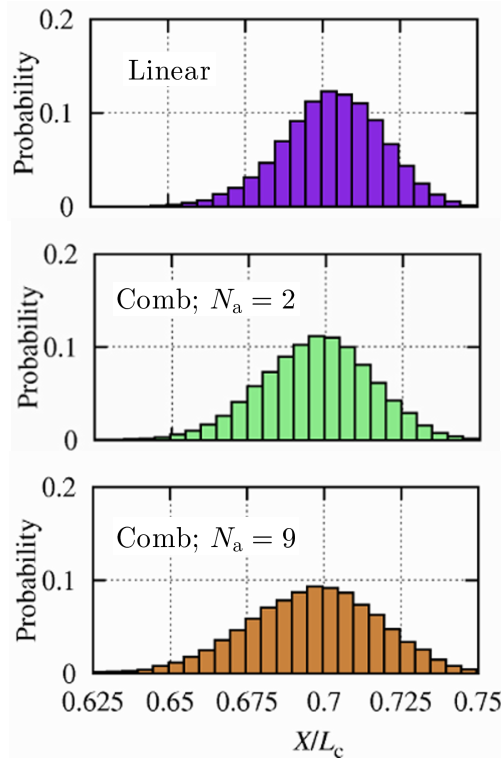
where  $B$  is the equilibrium value of mean-square end-to-end distance of  $X$  and  $A$  is a fitting constant. It is important to note that the beads in the arms are considered in the calculation of  $X$ . The longest relaxation time of comb polymers with short branches (2200 bps) is slightly increased compared to linear chains (data not shown).

Based on the starting configuration and the history of flow, different conformation types are formed during the simulation, including kinked, half dumbbell, dumbbell, coiled, extended, and folded. This is a signature of molecular individualism (see Figure 6.1).

The initial coiled conformation eventually reaches the extended state after about 12 Hencky strains. The folded and dumbbell conformations persist longer in the transient unstretched state. A large percentage of the trajectories experience folded conformations. Hence, the effect of grafted arms on the unfolding mechanism is of major importance in the coil-stretch transition of molecules in extensional flow. To this end, the transient behavior of linear and comb DNA with 2 and 9 branches are compared in Figure 6.2.



**Figure 6.2:**  $X/L_c$  as a function of Hencky strain for linear and comb DNA molecules with 2 and 9 branches at  $Wi = 2$ . The snapshots of colored trajectories are shown in [Figure 6.4](#). The insets demonstrate the probability of different end-to-end distance at the steady state condition, i.e.,  $\epsilon$  in the range of 13 to 18.

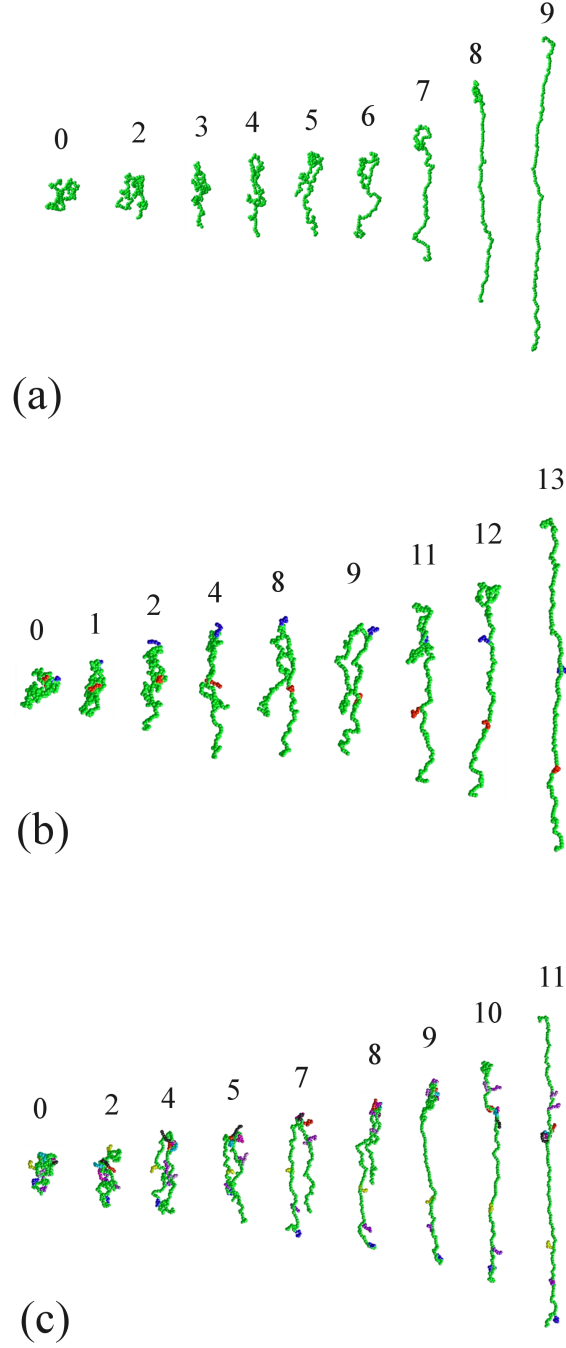


**Figure 6.3:** The probability of different end-to-end distance at the steady state condition and  $\epsilon$  in the range of 13 to 18.

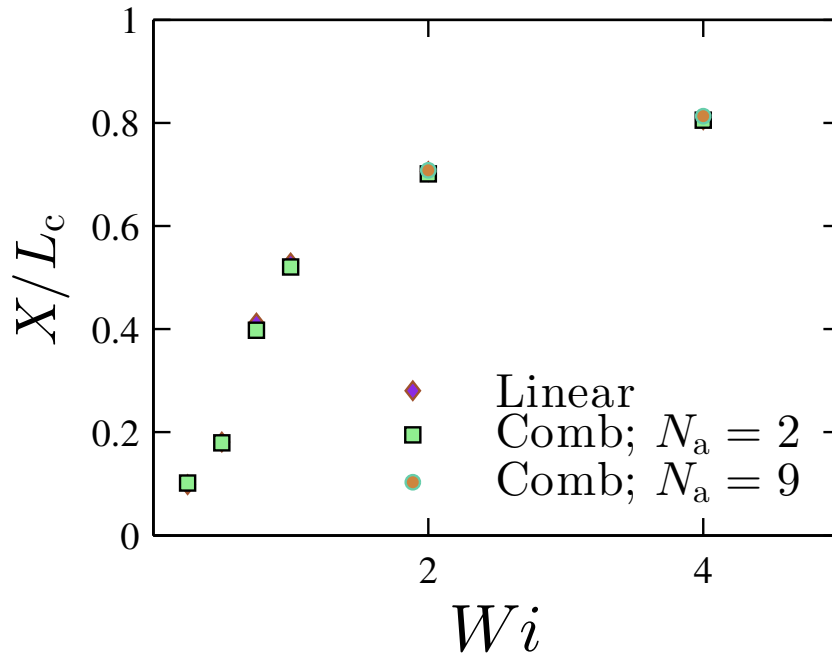
Interestingly, several comb trajectories remain in the low extension state for more than 8 Hencky strains. Moreover, the diversity of the steady state end-to-end distance increases as the number of branches is increased (see [Figure 6.3](#)).

Based on the visualization of configuration evolution of individual macromolecules, a totally different unfolding pathway is shown to exist for comb polymers (see [Figure 6.4](#)). In particular, the branches were found to prevent smooth translation of the fold apex along the backbone of the chain. The resulting chain meta-stable folded conformations unfold through an unusual mechanism. Specifically, the drag on the accumulated mass behind the apex of the two main sides of the fold gradually increases. This continues until one side of the fold (the one which is straightening out) exchanges a segment of the length larger than or equal to the extended arm with the other side of the fold. This is fundamentally different than the





**Figure 6.4:** Snapshots of colored trajectories represented in [Figure 6.2](#). Linear chain in part (a) shows a smooth unfolding behavior, while the presence of 2 (part (b)) and 9 (part (c)) branches, act as a constraint for the translation of the fold apex along the backbone. The numbers above the snapshots are the corresponding strain values.



**Figure 6.5:** Steady state fractional extension as a function of  $Wi$  for linear and comb DNA polymers.

case of linear chains, where the apex of the fold has a smooth exchange of segments during the unfolding even ([Figure 6.4\(a\)](#)).

The resulting steady state extension as a function of  $Wi$  is depicted in [Figure 6.5](#). Although the dynamics of unfolding is radically different for the linear and comb macromolecules, the steady state coil-stretch transition for linear and comb DNA molecules with 2 and 9 branches is very similar. It will be shown in [section 6.3.3](#) that increasing the length of the branches results in a much more pronounced influence of side chains on the relaxation behavior of the chain backbone. Hence, it is expected that DNA molecules with longer arms allow more precise examination of the effect of branches on the ensemble averaged stretching dynamics of the backbone.

### 6.3.3 Relaxation dynamics of comb DNA with long branches

In [section 6.3.2](#), it was found that the presence of relatively short branches slightly increases the longest relaxation time. However, the origin of this altered relaxation mechanism was not investigated. In this section, the influence of longer branches (10 kbp) on the relaxation behavior of comb DNA molecules is evaluated.

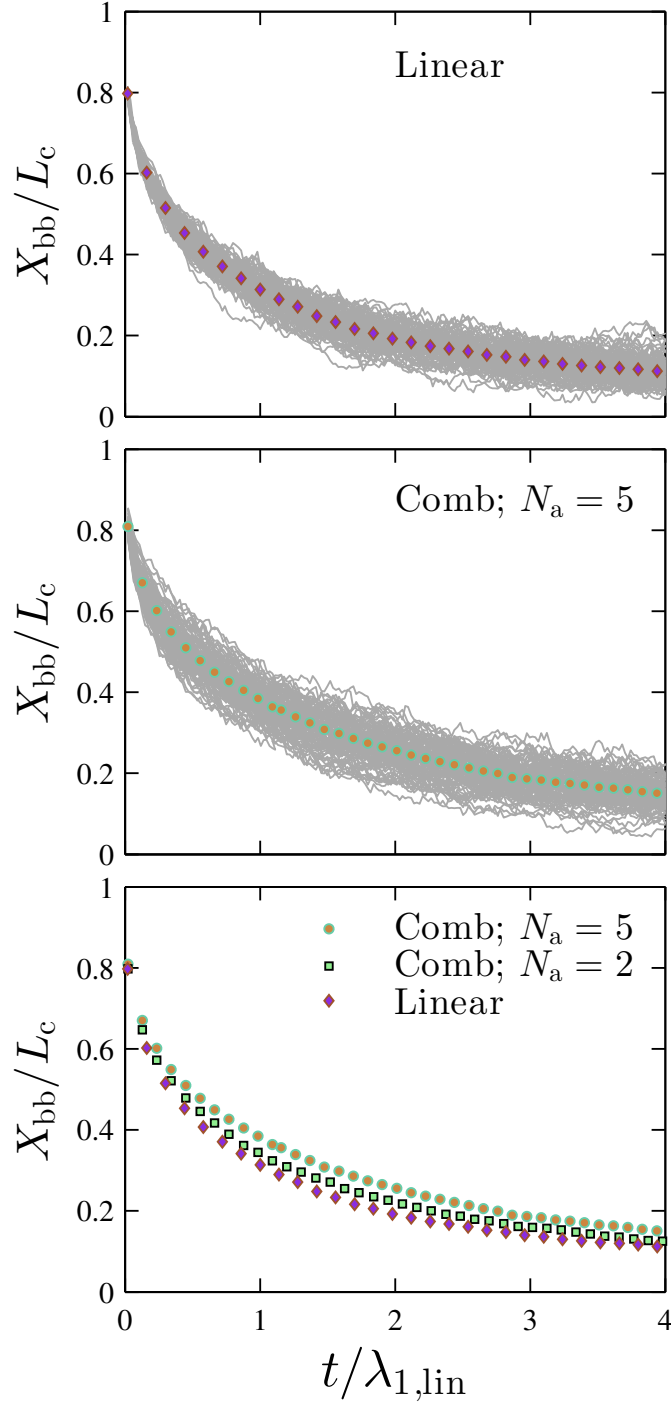
The projected extension is redefined to include the backbone beads only,

$$X_{\text{bb}} = \left\langle \max_{\mu, \nu \in \text{backbone}} (r_{\mu, x} - r_{\nu, x}) \right\rangle \quad (6.8)$$

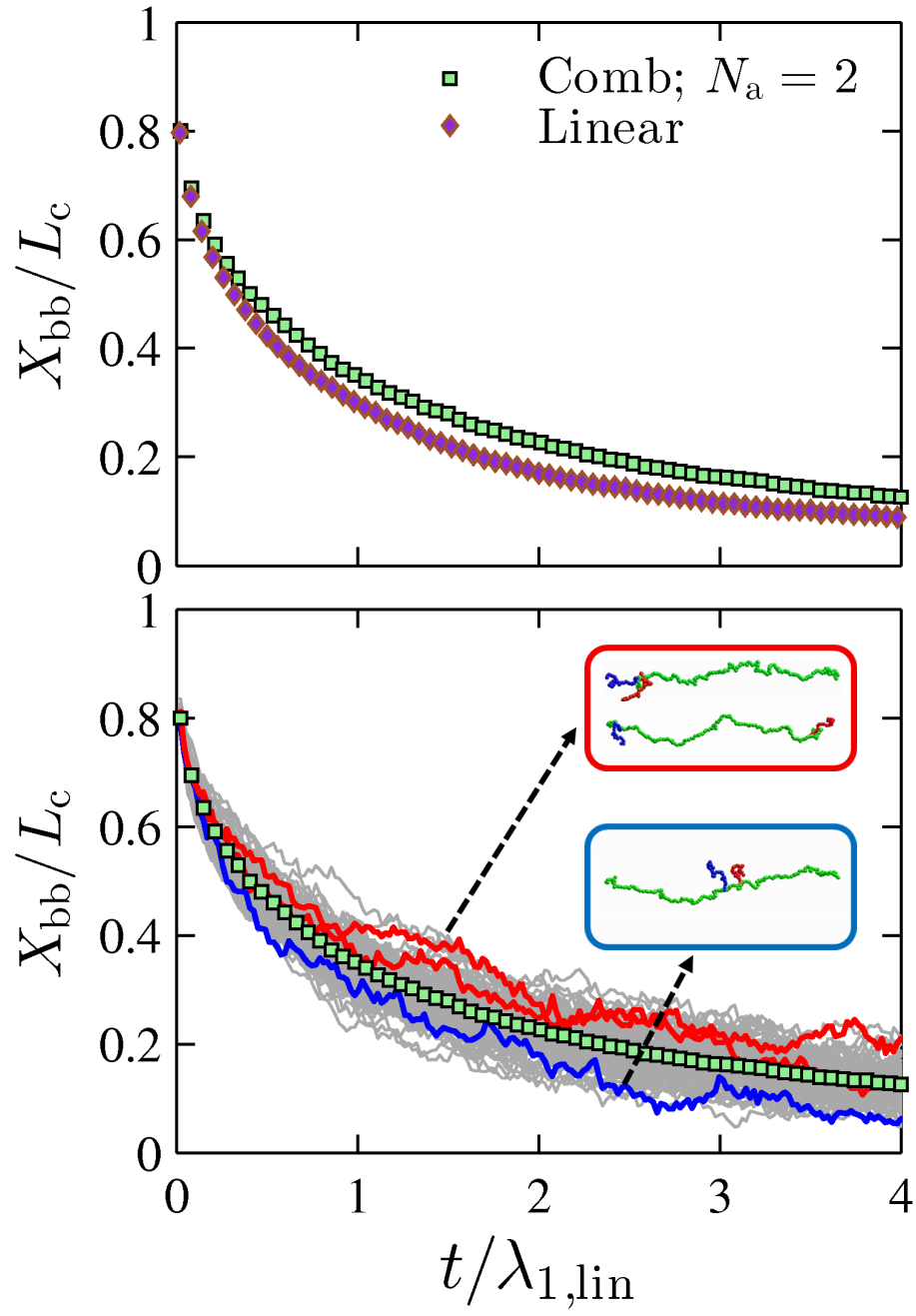
The definition of  $X_{\text{bb}}$  eliminates the influence of increasing the effective chain extension  $X$  on the relaxation behavior due to the presence of long branches. The individualistic relaxation behavior of linear and comb DNA with 5 branches is depicted in [Figure 6.6](#).

Consistent with the results shown in [section 6.3.2](#), the presence of branches hinders the relaxation of the backbone compared to the linear chain. This delayed relaxation may be attributed to several effects; the spatial hindrance of relatively bulky side branches (due to the EV effects), the hydrodynamic interactions between branches and the backbone, or the entropic (bonded and bending) forces translated from the branches to the backbone through the grafting points. To further investigate the slow-down of relaxation mechanism, simulations in the absence of HI and EV were performed (see [Figure 6.7](#)).

Clearly, the relaxation of comb DNA molecules with two branches is slower than linear chains even if HI and EV are neglected. Again, a larger window of extension for the case of comb-shaped molecules is observed. Visualizing relaxing trajectories in the two extremes, namely the slowest and the fastest, revealed that the slow-down effect is the most appreciable when the arms are closer to the ends of the backbone. This is further evidenced by the fact the fastest relaxing trajectories are those with branches in the middle section of the backbone.



**Figure 6.6:** Relaxation dynamics of linear and comb polymers. The normalized fractions extension is depicted as a function of time normalized by the longest relaxation of the linear chain  $\lambda_{1,\text{lin}}$ .



**Figure 6.7:** Relaxation dynamics of linear and comb polymers in the absence of HI and EV. The normalized fractions extension is depicted as a function of time normalized by the longest relaxation of the linear chain  $\lambda_{1,lin}$ . Configuration snapshots for the colored trajectories are given in the inset.

## 6.4 Conclusions

The WLC-SK model is utilized in Brownian dynamics (BD) simulation of DNA molecules. The relaxation and stretching dynamics of linear and comb DNA molecules are evaluated and compared against experimental data. Both transient and steady state fractional extension obtained using BD simulations for linear and comb-shaped chains with different degree of branching (low branching with up to 4 branches per backbone and high branching with 5 to 9 branches) are in good agreement with experimental results (yet to be published). Moreover, a mechanism for the unusual slow-down of the unfolding events is observed.

Existence of relatively long branches have a profound influence on the relaxation dynamics of comb molecules. In particular, the transient fractional extension in stretch-relaxation tests revealed a slower relaxation of the backbone when the branches are placed near the ends of the molecule. Moreover, the presence of side branches diversifies the molecular individualism.

# Chapter 7

## Conclusions

In this study I have developed a number of BD algorithms for bead-spring micromechanical model of polymers in dilute and semidilute regimes that utilized either the Chebyshev or the Krylov framework. Krylov subspace method, the algorithm with the highest efficiency and fidelity, enables fast calculation of single chain dynamics with simulation time scaling of  $\mathcal{O}(N_b^2)$  where  $N_b$  is the number of beads in the bead-spring micromechanical model. For simulations of coupled multichain systems, a matrix-free approach for calculation of HI was implemented which lead to  $\mathcal{O}(N \log N)$  scaling of simulation time, where  $N$  is the total number of beads in the periodic box.

In turn, the Krylov framework and the semi implicit predictor-corrector scheme was used to study the behavior of dilute solutions of high molecular weight polystyrene in a  $\theta$ -like solvent under uniaxial extensional flow. The influence of key parameters, namely appropriate inclusion of HI and EV, the level of fine-graining, and the flow strength on the observed extensional hardening of the dilute solutions over a broad molecular weight range was considered. Specifically, it was demonstrated that the combination of HI and successive fine-graining (SFG) results in a very good prediction of rheological properties of solutions containing 1.95, 3.9, and 10.2 million molecular weight macromolecules. The remarkable agreement between simulation and experiment was attributed to the novel parameter-free SFG approach for bead-spring chains with up to 609 beads, with  $h^*$  specified based on

Batchelor’s theory. Moreover, the appropriate incorporation of EV for different molecular weights but identical chemical structure was discussed.

Further, a new bead-spring model (denoted by WLC-SK) for semiflexible macromolecules was developed to ensure a better physical picture of real WLC model. This has been achieved through incorporation of a bending potential which was parametrized using the properties of the real WLC model. The accuracy of the theoretical model was further examined using BD simulations. All evaluated properties at different length scales ranging from the length scale of a single spring to the end-to-end distance of the macromolecules were found to be in excellent agreement with real WLC model. In turn, WLC-SK model was applied to BD simulations of DNA molecules with different architectures, namely, linear and comb. In particular, the relaxation and stretching dynamics of DNA molecules were evaluated and compared with the experimental results of single molecule visualization in cross-slot device [99, 100]. The transient and steady state stretching dynamics were simulated using BD, and an unusual slow-down of unfolding event was observed for polymers with grafted side chains. Moreover, it was observed that relatively long branches have a profound influence on the relaxation dynamics of comb molecules. In particular, the presence of branches as large as 10 kilo-base-pairs resulted in a more diversified molecular individualism and also slower relaxation of the backbone when the branches were placed near the ends of the molecule. Overall, these results are in good agreement with experimental findings of Schroeder and coworkers [99, 100].

For multichain interacting systems, the fidelity and computational efficiency of the matrix-free approach at equilibrium was evaluated by examining the mean-square-displacement and the averaged diffusivity of the center of mass over a broad range of concentrations in a  $\theta$ -solvent. In addition, the mean-square end-to-end distance and the mean-square radius of gyration for chains was obtained at different concentrations, i.e.,  $0.1c^*$  and  $5c^*$ , in theta and good solvents. The matrix-free results for center of mass diffusivity were found to be in excellent agreement with the ones obtained using the standard Ewald summation technique. Moreover, the asymptotic values of diffusivity at very low concentrations correctly



approached the infinite dilution value. At higher concentration, namely  $c/c^* = 5$ , the results of  $\langle R_g^2 \rangle$  were in a very good agreement with the values predicted by blob theory.

# Chapter 8

## Future prospects

### 8.1 Physical problems

The benchmarked codes in BDpack lay the foundation for numerous fundamental studies of polymeric systems, a few of which is considered in this section.

#### 8.1.1 Universal transient stretching in planar shear flow

It has been shown by Hur *et al.* [62] that in planar shear flow, the transient extension at different concentrations and up to  $6c^*$  is universal. This is an important experimental observation for semidilute solutions that requires further theoretical and computational evidences.

#### 8.1.2 Concentration dependence of coil-stretch hysteresis

The hysteresis in the coil-stretch transition has been recently confirmed by experiment and BD simulations [137, 9]. Investigating the effect of concentration on this well-established phenomenon is essential in developing theories for dynamics of polymers in the semidilute and concentrated regimes.

## 8.2 Further modeling options

In spite of several modeling options provided in BDpack, there are many additional options that can be considered. Among these include polydispersity, polymers with charged backbone, and complex polymer architectures.

### 8.2.1 Polydispersity

In many experiments, the distribution of the molecular weight deviates from 1 (mono-disperse limit). Then, it becomes indispensable to take into account the effect of chains with different chain length. This is particularly important for accurate description of polymer dynamics as the concentration is increased above the overlap concentration.

### 8.2.2 Polyelectrolyte solutions

Polyelectrolytes are polymers with charged backbone. To overcome the computational intensity of calculating long-range electrostatic interactions, algorithms similar to those employed in this dissertation for calculating HI should be employed in BD simulations of these systems. Moreover, the presence of colloids in the simulation box (acting as counter ions) is another problem which should be taken into account [110].

### 8.2.3 Complex polymer architectures

Simulations of polymers with architectures other than linear and comb, e.g., H-shaped, stars, rings are very demanding [96, 100]. BD simulations should then be combined with single and multichain visualizations in microfluidic device to pave the way for mechanistic understanding of polymer dynamics with these architectures. BD can also be employed to ensure a consistency between simulations and theoretical values for dimensional properties of polymers with complex topology.

## 8.3 Enhancing fidelity and computational power

The tools developed in BDpack can be improved in two main aspects; fidelity and computational power.

### 8.3.1 Force-extension for flexible polymers in good solvent

Force-extension relationship for flexible macromolecules in  $\theta$ -solution is known to follow the inverse Langevin function (ILF) [11]. In the presence of repulsive EV forces in good solvents, another region in small to medium values of extension exists [128, 134, 124], which is called the Pincus regime. In this regime, the extension  $x$  scales with force as  $x \propto f^{2/3}$ . The effect of EV in BDpack is considered by introducing a repulsive force between the beads and the changes to the force law is assumed to remain negligible. Although, it has been shown that the simulations using this assumption produce consistent results with experimental measurements [83, 150], one would expect an error with respect to the correct force-extension behavior as the number of Kuhn steps per spring is increased dramatically [124, 107, 101]. Underhill and coworkers [124] and Malekzadeh Moghani [107, 101] have recently modified the spring force relation to capture the Pincus regime. It is yet required to have a careful implementation of these models in BD simulations of bead-spring chains and compare the results with those of bead-rod chains. The new force-extension relations can also be verified using the constant-extension ensemble [155] and constant-force ensemble [101] of very long bead-spring chains.

### 8.3.2 Preventing chain crossings

An important step towards enhancing the fidelity of the BD simulations in BDpack is to implement algorithms that prevent chain crossings [113, 78], both self crossings for long single chain simulations as well as inter-chain crossings for semidilute systems. There is very little existing knowledge on how the chain crossings will affect the equilibrium and non-equilibrium results obtained with regular BD algorithms [57]. It is crucial to inhibit (or at

least minimize) the chain crossings, in order to preserve the correct topological, dynamical, and rheological properties of polymeric solutions, in particular, in semidilute solutions with higher concentrations.

### **8.3.3 GPU enabled BDpack**

The current computational efficiency of BDpack can be further improved by using the state of the art computational accelerators, namely graphical processing units (GPUs). In particular, the computation of time consuming parts such as SPME method, i.e., spreading, forward and backward Fourier transforms, and interpolation, may be transferred to the GPUs.

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# Appendices

# Appendix A

## Decomposition algorithms

The decomposition procedures used as the Lanczos, the block Lanczos and the Chebyshev are outlined in Algorithms A.1-A.3, respectively.

---

**Algorithm A.1** Lanczos algorithm.

---

**INPUT:**  $m_{\text{initial}}$  and  $E_{\text{min}}$ **Require:**  $m_{\text{initial}} \geq 2$ 

```
1:  $m \leftarrow m_{\text{initial}} - 1$ 
2:  $k_0 \leftarrow 1$ 
3:  $\mathbf{v}_1 \leftarrow \Delta \mathbf{W} / \|\Delta \mathbf{W}\|_2$ 
4: exit=false
5: repeat
6:   for  $k = k_0 \rightarrow m$  do
7:      $\mathbf{w}' \leftarrow \mathbf{D} \cdot \mathbf{v}_k$ 
8:     if  $k > 1$  then
9:        $\mathbf{w}' \leftarrow \mathbf{w}' - h_{k-1,k} \mathbf{v}_{k-1}$ 
10:    end if
11:    if  $k \neq k_0$  or  $k_0 = 1$  then
12:       $h_{k,k} \leftarrow \mathbf{v}_k^T \mathbf{w}'$ 
13:    end if
14:    if  $k < m$  then
15:       $\mathbf{w}' \leftarrow \mathbf{w}' - h_{k,k} \mathbf{v}_k$ 
16:       $h_{k+1,k} \leftarrow h_{k,k+1} \leftarrow \|\mathbf{w}'\|_2$ 
17:       $\mathbf{v}_{k+1} \leftarrow \mathbf{w}' / h_{k+1,k}$ 
18:    end if
19:  end for
20:  Compute  $\Delta \tilde{\mathbf{S}}^{(m)} \leftarrow \|\Delta \mathbf{W}\|_2 \cdot \mathbf{V}_m \cdot \mathbf{H}_m^{1/2} \cdot \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ 
21:  if  $m \geq m_{\text{initial}}$  then
22:    Compute  $E^{(m)}$ 
23:    if  $E^{(m)} \leq E_{\text{min}}$  then
24:      exit=true
25:    end if
26:  end if
27:   $k_0 \leftarrow m$ 
28:   $m \leftarrow m + 1$ 
29: until exit
```

$\triangleright \begin{pmatrix} 1 \\ 0 \end{pmatrix}$  in line 20 is the first column of  $3N \times 3N$  unit matrix.

---

---

**Algorithm A.2** Block Lanczos algorithm.

---

**INPUT:**  $m_{\text{initial}}$  and  $E_{\text{min}}$ **Require:**  $m_{\text{initial}} \geq 2$ 

```
1:  $m \leftarrow m_{\text{initial}} - 1$ 
2:  $k_0 \leftarrow 1$ 
3:  $V_1 \cdot R = \Delta W$ 
4: exit=false
5: repeat
6:   for  $k = k_0 \rightarrow m$  do
7:      $W' \leftarrow D \cdot V_k$ 
8:     if  $k > 1$  then
9:        $W' \leftarrow W' - V_{k-1} \cdot H_{k-1,k}$ 
10:    end if
11:    if  $k \neq k_0$  or  $k_0 = 1$  then
12:       $H_{k,k} \leftarrow V_k^T \cdot W'$ 
13:    end if
14:    if  $k < m$  then
15:       $W' \leftarrow W' - V_k \cdot H_{k,k}$ 
16:       $V_{k+1} \cdot H_{k+1,k} = W'$ 
17:       $H_{k,k+1} \leftarrow H_{k+1,k}^T$ 
18:    end if
19:  end for
20:  Compute  $\Delta \tilde{S}_{bl}^{(m)} \leftarrow V_{ms} \cdot H_{ms}^{1/2} \cdot \begin{pmatrix} R \\ 0 \end{pmatrix}$ 
21:  if  $m \geq m_{\text{initial}}$  then
22:    Compute  $E^{(m)}$ 
23:    if  $E^{(m)} \leq E_{\text{min}}$  then
24:      exit=true
25:    end if
26:  end if
27:   $k_0 \leftarrow m$ 
28:   $m \leftarrow m + 1$ 
29: until exit
```

▷ Lines 3 and 16 are reduced QR factorization.

---

---

**Algorithm A.3** Chebyshev polynomial approximation to  $\Delta \mathbf{S} = \mathbf{C} \cdot \Delta \mathbf{W}$ .

---

**INPUT:**  $L_{\text{initial}}$  and  $E_{\text{min}}$ **Require:**  $0 < d_{\text{min}} < d_{\text{max}}$  and  $L_{\text{initial}} \geq 2$ 

```
1:  $L \leftarrow L_{\text{initial}} - 1$ 
2:  $k_0 \leftarrow 1$ 
3:  $a_- \leftarrow \frac{d_{\text{max}} - d_{\text{min}}}{2}$  and  $a_+ \leftarrow \frac{d_{\text{max}} + d_{\text{min}}}{2}$ 
4:  $\mathbf{D}_{\text{sh}} \leftarrow \frac{1}{a_-} \mathbf{D} - \frac{a_+}{a_-} \mathbf{I}$ 
5:  $\Delta \mathbf{V}_0 \leftarrow \Delta \mathbf{W}$ 
6:  $\Delta \mathbf{V}_1 \leftarrow \mathbf{D}_{\text{sh}} \cdot \Delta \mathbf{W}$ 
7: repeat
8:   Compute  $c_j$ ;  $j = 0, \dots, L$  using
9:    $\Delta \tilde{\mathbf{S}}_{Ch} \leftarrow \frac{c_0}{2} \Delta \mathbf{W} + c_1 \Delta \mathbf{V}_1$ 
10:  for  $k = 2 \rightarrow L$  do
11:    if  $k > k_0$  then
12:       $\Delta \mathbf{V}_k \leftarrow 2\mathbf{D}_{\text{sh}} \cdot \Delta \mathbf{V}_{k-1} - \Delta \mathbf{V}_{k-2}$ 
13:    end if
14:     $\Delta \tilde{\mathbf{S}}_{Ch} \leftarrow \Delta \tilde{\mathbf{S}}_{Ch} + c_k \Delta \mathbf{V}_k$ 
15:  end for
16:  if  $L \geq L_{\text{initial}}$  then
17:    Compute  $E_L^{\text{Ch}}$ 
18:    if  $E_L^{\text{Ch}} \leq E_{\text{min}}$  then
19:      exit=true
20:    end if
21:  end if
22:   $k_0 \leftarrow L$ 
23:   $L \leftarrow L + 1$ 
24:  return  $\Delta \tilde{\mathbf{S}}_{\text{Ch}}$ 
25: until exit
```

---

# Appendix B

## Further results on frequency of updating the diffusion tensor

The following tables, namely [Table B.1](#) and [Table B.2](#), provide complementary information regarding the error evaluation in predicting equilibrium and non-equilibrium physical properties when different sets of and are exploited.

**Table B.1:** (%)Error in  $\langle R_g^2 \rangle$  obtained with various time steps and update intervals relative to the results of Cholesky with unit block dimension and  $dt = 8 \times 10^{-4}$ .

| $N_b$ | Method   | $dt$               | $\lambda_{\text{RPY}}$ | $\lambda_{\text{RPY}}dt$ | $\langle R_g^2 \rangle$ | (%)Error        |
|-------|----------|--------------------|------------------------|--------------------------|-------------------------|-----------------|
| 50    | Cholesky | $8 \times 10^{-4}$ | 1                      | $8 \times 10^{-4}$       | $25.89 \pm 0.42$        | Ref. $\pm 1.64$ |
| 50    | Lanczos  | $1 \times 10^{-3}$ | 1                      | $1 \times 10^{-3}$       | $26.00 \pm 0.42$        | 0.42            |
| 50    | Lanczos  | 0.05               | 1                      | 0.05                     | $25.79 \pm 0.43$        | 0.39            |
| 50    | Lanczos  | 0.01               | 5                      | 0.05                     | $25.59 \pm 0.43$        | 1.16            |
| 50    | Lanczos  | 0.01               | 25                     | 0.25                     | $24.04 \pm 0.42$        | 7.15            |
| 50    | Lanczos  | 0.01               | 50                     | 0.5                      | $22.90 \pm 0.40$        | 11.55           |
| 50    | Lanczos  | 0.1                | 1                      | 0.1                      | $25.42 \pm 0.44$        | 1.82            |
| 50    | Lanczos  | 0.1                | 5                      | 0.5                      | $22.91 \pm 0.41$        | 11.51           |
| 50    | Lanczos  | 0.1                | 25                     | 2.5                      | $21.52 \pm 0.39$        | 16.88           |
| 50    | Lanczos  | 0.5                | 1                      | 0.5                      | $23.55 \pm 0.42$        | 9.04            |

**Table B.2:** (%)Error in transient fractional extension of molecules in planar extensional flow obtained with various time steps and update intervals relative to the results of Cholesky with unit block dimension and  $dt = 8 \times 10^{-3}$

| $N_b$ | Method   | $dt$               | $\lambda_{\text{RPY}}$ | $\lambda_{\text{RPY}} \times dt$ | (%)Error        |
|-------|----------|--------------------|------------------------|----------------------------------|-----------------|
| 50    | Cholesky | $8 \times 10^{-3}$ | 1                      | $8 \times 10^{-3}$               | Ref. $\pm 2.09$ |
| 50    | Lanczos  | 0.01               | 1                      | 0.01                             | 0.39            |
| 50    | Lanczos  | 0.01               | 5                      | 0.05                             | 2.47            |
| 50    | Lanczos  | 0.01               | 25                     | 0.25                             | 4.74            |
| 50    | Lanczos  | 0.01               | 50                     | 0.5                              | 8.40            |
| 50    | Lanczos  | 0.1                | 1                      | 0.1                              | 1.96            |
| 50    | Lanczos  | 0.1                | 5                      | 0.5                              | 6.71            |
| 50    | Lanczos  | 0.5                | 1                      | 0.5                              | 3.44            |

# Appendix C

## Calculation of bending force

The bending force acting on the bead  $\mu$  of the bead-spring chain has contributions from bending at bead  $\mu$  as well as beads  $\mu - 1$  and  $\mu + 1$ :

$$\mathbf{F}_\mu^b = \mathbf{F}_{\mu,\mu}^b + \mathbf{F}_{\mu,\mu-1}^b + \mathbf{F}_{\mu,\mu+1}^b \quad (\text{C.1})$$

where  $\mathbf{F}_\mu^b$  is the total bending force on bead  $\mu$  and  $\mathbf{F}_{\mu,\mu'}^b$  is the contribution of bending force on bead  $\mu$  due to the constraint angle at bead  $\mu'$ . The bending force is a function of unit connectivity vector of the spring, i.e.,  $\hat{\mathbf{e}}_\mu = \frac{(\mathbf{r}_{\mu+1} - \mathbf{r}_\mu)}{\{(\mathbf{r}_{\mu+1} - \mathbf{r}_\mu) \cdot (\mathbf{r}_{\mu+1} - \mathbf{r}_\mu)\}^{1/2}}$ , and the angle at bead  $\mu$ , i.e.,  $\theta_\mu = \arccos(\hat{\mathbf{e}}_{\mu-1} \cdot \hat{\mathbf{e}}_\mu)$ . Namely, [6, 79, 154, 67]

$$\mathbf{F}_{\mu,\mu}^b = -\frac{\partial \phi_{b,\mu}}{\partial \mathbf{r}_\mu} = -\frac{\partial \phi_{b,\mu}}{\partial \theta_\mu} \left\{ \frac{\partial \theta_\mu}{\partial \hat{\mathbf{e}}_\mu} \cdot \frac{\partial \hat{\mathbf{e}}_\mu}{\partial \mathbf{r}_\mu} + \frac{\partial \theta_\mu}{\partial \hat{\mathbf{e}}_{\mu-1}} \cdot \frac{\partial \hat{\mathbf{e}}_{\mu-1}}{\partial \mathbf{r}_\mu} \right\} \quad (\text{C.2})$$

$$\mathbf{F}_{\mu,\mu-1}^b = -\frac{\partial \phi_{b,\mu-1}}{\partial \mathbf{r}_\mu} = -\frac{\partial \phi_{b,\mu-1}}{\partial \theta_{\mu-1}} \frac{\partial \theta_{\mu-1}}{\partial \hat{\mathbf{e}}_{\mu-1}} \cdot \frac{\partial \hat{\mathbf{e}}_{\mu-1}}{\partial \mathbf{r}_\mu} \quad (\text{C.3})$$

$$\mathbf{F}_{\mu,\mu+1}^b = -\frac{\partial \phi_{b,\mu+1}}{\partial \mathbf{r}_\mu} = -\frac{\partial \phi_{b,\mu+1}}{\partial \theta_{\mu+1}} \frac{\partial \theta_{\mu+1}}{\partial \hat{\mathbf{e}}_\mu} \cdot \frac{\partial \hat{\mathbf{e}}_\mu}{\partial \mathbf{r}_\mu} \quad (\text{C.4})$$

where  $\phi_b$  is the bending potential defined in Equation (5.15). The total force is the sum of all contributions,



$$\begin{aligned} \frac{\mathbf{F}_\mu^{\text{b}}}{k_{\text{B}}T\mathcal{C}} = & \left[ \hat{\mathbf{e}}_\mu \left( \frac{1}{r_{\mu-1}} + \frac{\cos \theta_\mu}{r_\mu} \right) - \hat{\mathbf{e}}_{\mu-1} \left( \frac{1}{r_\mu} + \frac{\cos \theta_\mu}{r_{\mu-1}} \right) \right] + \\ & \left[ \frac{1}{r_{\mu-1}} (\hat{\mathbf{e}}_{\mu-2} + \cos \theta_{\mu-1} \hat{\mathbf{e}}_{\mu-1}) \right] + \left[ \frac{1}{r_\mu} (\cos \theta_{\mu+1} \hat{\mathbf{e}}_\mu - \hat{\mathbf{e}}_{\mu+1}) \right] \end{aligned} \quad (\text{C.5})$$

where  $C$  is the bending rigidity (see Equation (5.15))

# Appendix D

## Properties of real WLC

Consider two points, i.e.,  $s$  and  $p$ , along the contour of the WLC such that  $a \leq s, p \leq a + l$ , where  $a$  is an arbitrary starting point. The average correlation of the unit vectors tangent to the contour of WLC at points  $s$  and  $p$  decays exponentially as  $\langle \mathbf{t}(s) \cdot \mathbf{t}(p) \rangle = \exp(-2|s-p|/b_K)$ . The vector which connects the end positions of an arbitrary segment along the chain with contour length  $l$  is the sum over the tangent vectors between the two end points:

$$\hat{\mathbf{Q}}_{\text{wlc}} = \frac{1}{l} \int_a^{a+l} ds \mathbf{t}(s) \quad (\text{D.1})$$

Therefore,

$$\langle \hat{Q}_{\text{wlc}}^2 \rangle_{eq} = \frac{1}{l^2} \left\langle \int_a^{a+l} ds \int_a^{a+l} dp \mathbf{t}(s) \cdot \mathbf{t}(p) \right\rangle = \frac{1}{l^2} \int_a^{a+l} ds \int_a^{a+l} dp \exp(-2|s-p|/b_K) \quad (\text{D.2})$$

Integration of Equation (D.2) is simplified by splitting it into two identical integrals but with different limits:

$$\langle \hat{Q}_{\text{wlc}}^2 \rangle = \frac{2}{l^2} \int_a^{a+l} ds \left\{ \int_a^s dp \exp(-2(s-p)/b_K) \right\} \quad (\text{D.3})$$

It is straight forward to perform this integration which results in Equation (5.3) of the manuscript.

The correlation of two arbitrary consecutive segments  $i$  and  $i+1$  each with contour length  $l$  (Equation (5.4) of the manuscript) is found in a similar fashion,

$$\left\langle \hat{\mathbf{Q}}_{\text{wlc},i} \cdot \hat{\mathbf{Q}}_{\text{wlc},j} \right\rangle_{eq} = \frac{1}{l^2} \left\langle \int_a^{a+l} ds \int_{a+l+(j-i-1)l}^{a+2l+(j-i-1)l} dp \, \mathbf{t}(s) \cdot \mathbf{t}(p) \right\rangle \quad (\text{D.4})$$

# Vita

Mr. Amir Saadat began his college education in 2003 at Amirkabir University of Technology (Tehran Polytechnic). He received his BS and MS degrees with high honors in 2009. During his stay at Amirkabir University, he studied rheological properties of polymers and polymer nanocomposites using computational fluid dynamics, viscoelastic theories, and several experimental characterization techniques (e.g., linear/non-linear viscoelastic measurements and measuring extrusion). He started his Ph.D. in spring 2011 at the University of Tennessee. His doctoral research has mainly focused on the development of theoretical and computational models for simulation of macromolecular solutions with the aim of developing molecular understanding of the behavior of this class of complex fluids at equilibrium and under flow. It should also be noted that during his PhD studies, he received an MS in chemical engineering and a graduate minor in computational science.