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Contents

1	Introduction	5
2	Theoretical Foundation	8
2.1	Reduced Units	8
2.2	Multi-Particle Collision Dynamics	9
2.2.1	The Streaming Step	10
2.2.2	The Collision Step	10
2.2.3	Characteristic Quantities	12
2.2.4	Conservation of Quantities	16
2.3	Polymer Modelling	17
2.3.1	The Bead Concept	18
2.3.2	Velocity-Verlet Algorithm	21
2.3.3	Interaction Potential	21
2.3.4	Andersen Thermostat	25
2.3.5	Embedding the Polymer in an MPCD Fluid	26
2.4	Polymer Analysis	27
2.4.1	Characteristic Quantities	28
2.4.2	Principal Component Analysis	31
2.4.3	Simulation Testing	33
2.5	Non-Equilibrium Simulations	34
2.5.1	Lees-Edwards Boundary Conditions	35
2.5.2	Cell-Level Thermostating	38
2.5.3	Tumbling and Tank-Treading	43
3	Knot Analysis	45
3.1	Mathematical Knots	45
3.2	The Long Route to Knot Invariants	47
3.2.1	Knot Diagram and Reidemeister Moves	48
3.2.2	Bracket Polynomial	49
3.2.3	Writhe	50
3.2.4	Skein Relations and Jones Polynomial	52
3.2.5	Jones Polynomial of the Trefoil Knot	53
4	Program Design	56

5	Simulations	58
5.1	Equilibrium Simulations for Reference	58
5.1.1	Ring Polymer	58
5.1.2	3_1 -Knotted Polymer	61
5.1.3	Shape Parameters in Comparison	63
5.2	Simulations Under Shear	65
5.2.1	Shape Parameters	65
5.2.2	Angle Analysis	71
5.2.3	Knot-Exclusive Analysis	72
5.2.4	VMD Snapshots	81
6	Conclusions and Outlook	86
7	References	87
	Appendix A: Abstract (English)	92
	Appendix B: Abstract (German)	93

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1 Introduction

Nowadays, the knotting of macromolecules such as DNA or RNA is known not only to occur, with studies covering the trigger mechanisms for the knotting itself [60] [38], but also to have an important influence on various processes, such as RNA transcription [49] and mutation promotion [18]. [46] Since the first crystal structures of knotted proteins were analysed in the 1990's, the amount of known knotted proteins has grown to several hundred registered instances in the protein data bank PDB [7], featuring a wide variety of folds and functions [63]. [50] Undeniably, the knotting of macromolecules touches several branches of science, such as molecular biology, chemistry and polymer physics. Of special interest to us as physicists, however, is the implied impact of topology and mechanical properties on biological functionality of DNA and RNA. To bring up a brief example, DNA knotting has been observed in the context of viruses, with articles by Matthews et al. (2009) about knot-controlled polymer ejection from virus capsids [39] and by Marenduzzo et al. (2009) on topological friction affecting viral DNA ejection [37]. The fact that this whole branch of research has only come up in recent years as well as its potential influence on our understanding of molecular biology added further to a fascination which ultimately led to the creation of this thesis. On the other hand, colloidal suspensions under shear have impact on our day-to-day life, for example in the context of blood cell flow through our body or water-based painting of a wall. [45] As for technological importance, shear is essential for many applications of soft materials, "such as drug delivery systems [68] or as motor oil viscosity modifiers [66]". [45] Additionally, external fields such as shear have been used to orient microdomains [11] as mentioned by Chremos et al. (2012) [10]. There has also been research in recent years covering the self-organisation of suspensions under shear, for example by Myung et al. (2015) [41].

The effects of knots on polymer dynamics have been studied extensively in recent years. Localisation of knots has been studied by Metzler (2002) [40], scaling and equilibrium lengths were tabulated by Rawdon et al. (2008) [51] and additional properties of knotted rings have been studied by Mansfield et al. (2010) [35] [36]. Narros, Likos and Moreno (2013) have taken this further and studied interactions between knotted rings [42] and in solvents of varying quality [43]. Poier et al. (2014) deduced a study on the influence of rigidity and knot complexity on knotting [46]. The influence of stiffness on knots was, additionally, also discussed by Gallotti and Pierre-Louis (2007) [22].

Properties of knotted polymers have gained importance because of their relation to and occurrence on DNA strands. Rybenkov et al. (1993) introduced studies on random DNA knotting and helix diameter [56], quickly followed by studies by Stasiak et al. (1996) on electrophoretic mobility of DNA knots [61] and the geometry and physics of knots in general [28]. Katritch et al. (2000) observed the tightness of knots created by random

knotting [29], whereas Bao et al. (2003) conducted a study on knots in single DNA molecules [6]. Dimensions of DNA knots were again studied by Ercolini et al. (2007) [20].

Furthermore, altered polymer behaviour when subjected to shear-induced stress has been the topic of other recent computational science research. A study on linear polymer chains was conducted by Teixeira et al. (2005) with a focus on tumbling motion [64], followed by simulations of star polymers by Ripoll et al. (2006, 2007) [52] [53] and by Nikoubashman and Likos (2010) [45]. Similar observations were published for ring polymers by Chen et al. (2013), describing tumbling and tank-treading dynamics [8]. A more extensive study on ring polymers in shear flow was published by a larger group around Chen et al. (2015), presenting further observations on deformation, orientation and motion [9].

Finally, conformation and topology of polymer chains have gotten more important with a recent discovery by Eslami-Mossallam et al. (2016), suggesting that mechanical properties of DNA molecules may have an impact on chromatin function, and furthermore providing evidence that the way DNA is packed into nucleosomes invites the possibility for it to store a second layer of DNA information [21].

Following the studies conducted by Narros et al. (2013) [43] and by Chen et al. (2015) [9], this thesis aims to compute similarly the deformational and orientational characteristics of single flexible polymer rings embedded in a solvent and therefore subject to hydrodynamic interactions, with the addition of a 3_1 trefoil knot, with the addition of shear.

Looking at the aforementioned research on knots as well as polymers under shear, respectively, it seems quite remarkable that studies covering knotted rings under shear have not been conducted before. In this thesis, the topic was tackled using a hydrodynamic and molecular dynamics hybrid approach called Multi-Particle Collision Dynamics (MPCD), originally developed by Malevanets and Kapral (1999) [34], to simulate a solvent in which the knotted polymer ring was embedded. This hybrid approach allows for time- and resource-efficient coupling of the solvent's hydrodynamics with the polymer's molecular dynamics. MPCD may conveniently be extended to obey Lees-Edwards boundary conditions [31] and therefore to accurately represent a fluid under shear. The polymer itself has been simulated using the Velocity-Verlet algorithm [65], with the interaction potential suggested for flexible polymer chains by Poier et al. in [47].

The number of beads of the knot was measured as well as its radius of gyration and the angle between the vector between the knot's center of mass and the polymer ring's center of mass, and the ring's orientational axis (the first principal component). Correlations between the two quantities were analysed. Similarly, shape parameters anisotropy, prolateness, asphericity and acylindricity, as well as alignment angle and deformational resistance, have been computed and compared to respective values from rings under the same shear-induced stresses. All quantities have been calculated in dependency of the system's Weissenberg number Wi , but for a fixed number of simulated beads on the ring.

Special attention was directed towards finding a preferred positioning of the knot and any correlation between knot size and knot position on the ring, and consecutively a correlation between knot size and the degree to which the knot is aligned with the shear flow direction.

2 Theoretical Foundation

In this section, a theoretical background is provided for all employed algorithms alongside an overview on characteristic values and tools used for basic simulation analysis.

2.1 Reduced Units

Reduced units are a rather powerful tool commonly employed in many fields of physics, such as theoretical particle physics, where one usually assigns $c = h = 1$, special relativity, where convention denotes $c = 1$, and multiple other subjects of physical research where the SI system has proven impractical, such as electrodynamics and biophysics. In Molecular Dynamics simulations, the same impracticality arises from the small but widely-ranged scales of length, energy and mass of any observed systems, which, when using SI units for a simulation, might lead to numerically caused inaccuracies. Numerical reasons aside, reduced units allow to see similarities and equivalences in simulations of the same reduced unit values accounting for different basic units. For example, the reduced values T^* and ρ^* correspond to multiple possible values of temperature and density, uniquely defined by the choice of reduced units. For this thesis, following a long tradition in simulations of Lennard-Jones systems, the Lennard-Jones parameters σ and ϵ have been chosen as the units of length and energy, respectively, and the solvent particle mass m as the unit of mass. The Boltzmann constant k_B functions as a conversion factor between energy and temperature. Subsequently, these four quantities are assigned a value of unity.

Because of this system's simplicity and its matter-of-factly use in most publications in this field, reduced units will be used throughout the rest of this thesis unless indicated otherwise, and the superscript $*$ (asterisk) will be dropped. Table 1 shows some of the most important quantities expressed in reduced units. As a rule of thumb, any resulting quantity in reduced units should be described by the basic parameters which have been assigned values of unity.

Quantity	Reduced Units
Length	$l^* = \frac{l}{\sigma}$
Energy	$E^* = \frac{E}{\epsilon}$
Mass	$m^* = 1$
Temperature	$T^* = \frac{k_B T}{\epsilon}$
Time	$t^* = t\sigma \left(\frac{\epsilon}{m}\right)^{\frac{1}{2}}$
Density	$\rho^* = \rho\sigma^3$
Velocity	$v^* = v \left(\frac{m}{\epsilon}\right)^{\frac{1}{2}}$
Force	$F^* = F \left(\frac{\sigma}{\epsilon}\right)$
Viscosity	$\eta^* = \eta \left(\frac{\sigma^4}{\epsilon m}\right)^{\frac{1}{2}}$

Table 1: Transposition of real to reduced units.

2.2 Multi-Particle Collision Dynamics

Multi-Particle Collision Dynamics (MPCD) is a numerical approach developed by Malevanets and Kapral (1999) for the simulation and investigation of complex fluids, one of the main reasons for its original development being the task of studying the behaviour of biopolymers in solution. [34] Additionally, Gompper, Ihle, Kroll and Winkler (2008) claim that the field of applications for MPCD includes "amphiphilic mixtures, colloidal suspensions, and polymer solutions, as well as [...] chemically reactive flows (combustion), the fluid dynamics of self-propelled objects, and the visco-elastic behavior of networks in cells." Phenomena of interest studied with MPCD occur at length scales of nano- to micrometers and at energy scales of the same order of magnitude as the thermal energy $k_B T$. [23] (see citation for a historical overview on the development of MPCD) Derived for these purposes, MPCD is a method involving the simulation of a set of point-like fluid particles N_f , with N_f being several orders of magnitude larger than the number of simulated polymer beads N_b , possibly $N_f \sim 10^5 - 10^6$ while $N_b \sim 10^2 - 10^3$, depending largely on polymer topology and dimensions of the simulation box. A fluid simulated with the MPCD approach continually undergoes an alternation of two separate algorithmic steps, the *Streaming Step* and the *Collision Step*. While the *Streaming Step* (see section 2.2.1) serves the purpose of propagating fluid particle positions in time, the *Collision Step* (see section 2.2.2) governs the global conservation of energy and the cell-level conservation of momentum and enforces the time propagation of fluid particle velocities. Local

algorithms, such as MPCD, are approximations for compressible fluids, which means it takes some time for hydrodynamics interactions to fully develop and propagate over long distances. Thus, MPCD is rather inefficient for near-zero Reynolds number or high Mach number, and therefore should not be used under such circumstances. However, MPCD is best suited for simulations in which both hydrodynamics and thermal fluctuations are considered crucial. [25]

2.2.1 The Streaming Step

The MPCD Streaming Step propagates all fluid particles inside (and outside) a simulation box in time and space and enforces any applied boundary conditions. It therefore also governs changes in velocity due to boundary conditions. However, unless a particle has crossed any boundaries, the velocities of all fluid particles are invariant under the Streaming Step. It is important to note that particles, during the streaming step, move independently of one another and only experience external forces, if any are given. In the absence of such external forces, these particles of masses m_i move ballistically, their positions $\mathbf{r}_i(t)$ being updated according to

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \Delta t \mathbf{v}_i(t), \quad (1)$$

where $i = 1, \dots, N_f$, $\mathbf{v}_i$ is the velocity of particle i and Δt is the time interval between streaming steps. [25]

2.2.2 The Collision Step

The MPCD Collision Step governs time propagation of all fluid particle velocities $\mathbf{v}_i$ and also enforces energy- as well as momentum conservation on a cell level, that is to say, within cubic cells of a grid spread over the entire simulation box. All cubic cells are to have the same side length a . Only particles within the same cubic cell may interact with each other during the collision step. First, for all cubic grid cells, the center-of-mass velocity of that cell is computed by

$$\mathbf{v}_{cm} = \frac{\sum_{i=1}^{N_c} m_i \mathbf{v}_i}{\sum_{i=1}^{N_c} m_i}, \quad (2)$$

with $\mathbf{v}_i$ being the velocities and m_i being the masses of any of the N_c particles i within the

specified grid cell. Next, also for all cubic grid cells, the relative velocities of any particles are rotated with respect to their cell's $\mathbf{v}_{cm}$, and $\mathbf{v}_i(t)$ is updated according to

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + (\mathbb{R}(\alpha) - \mathbb{1})(\mathbf{v}_i(t) - \mathbf{v}_{cm}(t)), \quad (3)$$

where $\mathbb{R}$ is the rotation matrix of a rotation around a randomly chosen axis $\hat{\mathbf{R}}$ by a fixed angle α and $\mathbb{1}$ the unit matrix. $\hat{\mathbf{R}}$ is computed individually for all grid cells according to

$$\begin{aligned} \hat{\mathbf{R}}_x &= \sqrt{1 - \theta^2} \cos(\phi), \\ \hat{\mathbf{R}}_y &= \sqrt{1 - \theta^2} \sin(\phi), \\ \hat{\mathbf{R}}_z &= \theta, \end{aligned} \quad (4)$$

ensuring any rotation axis is chosen uniformly distributed on a sphere of radius 1. One may write

$$\Delta \mathbf{v}_i(t) = \mathbf{v}_i(t) - \mathbf{v}_{cm}(t). \quad (5)$$

Then, the multiplication with the rotation matrix $\mathbb{R}$ can be expressed in a simplified way by

$$\begin{aligned} \mathbf{v}_i(t + \Delta t) &= \mathbf{v}_{cm}(t) + \cos(\alpha)[\Delta \mathbf{v}_i - (\Delta \mathbf{v}_i \hat{\mathbf{R}}) \hat{\mathbf{R}}] \\ &\quad + \sin(\alpha) \hat{\mathbf{R}} \times [\Delta \mathbf{v}_i - (\Delta \mathbf{v}_i \hat{\mathbf{R}}) \hat{\mathbf{R}}] \\ &\quad + (\Delta \mathbf{v}_i \hat{\mathbf{R}}) \hat{\mathbf{R}}. \end{aligned} \quad (6)$$

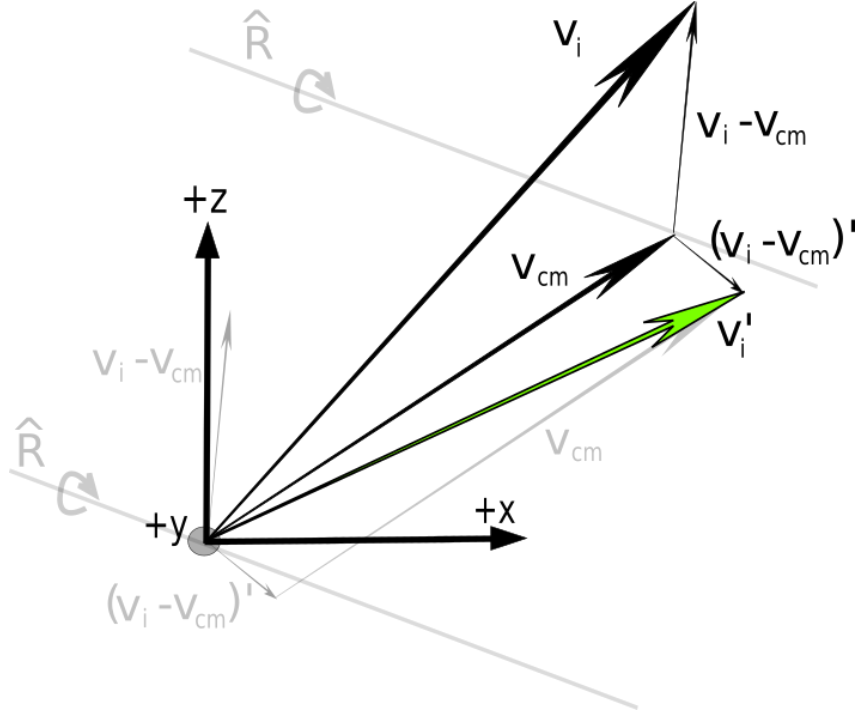


Figure 1: Vector $\Delta \mathbf{v}_i = \mathbf{v}_i - \mathbf{v}_{cm}$ is rotated around axis $\hat{R}$ by an angle of 130° to then obtain $\mathbf{v}_i' = \Delta \mathbf{v}_i' + \mathbf{v}_{cm}$. Figure done in Inkscape [12].

In its original form as proposed by Malevanets and Kapral [34], the MPCD algorithm is not invariant under change of reference frame. Especially at low temperatures or small time scales, the same particles interact with one another multiple times and therefore develop correlations. To restore Galilean invariance, a grid shift by a random vector with coordinates sampled uniformly from $[-a/2, +a/2]$ is employed previous to each collision step. This may be done either by shifting all particles by the same vector and keeping the grid fixed, and restoring the initial particle positions afterwards, or by shifting the grid, performing the collision step but preserving the initial grid position as the starting point for the next collision step grid shift. [25]

2.2.3 Characteristic Quantities

A fluid simulated using MPCD has its characteristics defined by several different quantities, some of which may be referred to as *basic quantities*. These are chosen directly by the programmer and may or may not influence program memory requirements and runtime (shape of the simulation box, number of grid cells, number of fluid "particles" per cell, dimensions and particle mass, temperature, but also the rotation angle of the MPCD *Collision Step*, among other quantities). There are also several defining quantities derived

from these *basic quantities*, including but not limited to fluid viscosity and the self-diffusion coefficient. A huge advantage of MPCD is that analytic expressions for transportation coefficients governing macroscopic laws can be derived. [25] In the following, the most influential of these both basic and derived quantities will be introduced.

The *rotation angle* of the MPCD *Collision Step* is one of the more important basic quantities because it has a crucial impact on transport coefficients and therefore may change the quality of the fluid acting as a solvent without increasing memory requirements or runtime. The rotation it governs is applied to the particle velocities relative to the center-of-mass velocities of their respective grid cells and thus provides a regulation tool for how strong particle interactions occur during the collision step.

The number N_c of fluid particles per cell provides a similar tool of regulating fluid particle interactions. Obviously, increasing N_c also increases runtime and memory requirements of the MPC algorithm, so choosing a higher N_c always comes at a price. Its importance for and its influence on MPCD accuracy, however, is trivial to see and a tradeoff between an increased value of N_c and therefore more accurate results and program runtime has to be accepted.

The *diffusion coefficient* D of a particle i is computed from the Green-Kubo relation as

$$D = \frac{\Delta t}{6} \langle \mathbf{v}_i(0)^2 \rangle + \frac{\Delta t}{3} \sum_{n=1}^{\infty} \langle \mathbf{v}_i(n \cdot \Delta t) \mathbf{v}_i(0) \rangle, \quad (7)$$

in accordance with [25], where one may also find the full derivation of the analytic expression for the diffusion coefficient D ,

$$D = \frac{\Delta t \langle \mathbf{v}_i(0)^2 \rangle}{3} \left(\frac{1}{\gamma} - \frac{1}{2} \right) = \frac{\Delta t k_B T}{m} \left(\frac{1}{\gamma} - \frac{1}{2} \right), \quad (8)$$

valid only under the molecular chaos assumption, with γ being defined as

$$\gamma = \frac{2(1 - \cos(\alpha))}{3 \langle N_c \rangle} \left(e^{-\langle N_c \rangle} + \langle N_c \rangle - 1 \right). \quad (9)$$

However, eq. (7)-(9) hold true only for $N_c \gtrsim 5$ and only if any correlations between particles can be neglected, which is not generally the case, but only for large collision time steps where $\Delta t / \sqrt{ma^2 / (k_B T)} = \lambda / a > 1$, where λ is called the mean-free path and a is the side length of each cubic grid cell. This ensures a new collision environment for

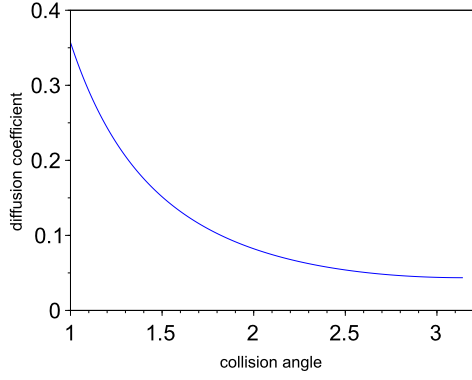


Figure 2: $D(\alpha)$ for $N_c = 5$, $\Delta t = 0.1$, $k_B T/m = 1$.

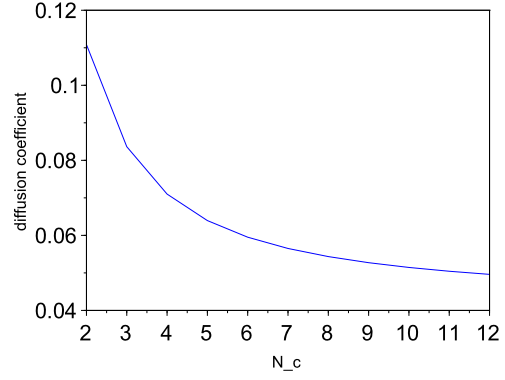


Figure 3: $D(N_c)$ for $\alpha = 130^\circ$, $\Delta t = 0.1$, $k_B T/m = 1$.

all particles at every collision step, therefore getting rid of any correlations which might otherwise stack up. For smaller values of λ , a correspondingly larger D may be obtained. [25]

Another important quantity which may be expressed analytically is the *shear viscosity* η which characterises the fluid's non-equilibrium behaviour. Usually, one obtains the viscosity of a fluid under shear in direction of the x-axis and gradient along the z-axis by calculating the stress tensor component σ_{xz} , with the relation

$$\eta = \lim_{\dot{\gamma} \rightarrow 0} \frac{\sigma_{xz}}{\dot{\gamma}}, \quad (10)$$

where $\dot{\gamma}$ is the shear rate along the x-axis. Analytic expressions for the stress tensor σ and the shear viscosity of a fluid in the absence of walls have been derived and discussed by Winkler in [25], and these quantities can be computed according to the therein obtained equations:

$$\sigma_{xz} = -\frac{1}{V} \sum_{i=1}^N m \hat{\mathbf{v}}'_{ix} \hat{\mathbf{v}}_{iz} - \frac{\dot{\gamma} \Delta t}{2V} \sum_{i=1}^N m \mathbf{v}_{iz}^2 - \frac{1}{V \Delta t} \sum_{i=1}^N \Delta \mathbf{p}_{ix} \mathbf{r}'_{iz}, \quad (11)$$

where V is the volume of the simulation box, quantities indexed with $'$ are quantities assigned to the particle mapped to the simulation box (whereas non-indexed quantities refer to the particle itself, i.e. $\mathbf{r}_i = \mathbf{r}'_i + \mathbf{R}_i$ where $\mathbf{R}_i = (n_{ix} \mathbf{L}_x, n_{iy} \mathbf{L}_y, n_{iz} \mathbf{L}_z)$ is the lattice vector to particle i , with $\mathbf{L}$ being the vector of box lengths along axis), $\hat{\mathbf{v}}_i$ denotes the

velocity vector of particle i after the streaming step, but before the collision, m is the mass of a solvent particle, and $\Delta \mathbf{p}_{ix} = m_f(\mathbf{v}_{ix} - \hat{\mathbf{v}}_{ix})$ is the momentum change due to collision. It is further obtained that

$$\eta = \eta_{kin} + \eta_{col}, \quad (12)$$

$$\eta_{kin} = \frac{Nk_B T \Delta t}{V} \left[\frac{5N_c}{(N_c - 1)(4 - 2\cos(\alpha) - 2\cos(2\alpha))} - \frac{1}{2} \right], \quad (13)$$

$$\eta_{col} = \frac{Nma^2}{18V\Delta t} (1 - \cos(\alpha)) \left(1 - \frac{1}{N_c} \right), \quad (14)$$

however one needs to keep in mind that these equations only hold true under the molecular chaos assumption, so for large mean-free paths $\lambda > 1$, and sufficiently many particles per grid cell, $N_c > 3$. Otherwise, fluctuations might be too large to obtain accurate results from the simulation.

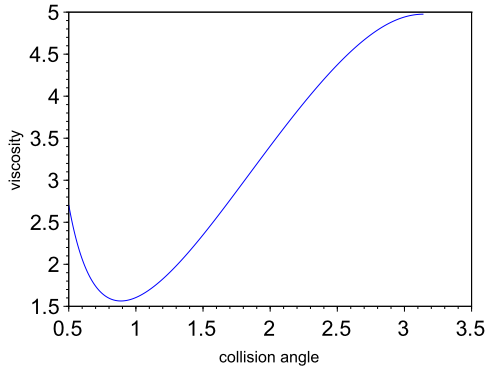


Figure 4: $\eta(\alpha)$ for $N_c = 5$, $a = 1$, $m = 1$, $k_B T = 1$.

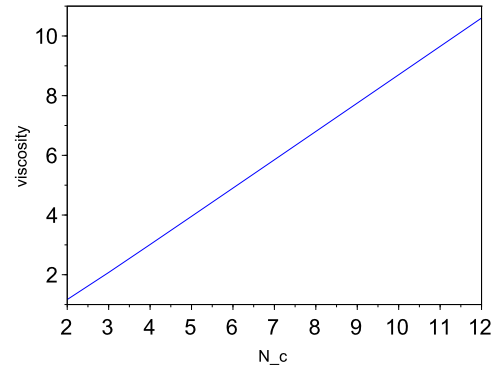


Figure 5: $\eta(N_c)$ for $\alpha = 130^\circ$, $a = 1$, $m = 1$, $k_B T = 1$.

In the context of shear flow simulations, one also needs to define the *shear rate* $\dot{\gamma}$, which is calculated from the velocity of the *moving walls* causing the shear as well as the dimensions of the simulation box. However, because the shear rate definition used for calculations within this thesis is heavily intertwined with a fitting choice of boundary conditions and is far easier visualised in this context, please refer to section 2.5.1 for a proper discussion and formula for the calculation of $\dot{\gamma}$.

2.2.4 Conservation of Quantities

In this section, we prove the conservation of energy and momentum by the MPCD algorithm, commencing with energy conservation:

$$\begin{aligned}
 E(t) &= \frac{1}{2} \sum_{i=1}^{N_c} m_i \mathbf{v}_i^2(t) \\
 &= \frac{1}{2} \sum_{i=1}^{N_c} m_i (\mathbf{v}_{cm}(t) + \Delta \mathbf{v}_i(t))^2 \\
 &= \frac{1}{2} \mathbf{v}_{cm}^2(t) \sum_{i=1}^{N_c} m_i + \mathbf{v}_{cm}(t) \sum_{i=1}^{N_c} m_i \Delta \mathbf{v}_i(t) + \frac{1}{2} \sum_{i=1}^{N_c} m_i \Delta \mathbf{v}_i^2(t),
 \end{aligned} \tag{15}$$

and the sum over $\Delta \mathbf{v}_i$ is zero for all $m_i = m$, but also for the case where a solvent consists of mixed particles, because $\mathbf{v}_{cm}$ takes different masses into account easily. Therefore,

$$E(t) = \frac{1}{2} \left(\mathbf{v}_{cm}^2(t) \sum_{i=1}^{N_c} m_i + \sum_{i=1}^{N_c} m_i \Delta \mathbf{v}_i^2(t) \right), \tag{16}$$

or, for solvents with all $m_i = m$, one may write a more compact form of:

$$E(t) = \frac{m}{2} \left(N_c \mathbf{v}_{cm}^2(t) + \sum_{i=1}^{N_c} \Delta \mathbf{v}_i^2(t) \right). \tag{17}$$

At time $t + \Delta t$, one may write, similarly:

$$\begin{aligned}
 E(t + \Delta t) &= \frac{1}{2} \sum_{i=1}^{N_c} m_i \mathbf{v}_i^2(t + \Delta t) \\
 &= \frac{1}{2} \left(\mathbf{v}_{cm}^2(t + \Delta t) \sum_{i=1}^{N_c} m_i + \sum_{i=1}^{N_c} m_i \Delta \mathbf{v}_i^2(t + \Delta t) \right)
 \end{aligned} \tag{18}$$

One may then consider that for $t \rightarrow t + \Delta t$, $\Delta \mathbf{v}_i(t) \rightarrow \mathbb{R}(\alpha) \cdot \Delta \mathbf{v}_i(t)$ which leaves the magnitude of $\Delta \mathbf{v}_i$ unchanged between two collision steps. $\mathbf{v}_{cm}^2$ does not change either:

$$\begin{aligned}
 \mathbf{v}_{cm}(t + \Delta t) &= \frac{\sum_{i=1}^{N_c} m_i (\mathbb{R}(\alpha) \cdot \Delta \mathbf{v}_i(t) + \mathbf{v}_{cm}(t))}{\sum_{i=1}^{N_c} m_i} \\
 &= \frac{\mathbb{R}(\alpha) \cdot \sum_{i=1}^{N_c} m_i \Delta \mathbf{v}_i(t)}{\sum_{i=1}^{N_c} m_i} + \frac{\mathbf{v}_{cm}(t) \sum_{i=1}^{N_c} m_i}{\sum_{i=1}^{N_c} m_i} \\
 &= \mathbf{v}_{cm}(t)
 \end{aligned} \tag{19}$$

Again, one makes use of $\sum_{i=1}^{N_c} m_i \Delta \mathbf{v}_i = 0$. With this knowledge, one may now rewrite equation 18:

$$E(t + \Delta t) = \frac{1}{2} \left(\mathbf{v}_{cm}^2(t) \sum_{i=1}^{N_c} m_i + \sum_{i=1}^{N_c} m_i \Delta \mathbf{v}_i^2(t) \right) = E(t), \tag{20}$$

by comparing to equation 16 and 17. Therefore, MPCD was proven to conserve energy within the system.

Conservation of momentum may be proven similarly. Let $\mathbf{P}(t)$ be the total momentum of the simulated solvent at time t . By comparison with equation 2, one obtains:

$$\mathbf{P}(t) = \sum_{i=1}^{N_c} m_i \mathbf{v}_i(t) = \sum_{i=1}^{N_c} m_i \mathbf{v}_{cm}, \tag{21}$$

$$\begin{aligned}
 \mathbf{P}(t + \Delta t) &= \sum_{i=1}^{N_c} m_i \mathbf{v}_i(t + \Delta t) \\
 &= \sum_{i=1}^{N_c} m_i (\mathbf{v}_{cm}(t) + \mathbb{R}(\alpha) \cdot \Delta \mathbf{v}_i(t)) \\
 &= \mathbf{P}(t) + \mathbb{R}(\alpha) \cdot \sum_{i=1}^{N_c} m_i \Delta \mathbf{v}_i(t) \\
 &= \mathbf{P}(t).
 \end{aligned} \tag{22}$$

2.3 Polymer Modelling

Seldom is there a simulation which is able to consider every tiny nuance enforced by nature. Almost any simulation has to rely on models and approximations. This is just as true for the simulation of polymers, as they have been modelled for this thesis. Segments of

any simulated macromolecule can be described as beads, connected by bonds which are likewise approximated to behave like springs. Chemical reactions are not considered, and the general shape of the polymer should therefore be conserved. As such, many quantities need to be chosen and considered to ensure a comparability between experiment and simulation. To explain such choices of quantities and to introduce the model itself is the aim of the following sections.

2.3.1 The Bead Concept

Polymer characteristics, such as microstructure and degree of polymerisation, are all decided upon polymerisation and may not be changed afterwards without potentially breaking up covalent bonds. However, a polymer could still adapt multiple conformations over time. "A conformation is the spatial structure of a polymer determined by the relative location of its monomers", say Rubenstein et al. in [55], meaning that a conformation is described by some n bonds between consecutive backbone monomers. It is a useful feature of polymers that they are, over a wide range of sizes, self-similar or *fractal*, showing the same internal structure or conformation from both macroscopic and microscopic points of view. This concept is easily illustrated by cutting a smaller sphere of radius r out of a bigger sphere of radius R . Both spheres will look the same, and their radii will be proportional to each other, as will be their masses and volumes. The same can be applied to polymers. One may therefore approximate a polymer chain segment of some length b longer than the average backbone bond length L , but shorter than the chain itself, by two consecutive beads connected by some bond of yet-to-be-calculated stiffness and strength. The specifics of this substitution are derived in the following equations for the simpler case without self-avoidance. In this approach, if M is the total mass of the polymer and m_a is the mass of an atomic backbone molecule, one may call m_b the mass of one of the newly-defined beads. If the microscopically observed chain consists of a number N of molecules connected by bonds of length L , one may define a number n of beads simulating a fractal chain on a more macroscopic scale, connected by bonds of length b . Consequently,

$$M = \sum_{i=1}^N m_{i,a} = \sum_{j=1}^n m_{j,b}, \quad (23)$$

thus the total mass of the chain is conserved. The end-to-end distance of such a polymer chain is computed from

$$\mathbf{R}_e = \sum_{i=1}^N \mathbf{r}_i, \quad (24)$$

and if one averages end-to-end distance over a large sample of polymer chains, because of isotropy, $\langle R_e \rangle = 0$. A more appropriate tool is therefore the mean-squared end-to-end distance, which is, in general, non-zero:

$$\langle \mathbf{R}_e^2 \rangle = \langle \mathbf{R}_e \cdot \mathbf{R}_e \rangle = \sum_{i=1}^N \sum_{j=1}^N \langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle. \quad (25)$$

For bonds with the same average length L , this can be further simplified by writing:

$$\langle \mathbf{R}_e^2 \rangle = L^2 \sum_{i=1}^N \sum_{j=1}^N \langle \cos(\theta_{ij}) \rangle, \quad (26)$$

and from here on, it is important to specify whether self-avoidance is considered or not. For no self-avoidance, equation (26) can be solved to become

$$\langle \mathbf{R}_e^2 \rangle = NL^2, \quad (27)$$

however with self-avoidance, scaling behavior changes to

$$\langle \mathbf{R}_e^2 \rangle = N^{2\nu} L^2, \quad (28)$$

and both equations only hold true if correlations between bonds can be neglected, as is the case for an ideal chain. One of the easiest models for such a chain is the freely-jointed chain model. [55] More generally, one may define the characteristic ratio C_n , with

$$C_n = \frac{1}{N} \sum_{i=1}^N C_i = \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^N \langle \cos(\theta_{ij}) \rangle, \quad (29)$$

where all C_i converge towards a value C_∞ for chains of infinite length, whereas real chains have a cutoff at finite j , resulting in smaller values of C_i . C_n can also be computed numerically and is dependent on local stiffness but is always larger than unity, with typical values being of order 10^1 . We now derive formulas for n and b without considering self-avoidance. For long chains, one may write:

$$\langle \mathbf{R}_e^2 \rangle \cong C_\infty N L^2. \quad (30)$$

In accordance with polymers' fractal nature, flexible chains have many characteristic quantities independent of local chemical structure. Any freely jointed chain may be described by an equivalent freely jointed chain, with the same $\langle R_e^2 \rangle$ and R_{max} , but with n freely-jointed bonds of length b . The effective bond length b is called *Kuhn length*, and one finds:

$$R_{max} = nb \quad (31)$$

$$\langle R_e^2 \rangle = nb^2 = bR_{max} = C_\infty N L^2 \quad (32)$$

Consecutively, the equivalent freely jointed chain consists of n bonds of Kuhn length b , with:

$$n = \frac{R_{max}^2}{C_\infty N L^2} \quad (33)$$

$$b = \frac{\langle R_e^2 \rangle}{R_{max}} = \frac{C_\infty N L^2}{R_{max}} \quad (34)$$

n and b are therefore not freely chosen, but depend on the conformation of the polymer on its original scale. [55] If there are n bonds of length b , there shall be a number of point-like, dimensionless beads of mass m_b simulated, with $n + 1$ beads for any linear or open polymer and n for any circular or closed polymer. The beads represent beginnings and ends for each bond and are treated as particles connected by some spring potential.

The bonds themselves do not have any mass, and for the purpose of this thesis, it will be assumed that the interaction between bonds is negligible. However, such an interaction could be easily added by considering angles between consecutive bonds and introducing rigidity, as suggested by Poier et al. (2015) [48]. Any consideration of bond angles would, however, lead to a more complicated chain model than the freely-jointed one, and may therefore be left for future studies.

2.3.2 Velocity-Verlet Algorithm

To simulate a bead-model polymer, one may find the Velocity-Verlet algorithm suitable to solve Newton's equations of motion whilst being a symplectic integrator and therefore conserving energy as well as linear and angular momentum. The Velocity-Verlet algorithm also does not depend on having access to positions and velocities at time $t = -\Delta t$ and is also more accurate than the semi-implicit Euler method. It has first been developed by Verlet (1982) [65] and is also explained in the appendix of [62]. One may therefore use the Velocity-Verlet algorithm to calculate bead position $\mathbf{r}_i$ and velocity $\mathbf{v}_i$ of any bead i at time $t + \Delta t$ according to

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \Delta t \mathbf{v}_i(t) + \frac{\Delta t^2}{2m} \mathbf{F}_i(t), \quad (35)$$

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + \frac{\Delta t}{2m} (\mathbf{F}_i(t) + \mathbf{F}_i(t + \Delta t)), \quad (36)$$

with $\mathbf{F}_i(t)$ being the force acting on a bead i . Note that this algorithm fails whenever the force model includes a dependence on velocity.

2.3.3 Interaction Potential

A fitting model for the interaction potential between two beads i and j (bonded as well as non-bonded) is the truncated and shifted Lennard-Jones potential as mentioned by Winkler in [25]:

$$U_{LJ}(r_{ij}) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 + \frac{1}{4} \right] & \forall r_{ij} \leq \sigma \sqrt[6]{2}, \\ 0 & \forall r_{ij} > \sigma \sqrt[6]{2}. \end{cases} \quad (37)$$

where r_{ij} is the distance between beads i and j , and σ and ϵ are the Lennard-Jones parameters. Additionally, $U_{LJ}(r_{ij}) = 0$ for any $r_{ij} > \sigma\sqrt[6]{2}$.

For consecutive beads, an additional additive bonding potential is introduced, simulating a spring of spring constant k and maximum bond length R_0 , called the FENE potential [48]:

$$U_{FENE}(r_{ij}) = \begin{cases} -\frac{kR_0^2}{2} \ln \left[1 - \left(\frac{r_{ij}}{R_0} \right)^2 \right] & \forall r_{ij} < R_0, \\ \infty & \forall r_{ij} \geq R_0. \end{cases} \quad (38)$$

As can be seen in eq. (38), U_{FENE} has a singularity at $r_{ij} = R_0$ and diverges for $r_{ij} \geq R_0$. Therefore, the time step Δt must be chosen sufficiently small to give the attractive U_{FENE} the necessary time to react to the repelling contribution of U_{LJ} so that the singularity is never encountered. Suggestions are made by Poier et al. in [48] to choose $\epsilon = k_B T$, $k = 30k_B T / \sigma^2$ and $R_0 = 1.5\sigma$. A different harmonic bond potential may also be used, as mentioned by Winkler in [25]:

$$U_{ALT}(r_{ij}) = \frac{k}{2} (r_{ij} - b)^2, \quad (39)$$

where k is again the spring constant and b the average bond length. Winkler also suggests values of $b = \sigma$ and $k = 5 \cdot 10^3 k_B T / a^2$. However, it can be seen from fig. 6 that the FENE potential offers a much smoother potential in the important range of values for the radius.

One may now derive $U_{tot} = U_{LJ} + U_{FENE}$ and the minimum of U_{tot} will influence the average bond length alongside the root of the total force, F_{tot} .

The force $\mathbf{F}_{ij}$ of bead j acting on bead i at time t is commonly calculated from

$$\mathbf{F}_{ij}(t) = -\nabla_{\mathbf{r}_i} U(|\mathbf{r}_i - \mathbf{r}_j|, t) = -\nabla_{\mathbf{r}_i - \mathbf{r}_j} U(|\mathbf{r}_i - \mathbf{r}_j|, t), \quad (40)$$

where $\mathbf{r}_j - \mathbf{r}_i = \mathbf{r}_{ij}$ is the distance vector pointing from bead i to bead j . One can then compute F_{LJ} and F_{FENE} to be

$$\mathbf{F}_{ij}^{LJ} = -\frac{24\epsilon}{r_{ij}} \left[2 \left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \frac{\mathbf{r}_{ij}}{r_{ij}}, \quad (41)$$

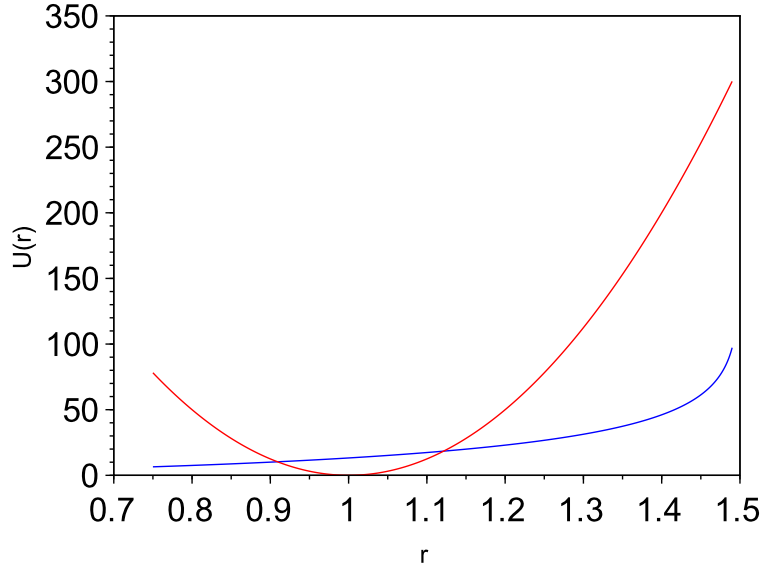


Figure 6: Direct comparison between the FENE potential (blue) with values suggested by Poier et al. [48] and the alternative bond potential (red) with values suggested by Winkler [25]. Plot done for $k_B T = 1$, $a = 1$, $\sigma = 1$.

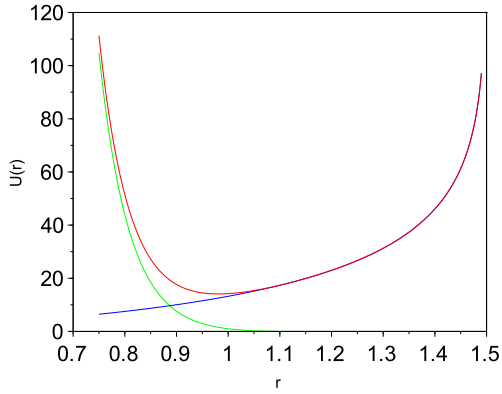


Figure 7: The Lennard-Jones (green, U_{LJ}) as well as the FENE (blue, U_{FENE}) and the combined (red, U_{tot}) potentials over a broader range of $r \in [0.75; 1.49]$. $\epsilon = 1$, $\sigma = 1$, $k = 30$, $R_0 = 1.5$.

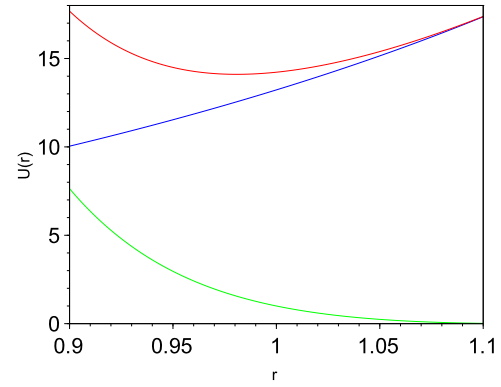


Figure 8: The Lennard-Jones (green, U_{LJ}) as well as the FENE (blue, U_{FENE}) and the combined (red, U_{tot}) potentials over a narrow range of $r \in [0.9; 1.1]$. Combined potential U_{tot} maximum is visible at around $r = 0.98$. $\epsilon = 1$, $\sigma = 1$, $k = 30$, $R_0 = 1.5$.

$$\mathbf{F}_{ij}^{FENE} = \frac{k}{\left[1 - \left(\frac{r_{ij}}{R_0}\right)^2\right]} \mathbf{r}_{ij}, \quad (42)$$

which already accounts for the direction of each force in relation to the distance vector $\mathbf{r}_{ij}$. Note that especially the Lennard-Jones force might be given with a different sign in different sources, depending on the derivation of $\mathbf{F}(r)$ and the orientation of the distance vector, which is sometimes defined as pointing towards particle i in literature.

A similar formula can be obtained for the alternative potential suggestion made by Winkler [25]:

$$\mathbf{F}_{ij}^{ALT} = -k(r_{ij} - b) \frac{\mathbf{r}_{ij}}{r_{ij}} \quad (43)$$

This force, however, is meant for non-flexible models, whereas the formula used by Poier et al. [48] corresponds to flexible polymer models, as seen in figures 9 and 10. Therefore, for this thesis, it was decided to employ the FENE potential for monomer-monomer bond interaction.

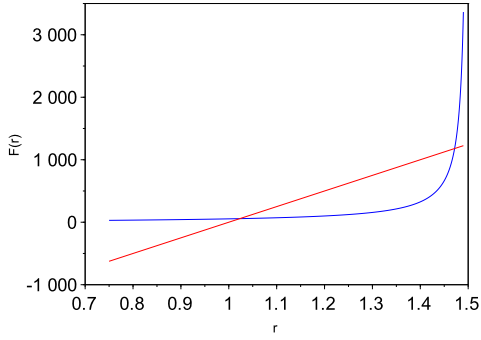


Figure 9: Direct comparison between the FENE force (blue) with values suggested by Poier et al. [48, p. 4985] and the alternative bond force (red) suggested by Winkler [25]. Plot done for $k_B T = 1$, $a = 1$, $\sigma = 1$.

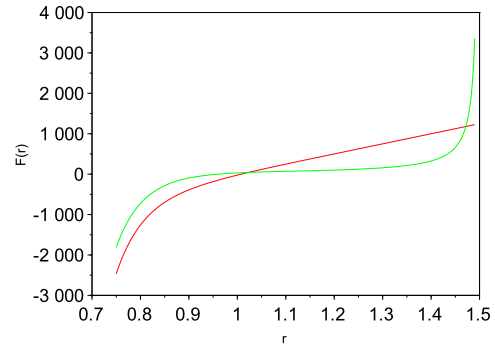


Figure 10: Direct comparison between $F_{LJ} + F_{FENE}$ (green) and $F_{LJ} + F_{ALT}$ (red), the forces acting on consecutive monomers. Plot done for $k_B T = 1$, $a = 1$, $\sigma = 1$, $\epsilon = 1$.

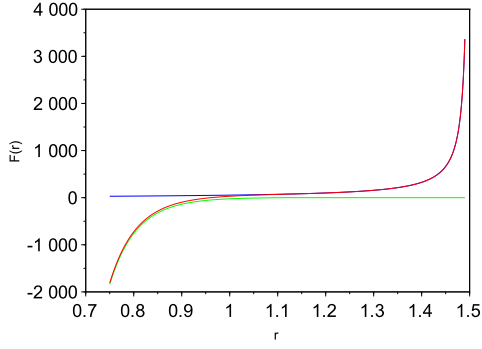


Figure 11: The Lennard-Jones (green, F_{LJ}) as well as the FENE (blue, F_{FENE}) and the combined (red, $F_{tot} = F_{FENE} + F_{LJ}$) forces over a broader range of $r \in [0.75; 1.49]$. $\epsilon = 1, \sigma = 1, k = 30, R_0 = 1.5$.

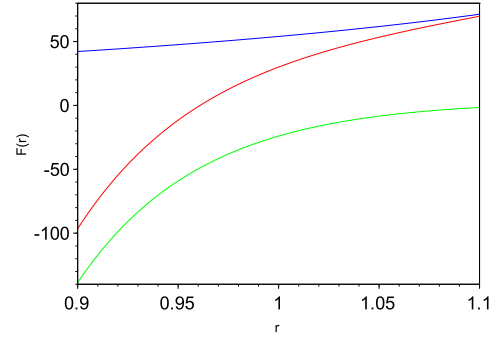


Figure 12: The Lennard-Jones (green, F_{LJ}) as well as the FENE (blue, F_{FENE}) and the combined (red, $F_{tot} = F_{FENE} + F_{LJ}$) forces over a narrow range of $r \in [0.9; 1.1]$. Force root $F(r) = 0$ is visible at around $r = 0.964$. $\epsilon = 1, \sigma = 1, k = 30, R_0 = 1.5$.

2.3.4 Andersen Thermostat

To achieve correct dynamical behavior, for equilibrium simulations as well as non-equilibrium simulations outside of MPC dynamics, the use of a thermostat is required to ensure the polymer's kinetic energy does not fluctuate or stray too wildly. A thermostat which is both effective and easy to implement is the Andersen thermostat as suggested by Andersen (1980) [5].

This thermostat works by, after some time τ , choosing random simulation particle and redistributing its velocity components according to a Maxwell-Boltzmann density distribution:

$$\wp(\mathbf{v}_{i,j}) = \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{1}{2}} \exp \left(-\frac{m_i \mathbf{v}_{i,j}^2}{2k_B T} \right), \quad (44)$$

where $\mathbf{v}_{i,j}$ is the j -th component of particle i 's velocity. Integration of the velocity distribution resulting from this yields the actual distribution:

$$f(v_i) = 4\pi \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} v_i^2 \exp \left(-\frac{m_i v_i^2}{2k_B T} \right), \quad (45)$$

which can also be written as a function of kinetic energy E_{kin} because $v_i^2 = 2E_{kin}/m_i$:

$$f(E_{kin}) = 4\pi \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \frac{2E_{kin}}{m} \exp \left(-\frac{E_{kin}}{k_B T} \right) \quad (46)$$

These thermostated particles then behave as if they had collided with a surrounding heat bath of temperature T . Eventually, if the frequency of particle velocity rescalings is chosen properly, this will ensure maintenance of the proper kinetic energy. τ may be chosen of a similar order as the molecular dynamics timestep, t_{MD} . However, true molecular kinetics are obviously disturbed by this thermostat. [58] Fortunately, in this case, the thermostat was only needed to fix the polymer's temperature, and analysis was done only of shape parameters, for which the preservation of exact kinetics is not important. Either way, its accuracy has been found sufficient for the purpose of this thesis. Alternatively, a Nosé-Hoover thermostat [58] should yield the same results while maintaining true kinetics. A test of this thermostat has been visualised in fig. 13.

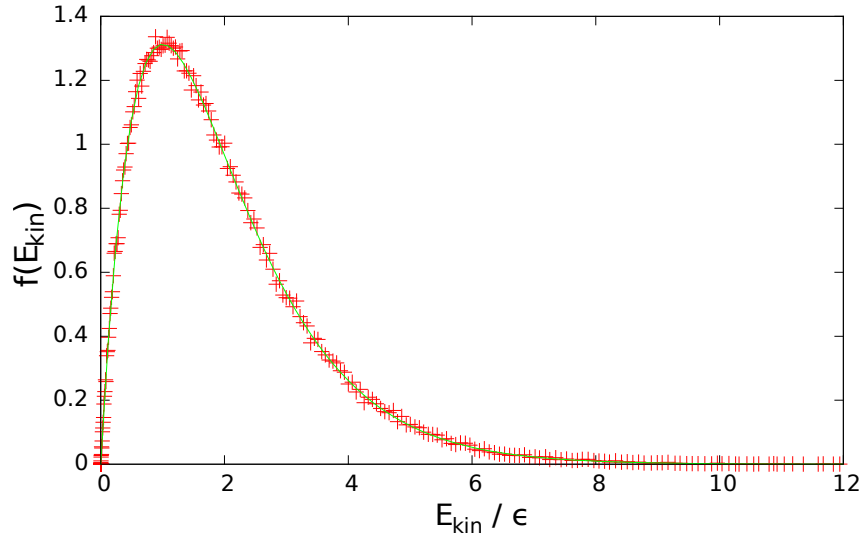


Figure 13: Kinetic energy distribution for polymer beads of mass $m_b = 5$. The green line is the analytic plot of eq. 45, fittingly adjusted to yield kinetic bead energy $E_{kin} = 0.5m_i\mathbf{v}_i^2$ according to eq. 46, while the red crosses represent simulation data.

The Andersen thermostat is replaced by a cell-level thermostat once the polymer is embedded into the MPCD solvent.

2.3.5 Embedding the Polymer in an MPCD Fluid

Embedding an object in an MPC dynamics-based solvent is rather straightforward. Most importantly, one needs to link MD integration with MPCD integration. Winkler explains

this approach thoroughly in [25]: Each monomer bead participates in the MPCD collision step (but not in the streaming step) as a particle of mass m_b of order $m_f \langle N_c \rangle$ (where m_f is the mass of a solvent particle) with dimensions zero, just like any solvent particle. Just like before, the center-of-mass velocity $\mathbf{v}_{cm}$ of some cubic grid cell can be calculated according to

$$\mathbf{v}_{cm} = \frac{\sum_{i=1}^{N_c^f} m_i^f \mathbf{v}_i^f + \sum_{i=1}^{N_c^b} m_i^b \mathbf{v}_i^b}{\sum_{i=1}^{N_c^f} m_i^f + \sum_{i=1}^{N_c^b} m_i^b}, \quad (47)$$

which results from the initial eq. 2 by splitting both sums into two and adding different labels to either contributions. All other steps of the MPCD Collision Step are applied to both solvent particles and polymer beads, although one has to be careful when applying a cell-level thermostat to consider both $N_c = N_c^f + N_c^b$ and $m_c = m_f N_c^f + m_b N_c^b$. For further discussion, please refer to section 2.5.2.

For the embedded object, the molecular dynamics step requires a significant amount of repetitions in between two MPCD collision steps to ensure all interaction potentials are considered properly despite fluctuations, so one demands $\Delta t_{MD} \ll \Delta t_{MPCD}$.

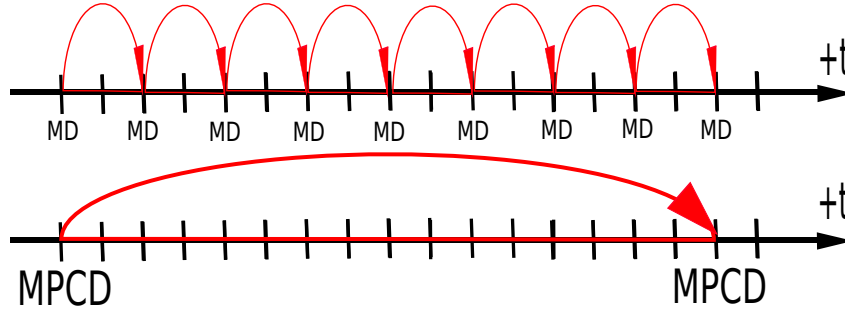


Figure 14: MD algorithm repeated 8 times, with $\Delta t_{MD} = 2$, whereas the MPCD algorithm takes place only once in the same time, with $\Delta t_{MPCD} = 16$.

2.4 Polymer Analysis

Because the main purpose of this thesis is the observation of dynamical modes and conformations of several topologies of polymers, much thought has been given to how to properly describe shape and orientation of polymers mathematically. The quantities presented in the following section will be extended by the quantities obtained from knot analysis in section 3.

2.4.1 Characteristic Quantities

Several quantities may be observed to determine polymer topology, conformation and general shape. Exclusively constant parameters characterising the polymer itself include the bead mass and the parameters of the interaction potentials, ϵ, σ, k and R_0 . These quantities may be adjusted to fit the individual needs of the simulation and account for a realistic model. For this thesis, quantities were chosen in accordance with the suggestion by Poier et. al. in [48] as stated explicitly in section 2.3.2. The bead mass m_b may be chosen freely, but is advisable to be of order $m_f N_c$ so that each bead is properly influenced by thermal fluctuations. On the choice of m_b should also depend the average bond length $\langle b \rangle$, which can be calculated from the interaction energy maximum (or, depending on frame, energy minimum) of the interaction potential and is directly dependent on the choice of the Lennard-Jones parameters ϵ and σ as well as k and R_0 . It should be noted that $\langle b \rangle$ should never be significantly smaller than the grid cell length a so that beads may only scarcely feel the proximity of other beads during the MPCD *Collision Step*.

A quite basic characteristic quantity whose average depends only on bead number N_b and solvent quality, described by the Flory exponent ν [55], is the radius of gyration R_g which is a measurement of size for the polymer, with

$$R_g^2 = \frac{1}{N_b} \sum_{i=1}^{N_b} (\mathbf{r}_i - \mathbf{r}_{cm})^2, \quad (48)$$

where $\mathbf{r}_{cm}$ is the chain's center of mass calculated by

$$\mathbf{r}_{cm} = \frac{\sum_{i=1}^N m_i \mathbf{r}_i}{\sum_{i=1}^N m_i}, \quad (49)$$

and, additionally,

$$\langle R_g \rangle \sim N^\nu, \quad (50)$$

in accordance with Rubinstein and Colby in [55], who offer a more detailed deduction and discussion of these quantities. Remember $\nu \approx 0.588$ for self-avoiding models and $\nu \approx 0.5$ for models without consideration of self-avoidance [55]. R_g , as can be seen from eq. (50), scales proportional to a power law and is therefore subject to minor fluctuations, but unfortunately not sensitive enough to measure and analyse changes in polymer shape.

Therefore, one may employ additional quantities which may be calculated from the so-called gyration tensor $\mathbb{M}$ in accordance with [44], where

$$\mathbb{M} = \frac{1}{N_b} \sum_{i=1}^{N_b} \mathbf{s}_i \otimes \mathbf{s}_i, \quad (51)$$

with $\otimes$ the dyadic product and $\mathbf{s}_i$ being the coordinate of bead i relative to the chain's center of mass. The gyration tensor $\mathbb{M}$ is derived in section 2.4.2, where it is proven to be identical to the covariance tensor $\text{cov}(X)$ for large enough N_b . Next, from the eigenvalues λ_i of $\mathbb{M}$ which are ordered such that $\lambda_1 \geq \lambda_2 \geq \lambda_3$, one may define invariants I_j :

$$I_1 = \lambda_1 + \lambda_2 + \lambda_3 \quad (52)$$

$$I_2 = \lambda_1 \lambda_2 + \lambda_2 \lambda_3 + \lambda_1 \lambda_3 \quad (53)$$

$$I_3 = \lambda_1 \lambda_2 \lambda_3 \quad (54)$$

Most conveniently, $I_1 = R_g^2$. From eigenvalues and invariants, the shape parameters can be defined:

$$\delta^* = 1 - 3 \left\langle \frac{I_2}{I_1^2} \right\rangle \quad (55)$$

$$S^* = \left\langle \frac{(3\lambda_1 - I_1)(3\lambda_2 - I_1)(3\lambda_3 - I_1)}{I_1^3} \right\rangle \quad (56)$$

$$b = \left\langle \lambda_1 - \frac{1}{2}(\lambda_2 + \lambda_3) \right\rangle \quad (57)$$

$$c = \langle \lambda_2 - \lambda_3 \rangle \quad (58)$$

where $\langle \dots \rangle$ denotes the average over all configurations. $\delta^* \in [0; 1]$ is called relative shape anisotropy, $S^* \in [-0.25; 2]$ is the prolateness, $b \geq 0$ is the asphericity and $c \geq 0$ the acylindricity. [44]

The polymer relaxation time τ_s has been described by Rubinstein and Colby in [55], and depends on solvent viscosity η_s and equilibrium radius of gyration R_g true to:

$$\tau_s \approx 0.163 \cdot \frac{\eta_s}{k_B T} \cdot R_g^3 \quad (59)$$

With this formula, one can then calculate the so-called Weissenberg number Wi originally introduced by White [67] and described in more detail by Dealy [17], which depends also on the applied shear rate $\dot{\gamma}$ (see section 2.5.1, equation (68)) by

$$Wi = \dot{\gamma} \cdot \tau_s, \quad (60)$$

and Wi is a measure for the shear impact on a given polymer.

Next, one may consider using the radial pair correlation function $g(|\mathbf{r}|)$ to analyse the polymer's conformation, which gives the probability of finding a particle at distance $|\mathbf{r}|$ from any other particle and is defined as

$$g(|\mathbf{r}|) = \frac{V}{N^2} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \delta(\mathbf{r} - \mathbf{r}_{ij}) \right\rangle. \quad (61)$$

$g(|\mathbf{r}|)$ may also be calculated from the structure factor $S(\mathbf{k})$ via a Fourier transform and thus, simulation results may directly be compared to experimental data.

Lastly, one may define the alignment angle χ between the gyration tensor's main axis and the shear flow direction according to [25]:

$$\tan(2\chi) = \frac{2\langle \mathbb{M}_{xz} \rangle}{\langle \mathbb{M}_{xx} \rangle - \langle \mathbb{M}_{zz} \rangle} \quad (62)$$

This formula, however, will cause a singularity for the Weissenberg number $Wi = 0$ and, therefore, no shear present. Thus, also calculated from the gyration tensor, one defines the deformation resistance m_G which prevents any singularities from occurring (although for

$Wi = 0$, the alignment angle is not uniquely resolved, and neither is m_G). But for linear shear flow along the x-axis and gradient along the z-axis, one may define uniquely

$$m_G = Wi \tan(2\chi) \quad (63)$$

as a final characteristic shape parameter.

2.4.2 Principal Component Analysis

While shape parameters certainly provide interesting information on polymer topology, for this thesis' aim of studying knots on polymers, a more direct method of expressing the position of the knot relative to the polymer's center of mass and its orientational axis was desirable. Expressing the relative knot position, $\hat{\mathbf{n}}_K$, to the polymer's center of mass is trivial:

$$\hat{\mathbf{n}}_K = \frac{\mathbf{r}_K^{cm} - \mathbf{r}_P^{cm}}{|\mathbf{r}_K^{cm} - \mathbf{r}_P^{cm}|}, \quad (64)$$

where $\mathbf{r}_K^{cm}$ is the center of mass of all beads part of the knot, and $\mathbf{r}_P^{cm}$ is the center of mass of the polymer itself. However, calculating the orientational axis of a polymer in $\mathbb{R}^3$ is not at all trivial and requires further theoretical knowledge. While a simple regression would suffice in $\mathbb{R}^2$, for $\mathbb{R}^3$, regression only yields the equation of a plane instead of an axis, and this is expected to become a problem for ring polymers under shear, which usually stretch, with all beads tending to rest in approximately the same plane. This would result in $\hat{\mathbf{n}}_K$ being almost perpendicular to $\hat{\mathbf{n}}_P$ most of the time. Therefore, a different approach is needed and provided by Principal Component Analysis (PCA) and one of its results is, for large enough N , the gyration tensor $\mathbb{M}$.

An excellent explanation of PCA is given by Smith (2002) [59]. Principal Component Analysis always yields d axes, with d being the number of variables to which PCA is applied. In $\mathbb{R}^3$, this of course means $d = 3$. However, for finding the main orientational axis of a set of coordinates (in this case, of polymer beads), calculating the first axis (first principal component) is perfectly sufficient. The first principal component may be interpreted of the slope of a line passing through the beads' center of mass, with the slope being chosen such that the sum of quadratic distances from this line is minimal for the given set of beads.

First, one needs to define variance $\text{var}(x)$ and covariance $\text{cov}(x, y)$ of a set of N points in $\mathbb{R}^3$ with components (x, y, z) :

$$\text{var}(x) = \frac{1}{N-1} \cdot \sum_{i=1}^N (x_i - \bar{x}) (x_i - \bar{x}) \quad (65)$$

$$\text{cov}(x, y) = \frac{1}{N-1} \cdot \sum_{i=1}^N (x_i - \bar{x}) (y_i - \bar{y}) \quad (66)$$

While the variance expresses how much one coordinate's values stray from its mean, the covariance expresses how much two coordinate's stray from their mean with respect to each other. It is also easy to see that $\text{cov}(x, y) = \text{cov}(y, x)$. One may define the covariance matrix $C(X)$ for a set of points X in $d = n$ as follows:

$$C_{ij}(X) = \text{cov}(X_i, X_j) \quad (67)$$

Comparing this equation with eq. 51 shows great similarity up to the prefactor. However, since for large N it holds true that $1/(N-1) \approx 1/N$, the gyration tensor $\mathbb{M}$ is given by the covariance matrix in this limit. Therefore, for a set of points X in $\mathbb{R}^3$, the PCA procedure can be outlined as follows:

1. Calculate the covariance matrix $C(X)$.
2. Compute the eigenvectors and eigenvalues of $C(X)$.
3. The set of eigenvectors $\{\hat{e}\}$, sorted by their eigenvalues $\{v_e\}$ in descending order, give the principal components in descending order.

Computing the eigenvectors and eigenvalues of a matrix is a simple enough task for most scientific computing programs. For this thesis, the Eigen library for C++ [19] was chosen for familiarity.

2.4.3 Simulation Testing

To check whether the code written for this thesis was accurate, the shape parameters given by the gyration tensor have been compared for linear polymer chains both embedded in an MPCD solvent (cell-level thermostat, green) and free (Andersen thermostat, blue) at equilibrium, depicted in figures 15 - 20. Simulations have been carried out at $T = 1$ and $m_b = 5$. Scaling time for the Andersen thermostat was set to $\tau = 0.1 \cdot \Delta t_{MPCD}$. The MPCD fluid was simulated at $a = 1$, $L = 50$ and $m_s = 1$. Possible inaccuracies might have arisen from relatively short simulations and the implementation of the Andersen thermostat, but also from the generally short chains. The Flory exponent ν could have been computed much more accurately for longer chains.

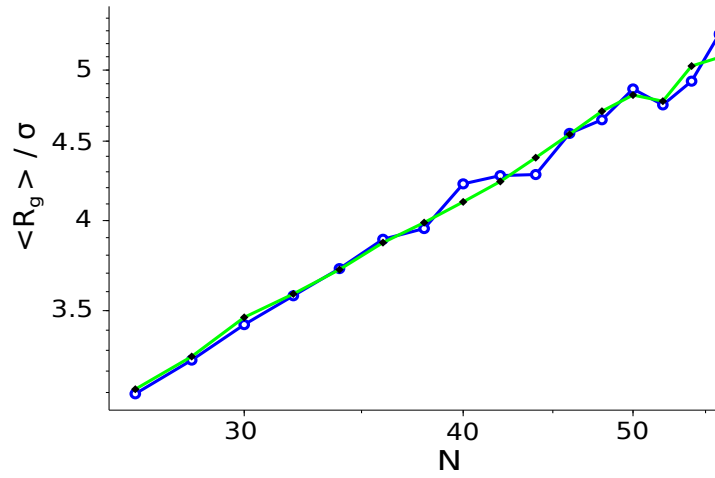


Figure 15: Gyration radii R_g as a function of chain length N , visualised in a double-logarithmic plot to stress scaling behaviour. The Flory exponent ν was calculated to be 0.652 for the free polymer chains (blue, empty circles), and 0.641 for the MPCD-embedded polymer chains (green, black squares).

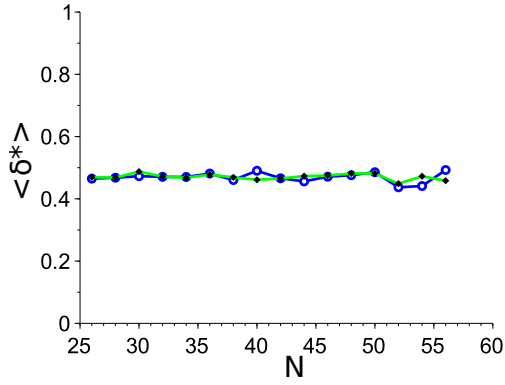
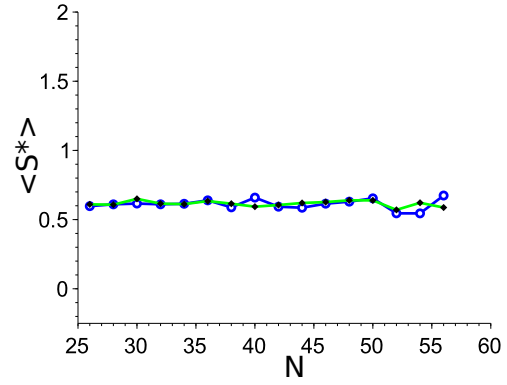
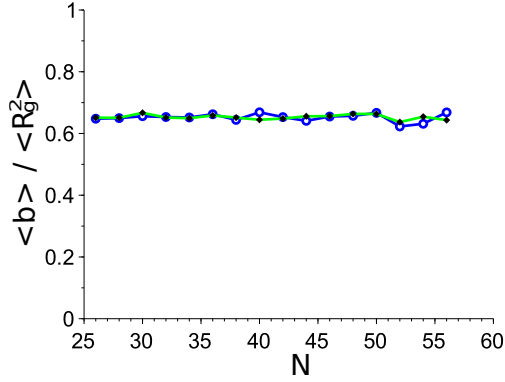
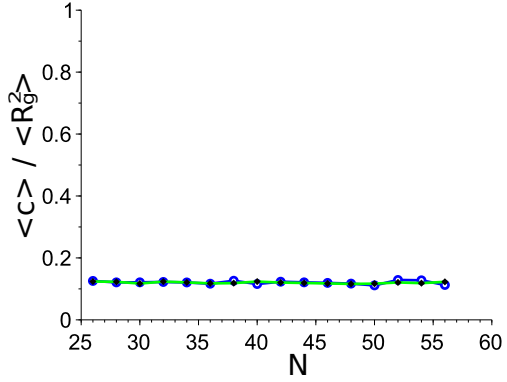
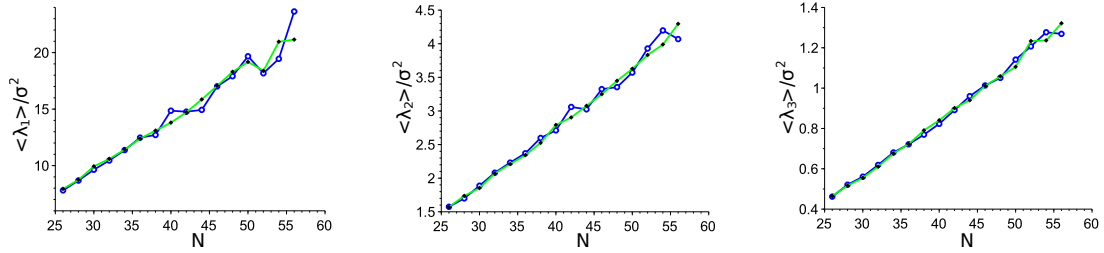

 Figure 16: Anisotropy $\delta^*(N) \in [0.0; 1.0]$.

 Figure 17: Prolateness $S^*(N) \in [-0.25; 2.0]$.

 Figure 18: Asphericity $b(N) \geq 0.0$.

 Figure 19: Acylindricity $c(N) \geq 0.0$.


Figure 20: Gyration tensor eigenvalues as a function of chain length, in descending order from left to right.

2.5 Non-Equilibrium Simulations

For this thesis, a shear was applied to an MPCD solvent. Therefore, periodic boundary conditions would no longer have accurately represented the system and Lees-Edwards

Boundary Conditions are employed instead. To prevent viscous heating of the local system, a cell-level thermostat is applied during the collision step.

2.5.1 Lees-Edwards Boundary Conditions

Lees-Edwards Boundary Conditions, introduced by Lees and Edwards (1972) [31], may be used to properly simulate shear flow in a system without abandoning the minimum image convention. They are visualised in fig. 21, with their basic idea being the introduction of layers of periodic box images. If the gradient is applied along the z-axis and the flow is linear in x-direction, with $\dot{\gamma}$ the shear rate, then one may write

$$\dot{\gamma} = \frac{u_x}{L}, \quad (68)$$

in which u_x is the average velocity of a layer at $z = L$. This relation also holds true if one calls L the length of the simulation box. For any added layer of periodic images, u_x is hence increased (or reduced, depending in which direction the layer is added) by $\dot{\gamma}L$. Therefore, the velocity of a particle leaving the simulation box in positive z-direction must be adjusted accordingly while remapping the particle into the simulation box. Lees-Edwards boundary conditions account for this $\mathbf{r}_z$ dependency of particle velocity by taking the movement of periodic box image layers relative to the simulation box into account. Each time step Δt_{MPCD} , the layer above moves $u_x \cdot \Delta t_{MPCD}$ along the x-axis, the layer below $-u_x \cdot \Delta t_{MPCD}$. Therefore, one may write the Lees-Edwards boundary conditions for a box centered at coordinate system origin as suggested by Allen and Tildesley (1987) [4] as

$$\mathbf{r}_{new} = \begin{pmatrix} \mathbf{r}_x - L_x \cdot \mathbf{round} :: \left(\frac{\mathbf{r}_x}{L_x} \right) - \delta_x \cdot \mathbf{round} :: \left(\frac{\mathbf{r}_z}{L_z} \right) \\ \mathbf{r}_y - L_y \cdot \mathbf{round} :: \left(\frac{\mathbf{r}_y}{L_y} \right) \\ \mathbf{r}_z - L_z \cdot \mathbf{round} :: \left(\frac{\mathbf{r}_z}{L_z} \right) \end{pmatrix} \quad (69)$$

where δ_x is the current displacement of the upper layer relative to the simulation box along the x-axis, with $\delta_x \in [-L/2; +L/2]$, and

$$\mathbf{v}_{new} = \begin{pmatrix} \mathbf{v}_x - u_x \cdot \mathbf{round} :: \left(\frac{\mathbf{r}_z}{L_z} \right) \\ \mathbf{v}_y \\ \mathbf{v}_z \end{pmatrix} \quad (70)$$

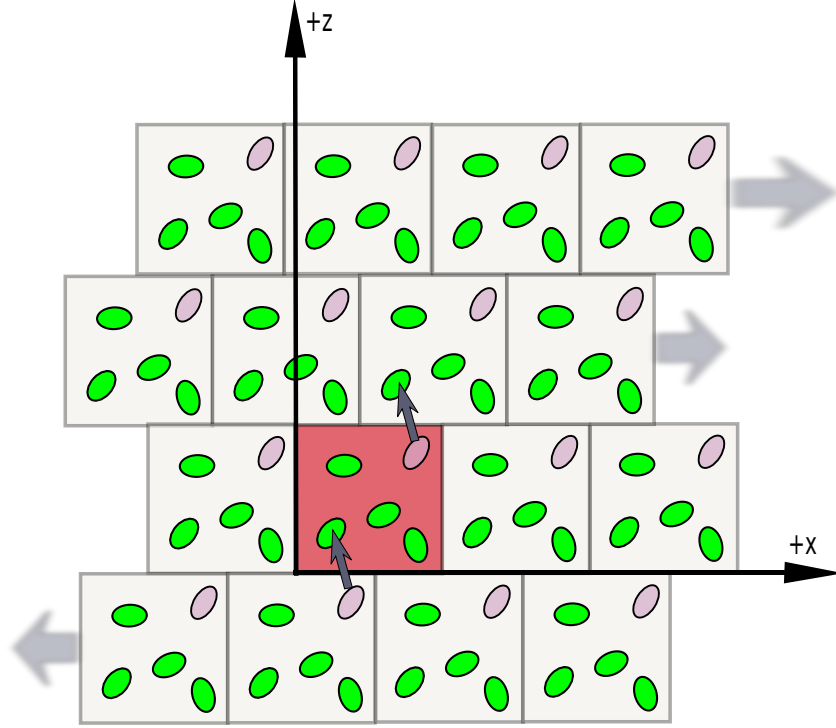


Figure 21: Lees-Edwards boundary conditions in a 2D system with shear flow in x -direction and the velocity gradient applied along the z -axis. The coloured box is the simulation box, resting in the static layer. Figure done in Inkscape [12], originally inspired by [4].

These equations may be adapted easily to reflect a different position of the simulation box, for example to adequately consider a simulation box centered at $(L/2, L/2, L/2)$, with the lower corner situated at the coordinate origin $(0, 0, 0)$. Similarly, one may modify the Lees-Edwards boundary conditions to consider the simulation box moving around a grid of shifting layers as would originally be assumed by Lees-Edwards boundary conditions. This is especially useful when linked to the MPCD algorithm, where a grid shift is employed before each collision step. It is even more important when embedding a moving polymer in the MPCD solvent, where it has proven beneficial both memory- and runtime-wise to center the simulation box around the polymer's center of mass $\mathbf{r}_{cm}$, shifted by a random vector in accordance with Winkler [25].

In such a scenario, where $\mathbf{L}_d$ is the position vector of the lower corner of the simulation box and $\mathbf{L}_u$ the diagonally opposite upper corner, and $\mathbf{L}_d^o = (0, 0, 0)$ for the equally sized static box defining the position of any periodic box images considered by Lees-Edwards boundary conditions, one may write

$$\mathbf{r}_{new} = \begin{pmatrix} \mathbf{r}_x - \left[\delta_x \cdot \mathbf{floor} :: \left(\frac{\mathbf{r}_z - \mathbf{L}_{d,z}}{L_z} \right) \right] \div L_z \\ \mathbf{r}_y - L_y \cdot \mathbf{floor} :: \left(\frac{\mathbf{r}_y - \mathbf{L}_{d,y}}{L_y} \right) \\ \mathbf{r}_z - L_z \cdot \mathbf{floor} :: \left(\frac{\mathbf{r}_z - \mathbf{L}_{d,z}}{L_z} \right) \end{pmatrix} \quad (71)$$

where $a \div b$ denotes a modulo operation of a modulo b . Furthermore,

$$\mathbf{v}_{new} = \begin{pmatrix} \mathbf{v}_x - u_x \cdot \mathbf{floor} :: \left(\frac{\mathbf{r}_z - \mathbf{L}_{d,z}}{L_z} \right) \\ \mathbf{v}_y \\ \mathbf{v}_z \end{pmatrix} \quad (72)$$

Afterwards, an additional correction must be applied to the position vector:

$$\mathbf{r}_{final} = \begin{pmatrix} \mathbf{r}_{new,x} - L_x \cdot \mathbf{floor} :: \left(\frac{\mathbf{r}_{new,x} - \mathbf{L}_{d,x}}{L_x} \right) \\ \mathbf{r}_{new,y} \\ \mathbf{r}_{new,z} \end{pmatrix} \quad (73)$$

This ensures a time- and memory-efficient handling of Lees-Edwards boundary conditions while storing only relevant solvent particle coordinates directly around the simulated polymer. For computation of any velocity-dependent quantities such as the velocity profile within the simulation box, it shall be advised to calculate and store the center-of-mass velocity $\mathbf{v}_{cm}$ of the entire simulation box, which can also be computed analytically via

$$\mathbf{v}_{cm} = \begin{pmatrix} u_x \left(\frac{\mathbf{L}_{d,z}}{L_z} \right) \\ 0 \\ 0 \end{pmatrix} \quad (74)$$

in any case where the velocity profile has its root at the center $(L/2, L/2, L/2)$ of the static simulation box with $\mathbf{L}_d^o = (0, 0, 0)$.

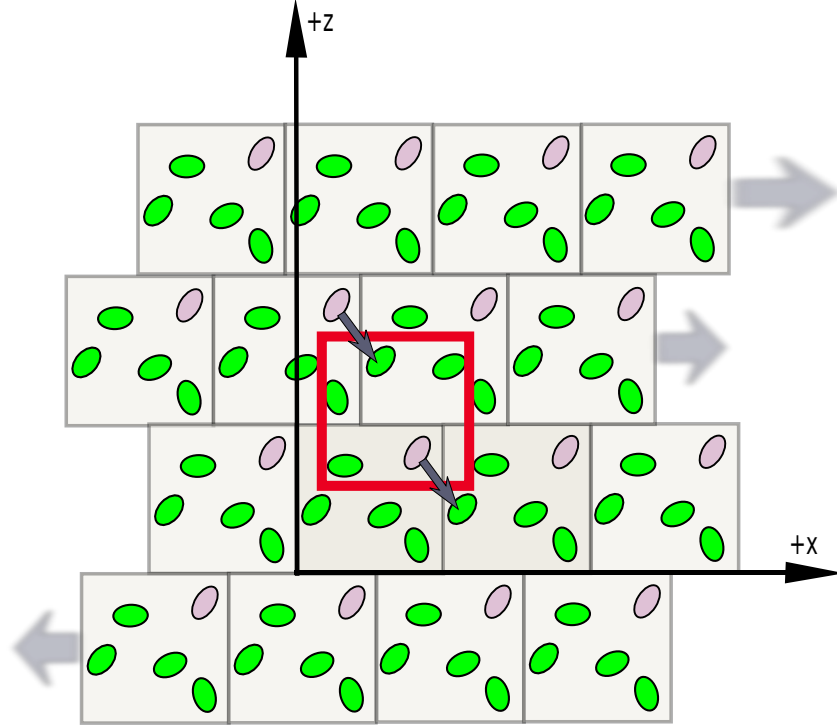


Figure 22: Modified Lees-Edwards boundary conditions in a 2D system with shear flow in x-direction and the velocity gradient applied along the z-axis. The box framed in red is the simulation box, but is not static. Figure done in Inkscape [12].

2.5.2 Cell-Level Thermostating

In shear flow simulations, energy is added constantly to the system, either by boundary conditions (as was the case in this thesis) or by a directly applied external force. One needs to apply a thermostat to control this so-called viscous heating and to ensure the desired strength and "shape" of the solvent's velocity gradient is maintained throughout the simulation and in the long run. The thermostat that was employed for this thesis worked on a cell-level basis. To understand the concept, one may consider the definition of what may be called "local temperature" or "relative kinetic energy". Because the contents of any layer of grid cells are supposed to be moving at some velocity fairly consistent throughout the same layer, one may take an individual particle i 's velocity relative to its grid cells center-of-mass velocity $\mathbf{v}_{cm}$ as a defining value for that particle's relative kinetic energy by

$$E_i^{kin,rel} = \frac{1}{2} m_i (\Delta \mathbf{v}_i)^2, \quad (75)$$

with the expectational value

$$\langle E^{kin,rel} \rangle = \frac{3}{2} N k_B T, \quad (76)$$

N being any number of particles included in the sum over relative kinetic energies, in accordance with the virial formula thoroughly discussed by Grimus (2010) [24]. The cell-level thermostat which can enforce this conservation of relative kinetic energy (and, therefore, local temperature) in the MPCD solvent must be applied during the collision step to the relative velocities $\Delta \mathbf{v}_i$. There have been several approaches to thermostating an MPCD fluid. For this thesis, the more sophisticated approach of Winkler [25] has been chosen because of its convenient canonical nature and efficiency due to directly scaling particle velocities. For this thermostat, a scaling factor κ is calculated for each grid cell and then applied to the relative particle velocities $\Delta \mathbf{v}_i$ before or after the rotation. In a homogeneous system, the computation of a single global scaling factor would be sufficient, however, that is not the case for inhomogeneous systems such as shear flow. One may calculate the cell-level scaling factor κ according to

$$\kappa = \left(\frac{2E_{kin}}{\sum_{i=1}^{N_c} m_i \Delta \mathbf{v}_i^2} \right)^{\frac{1}{2}}, \quad (77)$$

where N_c is the number of particles in that grid cell and E_{kin} is chosen from a Gamma distribution defined by

$$P(E_{kin}) = \frac{1}{E_{kin} \Gamma(f/2)} \left(\frac{E_{kin}}{k_B T} \right)^{f/2} \exp \left(-\frac{E_{kin}}{k_B T} \right), \quad (78)$$

with $f = 3(N_c - 1)$ being the degrees of freedom of the considered cell and $\Gamma(x)$ the gamma function. [25, p. 422f]

One may then consider the polymer's kinetic energy once embedded into the solvent. It was found that the polymer's relative kinetic energy will also oscillate around the desired value if no thermostat is applied to the polymer itself, but only through its interactions with the thermostated solvent during the collision step. However, in this case, a violation of the conservation of the solvent's center-of-mass velocity $\mathbf{v}_{cm}$ has occurred, resulting in a shift of the linear velocity gradient within the simulation box. This can be fixed quickly by also applying the cell-level scaling factor to each polymer bead's relative velocity

$\Delta \mathbf{v}_i$ before or after the rotation during the collision step. A direct comparison between simulations carried out with a non-thermostated and a thermostated embedded polymer, respectively, in a system subjected to shear flow is presented in figures 23 to 28 for a polymer ring with $N = 100$ beads in a solvent of $\langle N_c \rangle = 5$ and of dimensions $(50 \times 50 \times 50)$, with cell length $a = 1$, $k_B T = 1$ and $u_x = 1$, after $t = 50000 \Delta t_{MPCD}$.

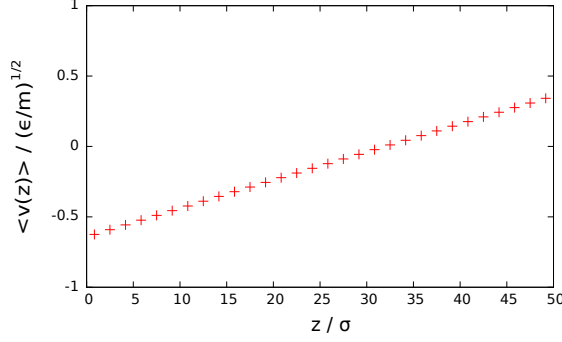


Figure 23: $\langle v(z) \rangle$ in dependency of z . Velocity profile along z -axis of a non-thermostated polymer. Shift is clearly visible and non-negligible.

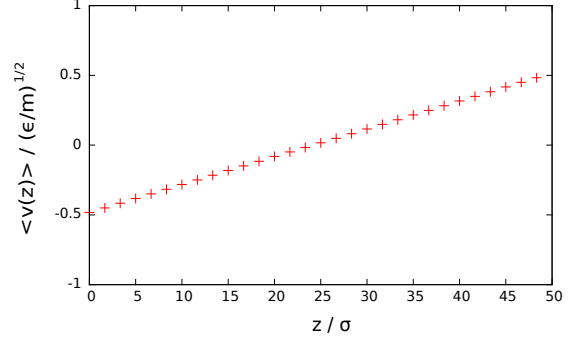


Figure 24: $\langle v(z) \rangle$ in dependency of z . Velocity profile along z -axis of a thermostated polymer ring. No gradient shift visible - the profile is perfectly symmetric and agrees with the predictions of Lees-Edwards boundary conditions.

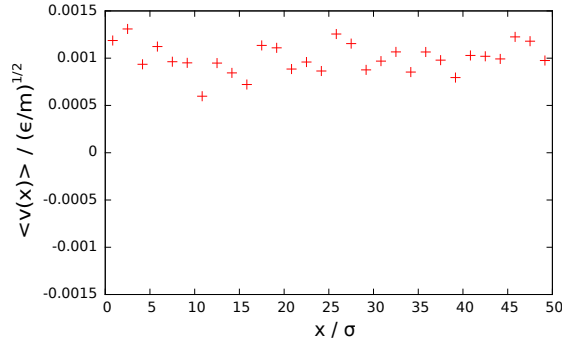


Figure 25: $\langle v(x) \rangle$ in dependency of x . Velocity profile along x -axis of a non-thermostated polymer ring. Average velocity does not converge towards zero.

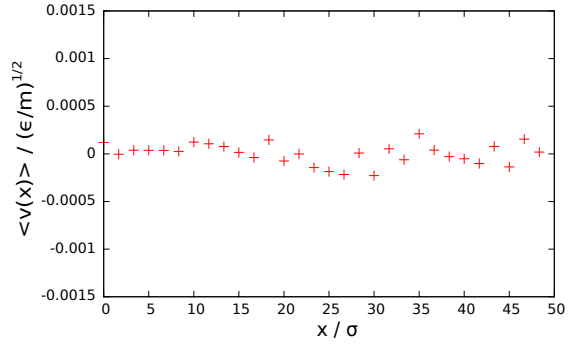


Figure 26: $\langle v(x) \rangle$ in dependency of x . Velocity profile along x -axis of a thermostated polymer ring. Average velocity converges towards zero for sufficiently long runtime.

Fig. 29 depicts the cell-level thermostat applied to the MPCD solvent, and a comparison of the cell-level thermostat (for the MPCD-embedded polymer) to the Andersen thermostat (for the free polymer) for a system at equilibrium can be found in figure 30.

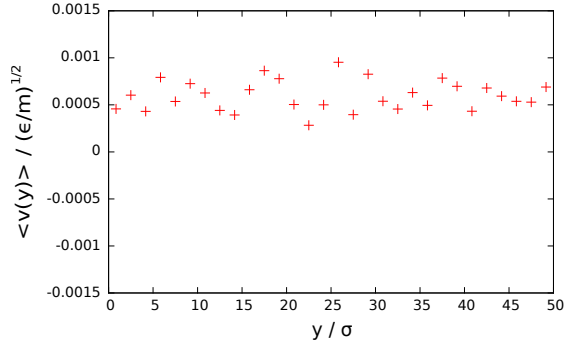


Figure 27: $\langle v(y) \rangle$ in dependency of y . Velocity profile along y -axis of a non-thermostated polymer ring. Average velocity does not converge towards zero.

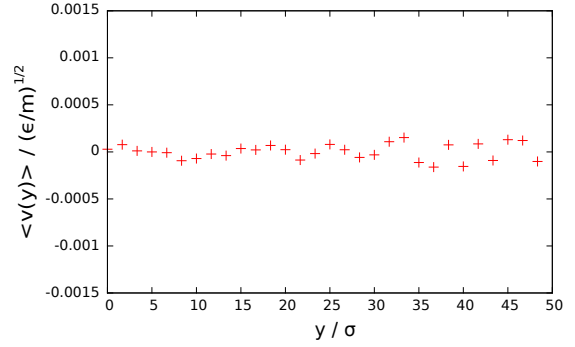


Figure 28: $\langle v(y) \rangle$ in dependency of y . Velocity profile along y -axis of a thermostated polymer ring. Average velocity converges towards zero for sufficiently long runtime.

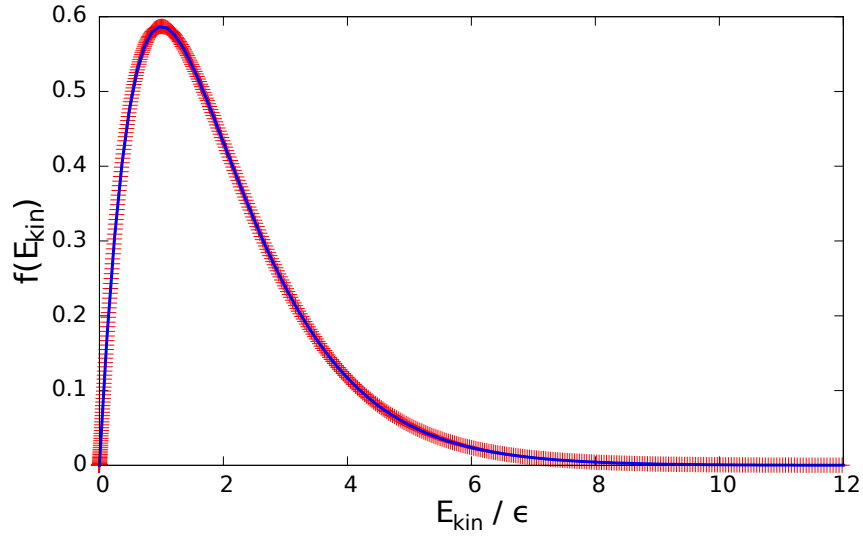


Figure 29: Kinetic energy distribution for solvent particles of mass $m_s = 1$, obtained from an MPCD simulation at equilibrium and $T = 1$ (red pluses). The blue line is the analytic plot of eq. (45), fittingly adjusted to yield kinetic particle energy $E_{kin} = 0.5m_i\mathbf{v}_i^2$ according to eq. (46).

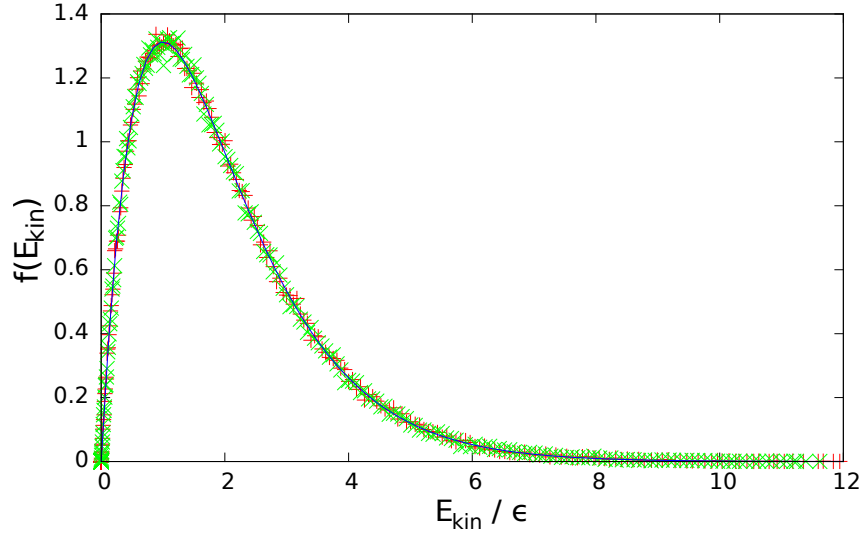


Figure 30: Kinetic energy distribution for polymer beads of mass $m_b = 5$, obtained from an MPCD simulation at equilibrium and $T = 1$ (green crosses), but also from an equilibrium MD simulation governed by the Andersen thermostat for beads of mass $m_b = 5$ and $T = 1$ (red pluses). The blue line is the analytic plot of eq. (45), fittingly adjusted to yield kinetic bead energy $E_{kin} = 0.5m_i\mathbf{v}_i^2$ according to eq. (46).

2.5.3 Tumbling and Tank-Treading

Polymer chains and rings under shear have been studied recently but extensively, and it is known that they both exhibit a curious behaviour [64] [8]: Both tend to perform tumbling (TB), a motion where both "ends" switch place (thinking of the ring polymer as a shear-stretched object with clearly identifiable ends and a unique orientation), and, exclusively seen for rings, tank-treading (TT), a motion where individual beads keep circulating around the ring's center of mass. Tumbling is caused by random movements causing either the "dragged" end to rise "above" the other end along gradient direction, or the "leading" end to sink "below" the other end along gradient direction, where it is either way accelerated and then causes the polymer to first collapse and then to spin 180° relative to its previous orientation. Tank-treading, on the other hand, is caused by larger segments of the polymer rising along the gradient direction and thus gaining higher velocity compared to other segments of the ring. This causes the ring to perform a spinning motion, clockwise or counter-clockwise, depending on shear orientation. Both motions occur more frequently under strong shears and for shorter chains [8].

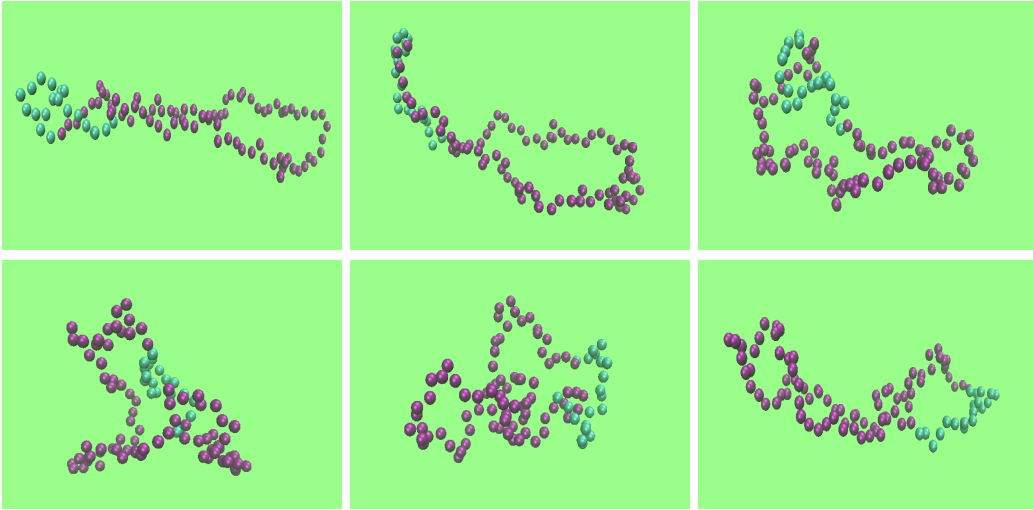


Figure 31: From left to right, top to bottom: A full tumbling (TB) cycle on a 100-bead ring under shear. The brightly-colored section of the ring changes from one side of the ring to the other while the whole polymer ring first collapses and then expands again.

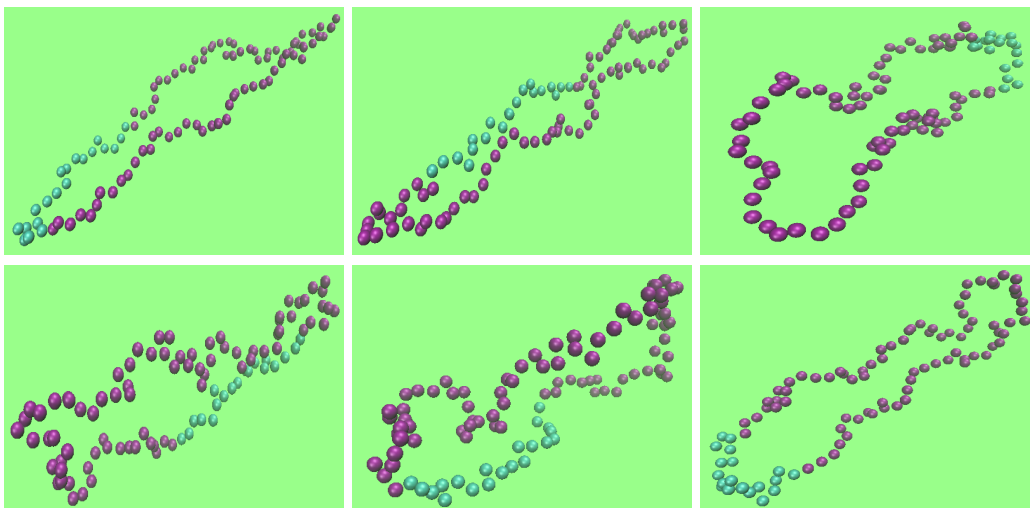


Figure 32: From left to right, top to bottom: A full tank-treading (TT) cycle on a 100-bead ring under shear. The brightly-colored section of the ring performs a full 360° circular motion around the ring's center of mass, without the ring collapsing.

3 Knot Analysis

This thesis aims to observe and analyse the behaviour of knotted polymers in shear flow. Therefore, a proper definition of the object "knot" is needed, as well as some tool of determining knot type and shape, as well as knot position. The branch of Knot Theory provided the insight needed to complete this thesis and shall be introduced briefly in the following sections.

3.1 Mathematical Knots

Most people, even outside the fields of physics, should be familiar with the more simple knots encountered in day-to-day life, such as the overhand knot (fig. 33) and the figure-eight knot (fig. 34). These are prime examples for two different physical knots, meaning one cannot be transformed into the other without untying and retying. [16] Angle of observation and thoroughness do not change the fact that both knots are different from each other, although one may clearly perceive both as "knots" in the common sense of the word. Also, failure to twist one knot onto another is no mathematical proof that both knots are not, in fact, the same.

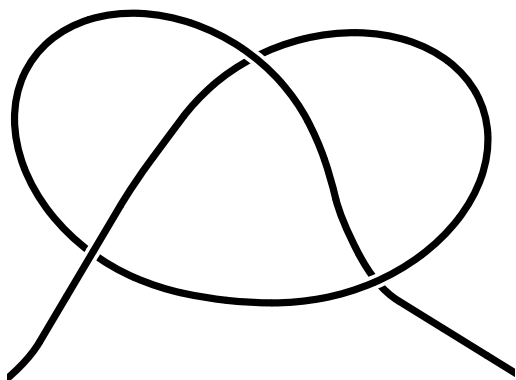


Figure 33: Overhand knot.

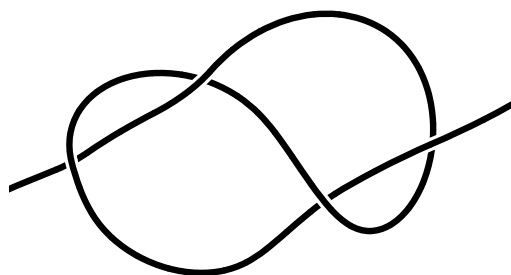


Figure 34: Figure-Eight knot.

Therefore, a mathematical definition of a knot is needed, and also, in this context, a mathematical definition of under which circumstances two knots could be considered identical. First, one needs to eliminate the possibility of untying a knot by that definition itself, otherwise, all mathematical knots would be identical in the sense that they could be easily transformed into one another by some set of transformations in $\mathbb{R}^3$. Basically,

one aims at getting rid of any ends which could be tied by merging two endings together, those closing a shape. A proper formal definition is given by Crowell and Fox: " K is a *knot* if there exists a homeomorphism of the unit circle C into three-dimensional space $\mathbb{R}^3$ whose image is K . By the circle C is meant the set of points (x, y) in the plane $\mathbb{R}^2$ which satisfy the equation $x^2 + y^2 = 1$." [16] A similarly formal definition may define whether two knots K_1 and K_2 are equivalent. Note that being equivalent does not follow from being homeomorphic, since two knots K_1 and K_2 are always automatically homeomorphisms to the unit circle and therefore to one another. The property of being knotted correlates to how a string is embedded in $\mathbb{R}^3$, and is therefore a matter of three-dimensional rather than one-dimensional topology. Crowell and Fox state: "Knots K_1 and K_2 are *equivalent* if there exists a homeomorphism of $\mathbb{R}^3$ onto itself which maps K_1 onto K_2 ." [16] Equivalent knots belong to the same *type*, an equivalence class of knots constitutes a *knot type*. Because the overhand knot and the figure-eight knot are different from one another, one may say they belong to different knot types.

Further distinction can be made by use of the attributes *tame* and *wild*, where a *tame knot* is one that has a polygonal equivalent knot. A polygonal knot consists of *edges* and *vertices*. As long as a knot is continuously differentiable, it is tame, and if this does not apply, then the knot is called *wild*. [16] Knot theory is usually not concerned with wild knots, and neither is this thesis, so for all intents and purposes, everything that follows may be true only for tame knots, especially the Jones polynomial introduced in section 3.2.

One may organise knot types by their characteristic minimal number of intersections visible to the observer. No matter how much one twists and bends a tame knot, this number will always remain the same. Such an approach has been chosen by Conway (1969) [15] after a table by Alexander and Briggs (1926-27) [3]. Said table has been visualised by and named after Rolfsen (2003) [54]. In its mathematically accurate form, the overhand knot, for example, is often referred to as trefoil knot and is also called the 3_1 knot, while the figure-eight knot is referred to as the 4_1 knot.

Figures 33 to 38 have been created with KnotPlot [57], which conveniently also offers to print bead configurations for further use.

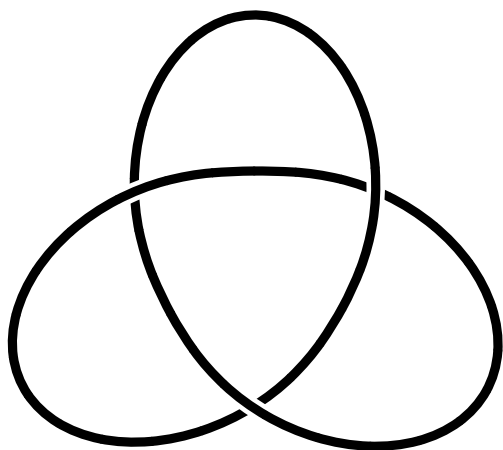


Figure 35: The 3_1 or trefoil knot.

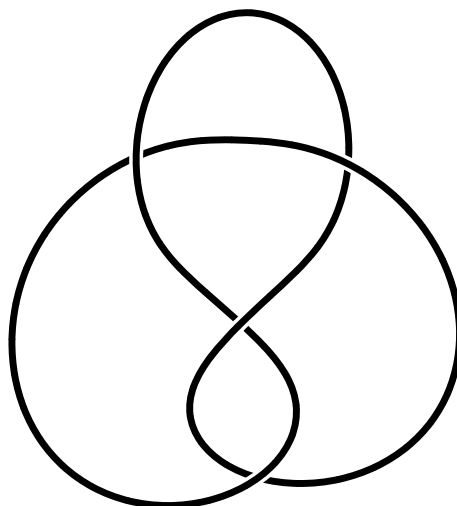


Figure 36: The 4_1 knot.

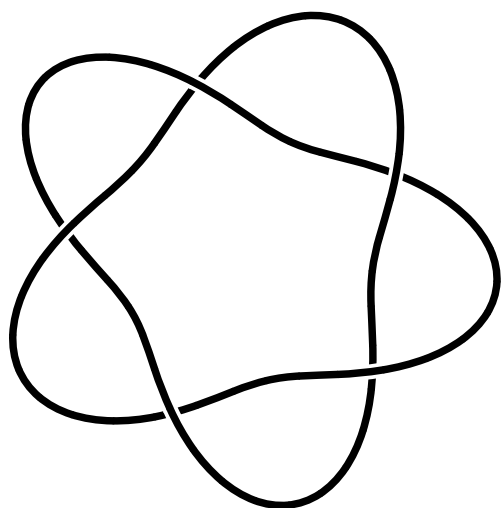


Figure 37: The 5_1 knot.

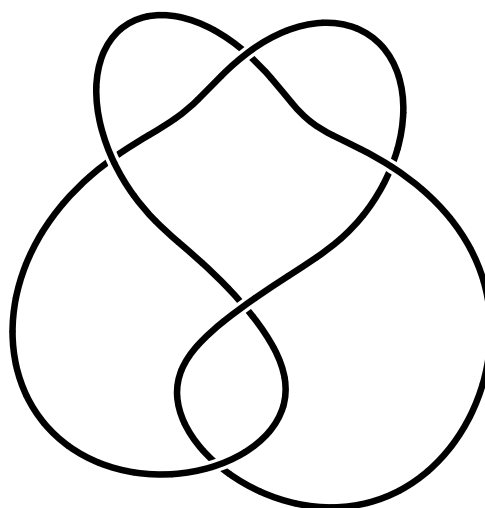


Figure 38: The 5_2 knot.

3.2 The Long Route to Knot Invariants

The Jones Polynomial is only one of several other numerical means to uniquely find the knot type of a set of connected points (x, y, z) in $\mathbb{R}^3$. Not only can the polynomial be employed to determine the knot type of a certain configuration, but it may also be used to determine the position of a knot on an object in $\mathbb{R}^3$. Subsequently disregarding segments of the object and closing newly generated open ends at a far distance from the observed object (ideally but numerically impossible at infinite distance to ensure the remaining parts of the object are in no way penetrated by the closing line) will yield the same

Jones polynomial until the same test is run from inside the knot, resulting in the Jones polynomial of a configuration with fewer cross-sections and thereby providing a possible means to determine whether a bead is part of a knot, and also providing additional information on the position and tightness of said knot.

A few additional definitions are needed to understand the calculation of the Jones Polynomial as a knot invariant. An excellent introduction is provided by The Knot Book by Colin C. Adams [1], which shall be recounted here.

3.2.1 Knot Diagram and Reidemeister Moves

First, any given knot may be turned into a 2-dimensional *knot diagram*, which is done most simply by abandoning one of the three coordinates of any beads given on the knot. The resulting figure is a projection onto a plane, and one may observe a number of crossings in that projection, the number of which may or may not be representative of the type of knot. Each crossing needs to be indexed properly, with the upper branch being marked as such. Additionally, each crossing has to be uniquely assigned to no more than two branches.

Secondly, one defines the so-called Reidemeister moves in accordance with [33]. Reidemeister moves are actions which one may perform on crossings on a knot without altering the type of said knot. There are three such actions, and all of them can be used to simplify a knot diagram until all remaining crossings are vital for the identity of the given knot. These three moves are depicted in figures 39 to 41.

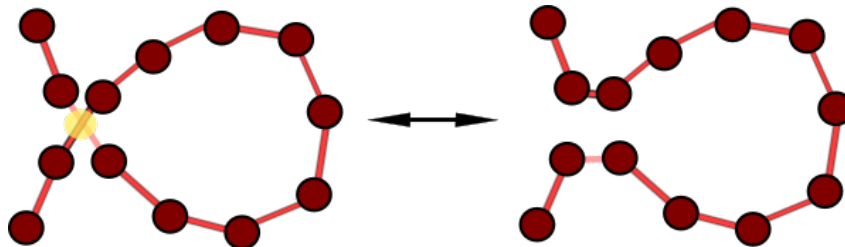


Figure 39: Reidemeister-I move performed on a bead-model polymer. The yellow-marked crossing is reduced to no crossings and vice-versa. This move is the equivalent of twisting a loop once by 180° with fixed ends.

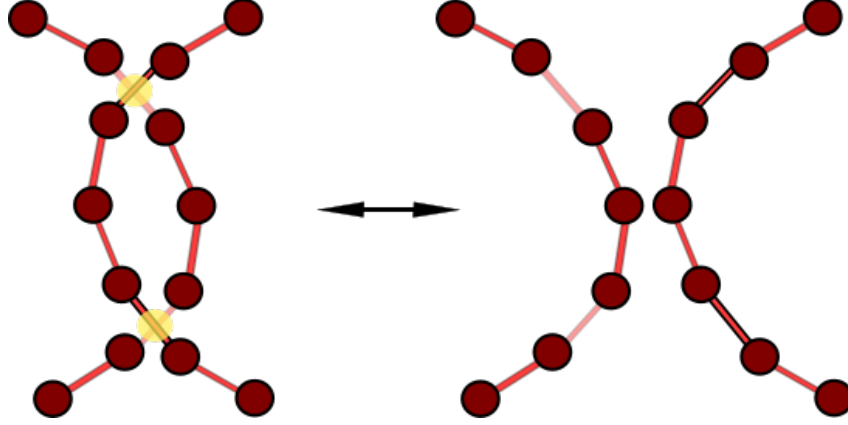


Figure 40: Reidemeister-II move performed on a bead-model polymer. The yellow-marked crossings originate from overlapping branches, the right branch being above the left branch in this picture. Crossings are reduced by separating both branches.

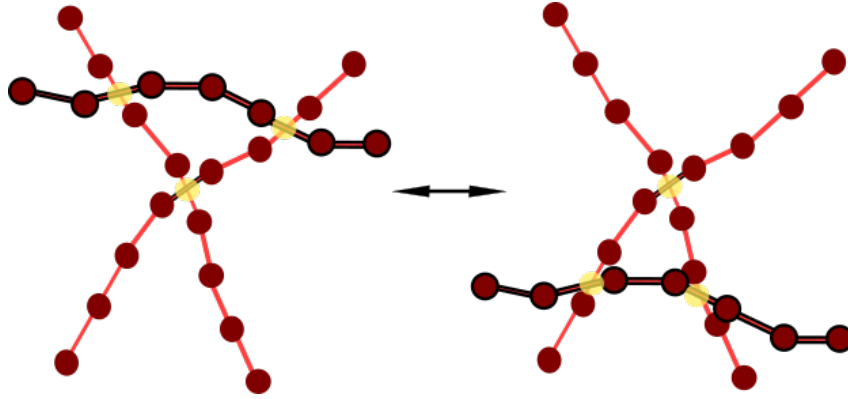


Figure 41: Reidemeister-III move performed on a bead-model polymer. The two yellow-marked crossings belonging to overpasses on the same branch switch locations. This is done by shifting the branch (overpassing) to the other side of a third crossing (below).

3.2.2 Bracket Polynomial

Next, one may define the bracket polynomial $\langle L \rangle$ of a structure L as follows:

1. $\langle \bigcirc \rangle = 1$
 2. $\langle \times \rangle = A \cdot \langle \rangle + B \cdot \langle \rangle$
 3. $\langle L \cup \bigcirc \rangle = C \cdot \langle L \rangle$
- (79)

Here, A , B and C are fittingly chosen constants. An example for such a choice is given in section 3.2.4. From eq. (79), one may derive a polynomial for any given knot diagram

by reducing crossings and thereby gaining simpler configurations, until all that is left are a series of unknots. Each attempt to reduce a crossing should result in a structure with less crossings, otherwise, the move should be reversed. Constants B and C are chosen such that Reidemeister-II and -III moves do not change the polynomial. The Bracket polynomial is, however, not invariant under the Reidemeister-I move and is therefore no knot invariant. Nonetheless, from it, one may calculate different polynomials which indeed may serve as knot invariants, such as the Alexander polynomial or the Jones polynomial.

3.2.3 Writhe

Next, one considers the *writhe* of a knot diagram [2]. In a crossing of two branches in a knot diagram, the branch closer to the viewer is called the overpass, the one more distant to the viewer is called the underpass. A starting point on the knot diagram is chosen freely, as well as a traverse direction for the diagram. One may count, by convention, a crossing as $+1$ if the orientated overpass can be rotated counter-clockwise by an angle between 0 and π to align it with the orientated underpass (right-handed intersection, L_+), and as -1 if this rotation needs to be clockwise (left-handed intersection, L_-). The Tait or directional writhing number $D\omega$ is the sum over all intersections' contributions, and depends on the plane on which the knot was projected. If the normal vector to this plane is called $\hat{\mathbf{z}}$, one defines the writhe Wr as the average directional writhing number as follows:

$$\omega = \frac{1}{4\pi} \int_{\mathbb{S}^2} D\omega(\hat{\mathbf{z}}) d\hat{\mathbf{z}} \quad (80)$$

There exists a numerical solution to calculating the writhe, developed by Levitt in [32] and employed by Klenin and Langowski in [30]. Additional approaches, both analytical and numerical, are also covered in [30].

Following Levitt's approach [32], one starts with a numerical formulation of eq. (80):

$$\omega = \frac{1}{4\pi} \int_{\mathbb{S}^2} \sum_{i,j>i}^n \delta_{ij}(\hat{\mathbf{z}}) d\hat{\mathbf{z}}, \quad (81)$$

with, considering two segments i and j , numbered in traverse direction, $\delta_{ij} = 0$ for over- or underpassing segments i and j , and $\delta_{ij} = \pm 1$ for intersecting segments in accordance with right- and left-handedness of intersections (as defined previously). This can be further simplified to

$$\omega = \sum_{i,j>i}^n \frac{1}{4\pi} \int_{\mathbb{S}^2} \delta_{ij}(\hat{\mathbf{z}}) d\hat{\mathbf{z}} = \sum_{i,j>i}^n \omega_{ij}, \quad (82)$$

and an analytical formula is provided for ω_{ij} :

$$\omega_{ij} = \frac{2\Omega_{ij}}{4\pi} = \frac{\Omega_{ij}}{2\pi} \quad (83)$$

One may by convention define a traverse direction for the polygonal knot, as well as a starting point. Let any two segments i and j be denoted by the vectors pointing to the segments' beginnings and endings. One writes:

$$\begin{aligned} \mathbf{a} &= (\mathbf{r}_i - \mathbf{r}_{j+1}) \times (\mathbf{r}_i - \mathbf{r}_j) \\ \mathbf{b} &= (\mathbf{r}_i - \mathbf{r}_{j+1}) \times (\mathbf{r}_{i+1} - \mathbf{r}_{j+1}) \\ \mathbf{c} &= (\mathbf{r}_{i+1} - \mathbf{r}_j) \times (\mathbf{r}_{i+1} - \mathbf{r}_{j+1}) \\ \mathbf{d} &= (\mathbf{r}_{i+1} - \mathbf{r}_j) \times (\mathbf{r}_i - \mathbf{r}_j) \end{aligned} \quad (84)$$

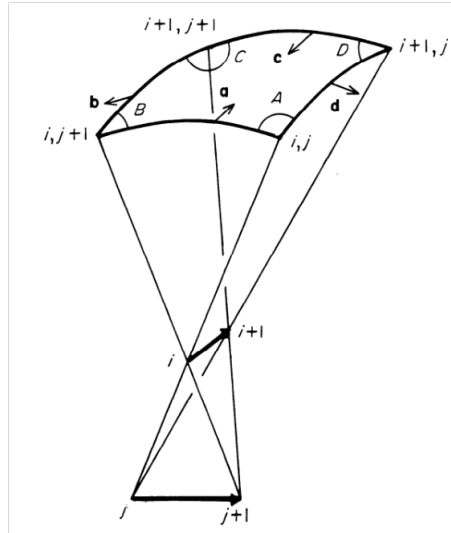


Figure 42: Figure taken out of Levitt's article on numerical writhing number calculation [32]. ω_{ij} can be computed from $\mathbf{r}_{i,i+1}$ and $\mathbf{r}_{j,j+1}$. Both segments are overlapping if viewed from a direction $\hat{\mathbf{z}}$ passing through the depicted spherical quadrilateral.

The angles A, B, C and D can be calculated easily by using the visualisation in figure 42:

$$\begin{aligned}
 A &= \cos^{-1}(\mathbf{a} \cdot \mathbf{d}/(|\mathbf{a}| \cdot |\mathbf{d}|)) \\
 B &= \cos^{-1}(\mathbf{a} \cdot \mathbf{b}/(|\mathbf{a}| \cdot |\mathbf{b}|)) \\
 C &= \cos^{-1}(\mathbf{c} \cdot \mathbf{b}/(|\mathbf{c}| \cdot |\mathbf{b}|)) \\
 D &= \cos^{-1}(\mathbf{c} \cdot \mathbf{d}/(|\mathbf{c}| \cdot |\mathbf{d}|))
 \end{aligned} \tag{85}$$

From there, one may finally calculate the angle Ω_{ij} :

$$\Omega_{ij} = A + B + C + D - 2\pi \tag{86}$$

3.2.4 Skein Relations and Jones Polynomial

With any obstacle to calculating the writhe ω out of the way, an auxiliary polynomial $X(L)$ may now be defined as follows:

$$X(L) = \left(-A^3\right)^{-\omega(L)} \langle L \rangle, \tag{87}$$

with L the respective knot diagram and $\omega(L)$ that diagram's writhe. $X(L)$ becomes the Jones polynomial $V(L)$ for $A = t^{-1/4}$. The writhe $\omega(L)$ is invariant under Reidemeister-II and -III moves, but is altered by Reidemeister-I by ± 1 . However, Reidemeister-I also changes $\langle L \rangle$ by a factor $(-A^{\mp 3})$ and therefore, $X(L)$ is a true knot invariant. It is, however, important to note that the Jones polynomial does not differentiate between two orientated knot diagrams, even though they may be non-invertible and different from each other. [1] This inconvenience fortunately was of no significance for this thesis.

A Skein relation is tool to analyse knots, exclusive to certain polynomials. Let there be given the following Skein relations for the Bracket polynomial [1]:

$$\begin{aligned}
 \left\langle \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} \right\rangle &= A \cdot \left\langle \begin{array}{c} \diagup \diagdown \\ \diagup \diagdown \end{array} \right\rangle + \frac{1}{A} \cdot \left\langle \begin{array}{c} \diagdown \diagup \\ \diagdown \diagup \end{array} \right\rangle \\
 \left\langle \begin{array}{c} \diagdown \diagup \\ \diagup \diagdown \end{array} \right\rangle &= \frac{1}{A} \cdot \left\langle \begin{array}{c} \diagup \diagdown \\ \diagup \diagdown \end{array} \right\rangle + A \cdot \left\langle \begin{array}{c} \diagdown \diagup \\ \diagdown \diagup \end{array} \right\rangle
 \end{aligned} \tag{88}$$

To derive the Skein relation of the Jones polynomial, one first has to define signs for the writhe:

$$\begin{aligned}\omega\left(\begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array}\right) &= +1 \\ \omega\left(\begin{array}{c} \diagdown \diagup \\ \diagup \diagdown \end{array}\right) &= -1\end{aligned}\tag{89}$$

With this convention, one proceeds and writes:

$$\begin{aligned}X\left(\begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array}\right) &= (-A^{-3})\left(A \cdot X\left(\begin{array}{c} \diagup \diagup \\ \diagdown \diagdown \end{array}\right) + \frac{1}{A} \cdot X\left(\begin{array}{c} \diagdown \diagdown \\ \diagup \diagup \end{array}\right)\right) \\ X\left(\begin{array}{c} \diagdown \diagup \\ \diagup \diagdown \end{array}\right) &= (-A^{+3})\left(A \cdot X\left(\begin{array}{c} \diagdown \diagdown \\ \diagup \diagup \end{array}\right) + \frac{1}{A} \cdot X\left(\begin{array}{c} \diagup \diagup \\ \diagdown \diagdown \end{array}\right)\right) \\ \Rightarrow X\left(\begin{array}{c} \diagdown \diagdown \\ \diagup \diagup \end{array}\right) &= -A^4 \cdot X\left(\begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array}\right) - A^2 \cdot X\left(\begin{array}{c} \diagup \diagup \\ \diagdown \diagdown \end{array}\right) \\ \Rightarrow X\left(\begin{array}{c} \diagup \diagup \\ \diagdown \diagdown \end{array}\right) &= -A^{-4} \cdot X\left(\begin{array}{c} \diagdown \diagup \\ \diagup \diagdown \end{array}\right) - A^{-2} \cdot X\left(\begin{array}{c} \diagup \diagup \\ \diagdown \diagdown \end{array}\right)\end{aligned}\tag{90}$$

Finally, comparing equations and substituting $A = t^{-1/4}$ yields the Skein relation for the Jones polynomial:

$$t^{-1} \cdot V\left(\begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array}\right) - t^1 \cdot V\left(\begin{array}{c} \diagdown \diagup \\ \diagup \diagdown \end{array}\right) = (t^{1/2} - t^{-1/2}) \cdot V\left(\begin{array}{c} \diagup \diagup \\ \diagdown \diagdown \end{array}\right),\tag{91}$$

with the actual Jones polynomial, $V(L)$, defined by:

$$V(L) = \left(-t^{3/4}\right)^{\omega(L)} \langle L \rangle\tag{92}$$

It can be easily shown from this equation that $V(L) = 1$ for any L that is an unknot. With this knowledge, it can be proven that it is always possible to calculate the Jones polynomial of any polygonal knot, starting from the Skein relation given in equation (91). [1].

3.2.5 Jones Polynomial of the Trefoil Knot

To further illustrate this procedure, a derivation of the Jones polynomial for the trefoil knot shall be given below, following lectures by Jones at the University of California at

Berkeley [27]:

One starts with considering the most simple knot components possible, depicted in fig. 43.

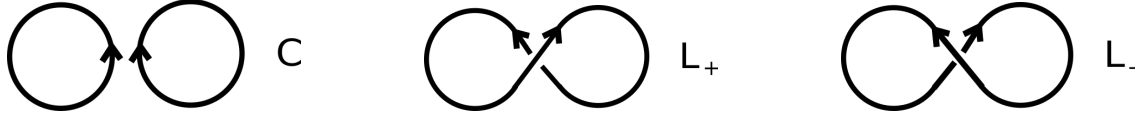


Figure 43: From left to right: Two disentangled unknots, an unknot with a right-handed crossing, and an unknot with a left-handed crossing. Illustrations done with Inkscape [12].

Given the Skein relation of equation 91, one may conclude that for the set of Jones polynomials $V(L_+)$, $V(L_-)$ and $V(C)$, the following must also hold true:

$$t^{-1} \cdot V(L_+) - t^{+1} \cdot V(L_-) = (t^{1/2} - t^{-1/2}) V(C), \quad (93)$$

$$V(C) = - (t^{1/2} + t^{-1/2}), \quad (94)$$

with the formula for $V(C)$ following from $V(L_+) = V(L_-) = 1$. Next, one considers the more complicated Hopf link H as depicted in fig. 44, which has two crossings.

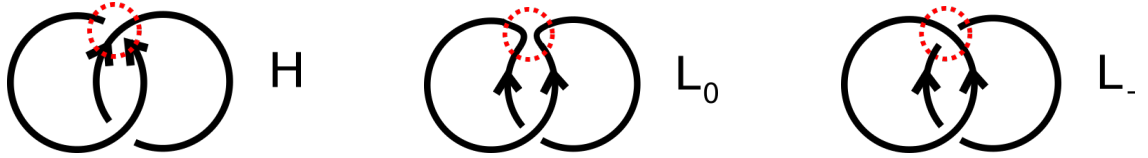


Figure 44: From left to right: The hopf link (two entangled unknots), an unknot with a right-handed crossing, and two overlapping unknots with one right-handed and one left-handed crossing. Illustrations done with Inkscape [12].

Once more, using equation 91, a Skein relation can be written for this set of links as follows:

$$\begin{aligned} t^{-1} \cdot V(H) - t^{+1} \cdot V(L_-) &= (t^{1/2} - t^{-1/2}) V(L_0) \\ \implies t^{-1} \cdot V(H) - t^{+1} \cdot V(C) &= (t^{1/2} - t^{-1/2}) V(\bigcirc), \end{aligned} \quad (95)$$

$$V(H) = -t^{1/2} (1 + t^2), \quad (96)$$

by employing $V(\bigcirc) = 1$ and taking a closer look at fig. 44: L_- represents the two disentangled circles, C , from fig. 43, and L_0 is the unknot. One has now everything needed to calculate the Jones polynomial of the trefoil knot.

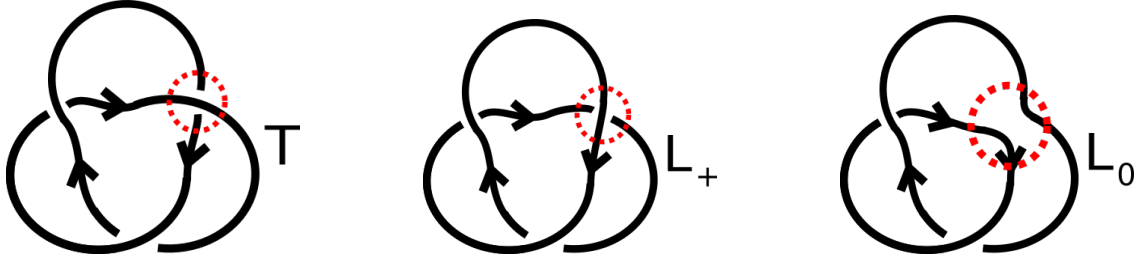


Figure 45: From left to right: The trefoil 3_1 knot, the unknot with two left-handed and one right-handed crossing, and two entangled unknots (hopf link). Illustrations done with Inkscape [12].

One last time, equation 91 is rewritten to fit this set of links, while considering that the L_+ link of fig. 45 is of reduced complexity in comparison to the trefoil knot, and therefore takes the place of L_- in the Skein relation, resulting in:

$$\begin{aligned} t^{-1} \cdot V(T) - t^{+1} \cdot V(L_+) &= (t^{1/2} - t^{-1/2}) V(H) \\ \Rightarrow t^{-1} \cdot V(T) - t^{+1} \cdot V(\bigcirc) &= (t^{1/2} - t^{-1/2}) V(H), \end{aligned} \tag{97}$$

$$V(T) = t + t^3 - t^4, \tag{98}$$

which concludes the derivation of the trefoil knot's Jones polynomial. The same approach can be pursued to derive the Jones polynomial of any other tame polygonal knot or, more generally speaking, any set of links.

4 Program Design

The main simulation has been written entirely in C++, which was chosen for familiarity and flexibility, as well as performance. While maintaining a time- and resource-efficient implementation of algorithms and structures, an object-oriented approach was chosen and carried out consequently throughout the whole program. A modular structure allowed for easier code maintenance, improved readability and reusability. The program in its current form could be adapted easily to carry out more sophisticated calculations with different boundary conditions, another time integration algorithm or more complicated polymer structures. Most importantly, parts of the program can be switched on and off without much effort and without influencing program functionality (at the user's discretion and convenience).

In order to visualise the program's structure, a class-diagram is depicted in figure 46. Getter- and Setter-functions have been excluded from the diagram, as well as all functions dedicated to result analysis and monitoring for reasons of readability. The same applies to any quantities not crucial to the understanding of the general program structure, such as timesteps, probability distributions and similar objects. This does not mean that such quantities are not required for the algorithms employed, but simply that their inclusion would have unnecessarily lengthened the diagram. Additionally, all function arguments, unless absolutely crucial, have been abandoned for improved visualisation. In general, almost all functions have a list of several input parameters provided by other classes or structures. This small tradeoff in performance and structure was chosen to improve readability and maintainability of the program itself.

The crucial importance of classes *ParticleSystem* and *Polymer* is clearly visible. The function *main()* accounts for the general functionality of the program and handles the most basic function calls, enforcing both Molecular Dynamics and MPCD simulations being carried out. In general, the program structure allows for easy calculation of class properties within the class and aims to prevent uncalled interference from outside the class. This is especially true for the two main classes, *ParticleSystem* and *Polymer*, but less for the minor classes *RotationSimulator* and *Thermostat* which need to be accessed during the MPCD Collision Step and serve no other purpose.

The class *ParticleSystem* stores all information on the fluid, such as fluid particle positions, velocities and other important data. For practical and performance reasons, it also handles all functions specifically assigned to the time propagation of the fluid particles and therefore includes the algorithm enforcing boundary conditions, *RemapParticles()*, as well as integrators *StreamingStep()* and *CollisionStep()*, whereas the latter also depends on the *Polymer* class.

The *Polymer* class fills a similar roll, handling all functions related to Molecular Dynamics

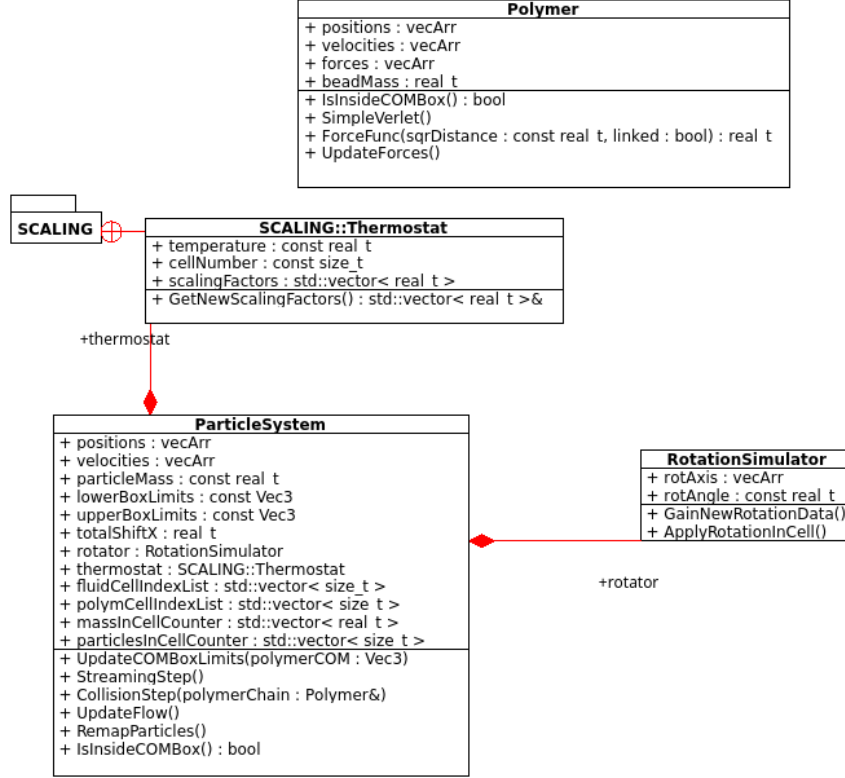


Figure 46: Class diagram (simplified) of main C++ program.

and storing bead positions, velocities and other variables crucial for function calls and calculations within the class.

The initial construction of the knot configuration was done by the RKnots [13] [14] package, which was accessed by a small Python script. The obtained configuration of the 3_1 knot was scaled and adapted before being equilibrated at a much smaller MD timestep of $\delta t^* = 0.001$ to avoid singularity-like behavior. The final configuration was stored and reused for all 3_1 knot simulations for this thesis.

5 Simulations

In this section, simulation results are presented. We first focus on obtaining reference values for the unknotted (O_1) ring and the 3_1 -knotted ring in equilibrium (section 5.1), and then proceed to analysing and comparing behavior of the two under shear (section 2.5).

5.1 Equilibrium Simulations for Reference

First, simulations at equilibrium for both an unknotted polymer ring and a 3_1 -knotted ring have been carried out to provide comparative options for analysis of behavior under shear. Of importance was, for example, the computation of the radius of gyration and, from it, the relaxation time τ_s . Simulations have performed for polymers embedded in an MPCD solvent with $N_c = 5$, $a = 1$, $m_f = 1$, $k_B T = 1$, at equilibrium and $\Delta t_{MPCD} = 0.1$ for a simulation box of dimensions $(50 \times 50 \times 50)$. The polymers were simulated as flexible, with $m_b = 5$, $\Delta t_{MD} = 0.002$, LJ parameters $\sigma = 1$, $\epsilon = k_B T = 1$ and the FENE potential parameters $R_0 = 1.5\sigma$ and $k = 30k_B T/\sigma^2$ as discussed in section 2.3.3. For further reference for 3_1 -knotted rings at equilibrium, we refer to [43].

5.1.1 Ring Polymer

A basic simulation has been carried out for a polymer ring with $N = 100$ beads in a solvent at equilibrium, over a period of 10^6 MPCD steps. First, we look at the three eigenvalues of the gyration tensor over time, as seen in fig. 47-49. All eigenvalues fluctuate similarly around their averages. A similar conclusion has been drawn for the knotted polymer in section 5.1.2.

We have also analysed the shape parameters for the ring polymer, which are presented in table 2. From the radius of gyration, one can now calculate the relaxation time τ_s according to eq. (59): $\tau_s \approx 0.163 \cdot (\eta_s/(k_B T)) \cdot R_g^3 = 130.154$.

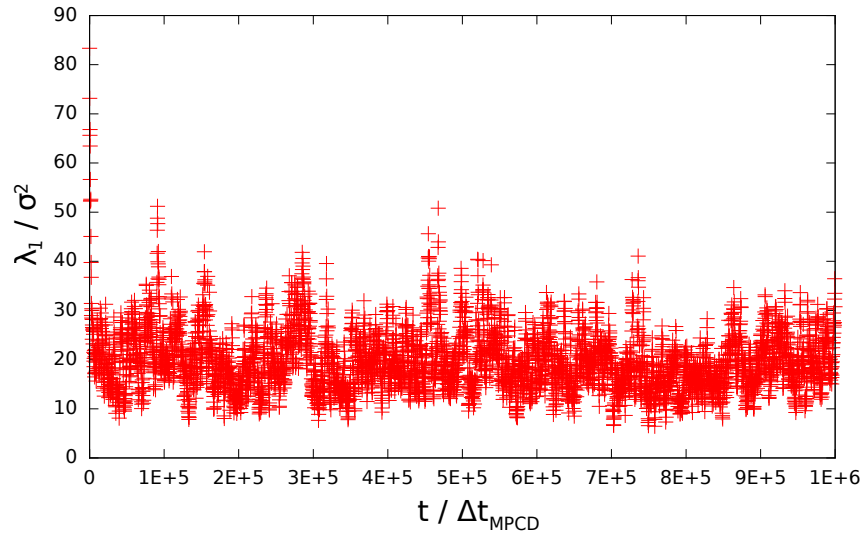


Figure 47: Largest eigenvalue of the gyration tensor for the unknotted 100-bead ring at equilibrium over time.

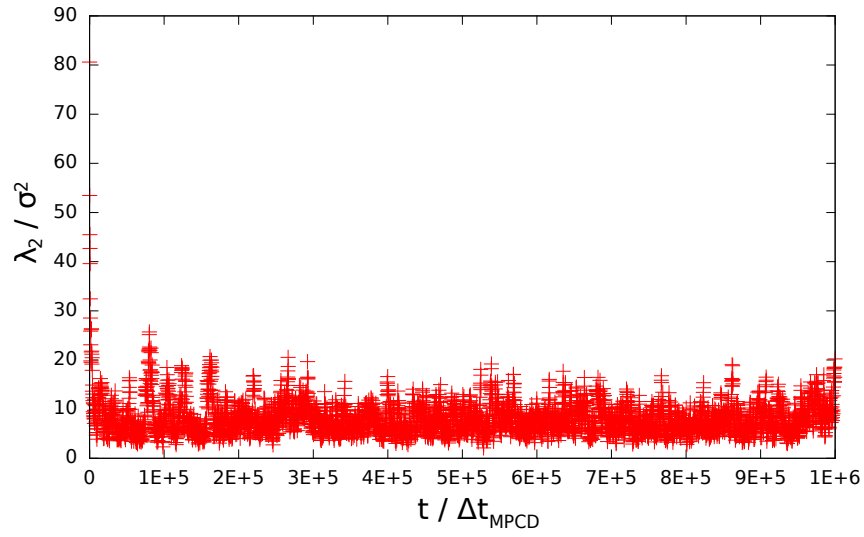


Figure 48: Second-to-largest eigenvalue of the gyration tensor for the unknotted 100-bead ring at equilibrium over time.

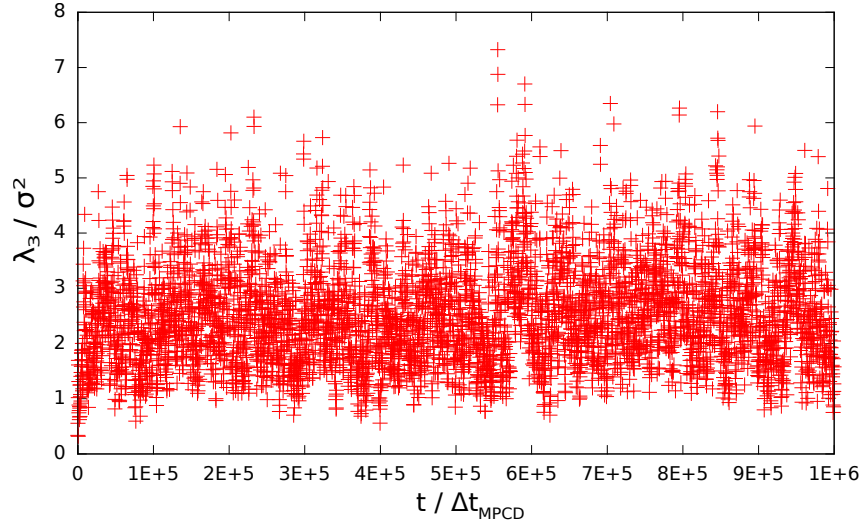


Figure 49: Third and smallest eigenvalue of the gyration tensor for the unknotted 100-bead ring at equilibrium over time.

Quantity	Abbr.	Value $\pm$ Std.-Deviation
Gyration Radius	$\langle R_g \rangle / \sigma$	5.4951 ± 0.6504
Anisotropy	δ^*	0.2645 ± 0.1144
Prolateness	S^*	0.1817 ± 0.2246
Asphericity	$b / \langle R_g^2 \rangle$	0.4661 ± 0.1330
Acylicity	$c / \langle R_g^2 \rangle$	0.1770 ± 0.0897

Table 2: Shape parameters of a 100-bead polymer ring in equilibrium, with the standard deviation of the respective data sample.

5.1.2 3_1 -Knotted Polymer

A comparative basic simulation has been carried out for a 3_1 -trefoil-knotted polymer ring with $N = 100$ beads in a solvent at equilibrium over a period of 10^6 MPCD steps. A lower number of $8.4 \cdot 10^5$ MPCD steps was used for any knot position- or angle-related calculations due to time issues with the computation of the knot's location. Again, we first look at the three eigenvalues of the gyration tensor over time, as seen in fig. 50-52. All eigenvalues fluctuate similarly around their averages. The behavior is very similar to the one observed for the unknotted ring in section 5.1.1.

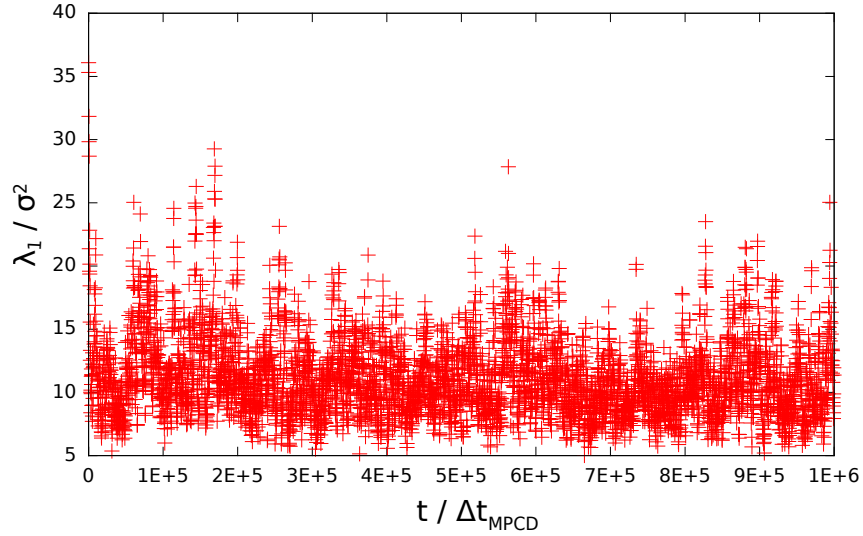


Figure 50: Largest eigenvalue of the gyration tensor for the 3_1 -knotted 100-bead ring at equilibrium over time.

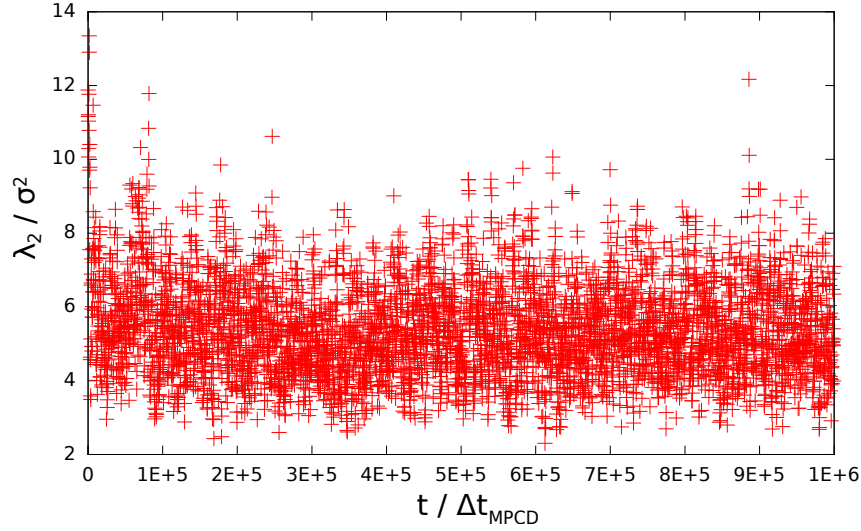


Figure 51: Second-to-largest eigenvalue of the gyration tensor for the 3_1 -knotted 100-bead ring at equilibrium over time.

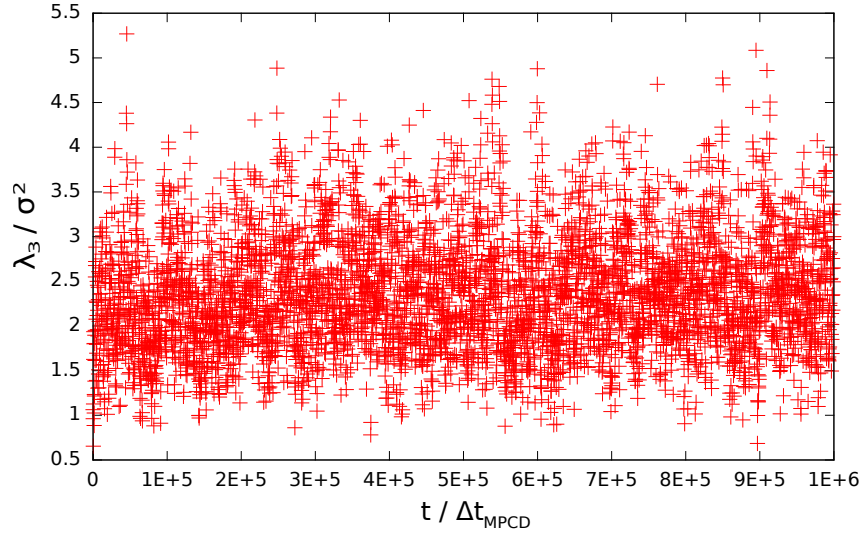


Figure 52: Third and smallest eigenvalue of the gyration tensor for the 3_1 -knotted 100-bead ring at equilibrium over time.

We have analysed the shape parameters for the 3_1 -knotted ring polymer, which are presented in table 3. Comparing table 3 to table 2, one finds generally smaller and more accurate values for all shape parameters. This shows most prominently in the standard deviation of the radius of gyration, which is almost half the value of the standard deviation for R_g of the normal ring (table 2). From the radius of gyration, one can now calculate the relaxation time τ_s according to eq. (59): $\tau_s \approx 0.163 \cdot (\eta_s/(k_B T)) \cdot R_g^3 = 64.821$.

Quantity	Abbr.	Value $\pm$ Std.-Deviation
Gyration Radius	$\langle R_g \rangle / \sigma$	4.3558 ± 0.3645
Anisotropy	δ^*	0.1774 ± 0.0887
Prolateness	S^*	0.0899 ± 0.1361
Asphericity	$b / \langle R_g^2 \rangle$	0.3738 ± 0.1191
Acylicity	$c / \langle R_g^2 \rangle$	0.1605 ± 0.0748

Table 3: Shape parameters of a 100-bead 3_1 -knotted polymer ring in equilibrium, with the standard deviation of the respective data sample.

5.1.3 Shape Parameters in Comparison

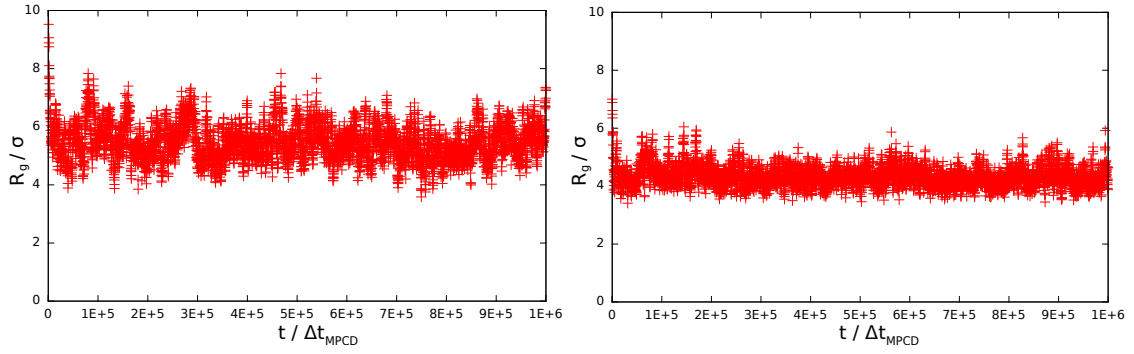


Figure 53: Radius of gyration R_g of a 100-bead polymer ring (left) and a 100-bead ring with a 3_1 trefoil knot (right) in equilibrium.

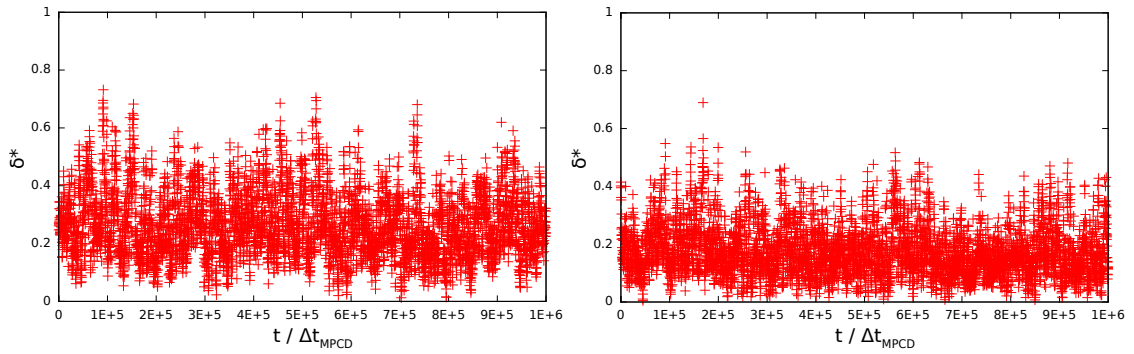


Figure 54: Anisotropy δ^* of a 100-bead polymer ring (left) and a 100-bead ring with a 3_1 trefoil knot (right) in equilibrium.

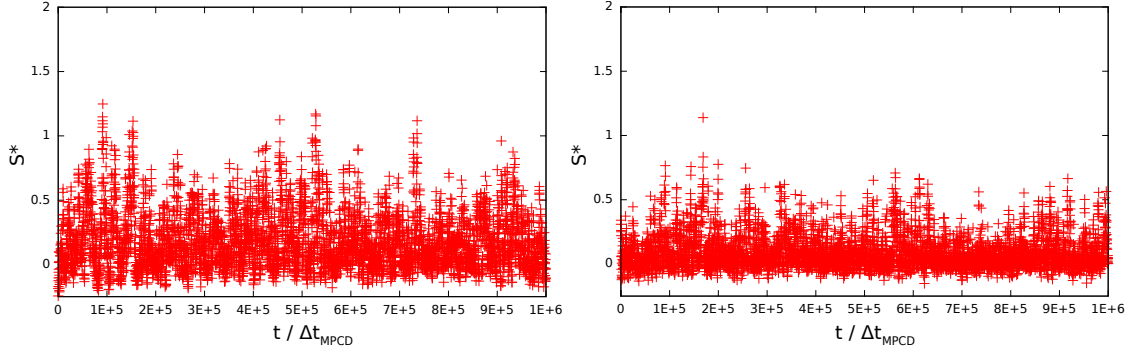


Figure 55: Prolateness S^* of a 100-bead polymer ring (left) and a 100-bead ring with a 3_1 trefoil knot (right) in equilibrium.

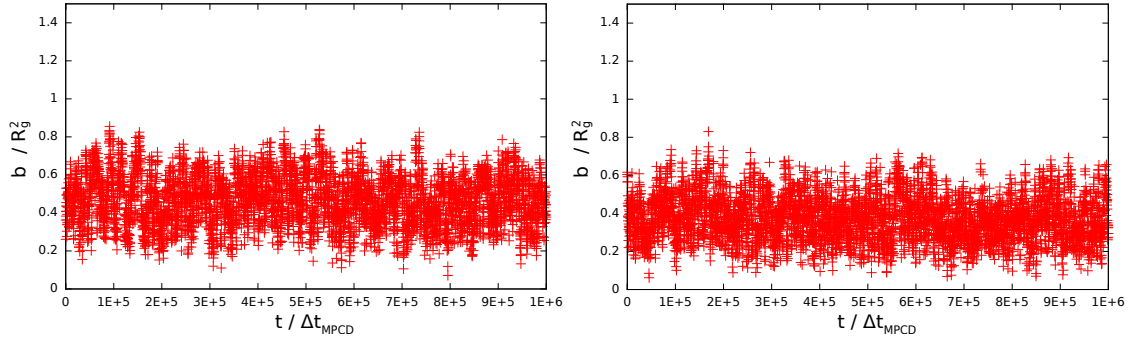


Figure 56: Asphericity b of a 100-bead polymer ring (left) and a 100-bead ring with a 3_1 trefoil knot (right) in equilibrium.

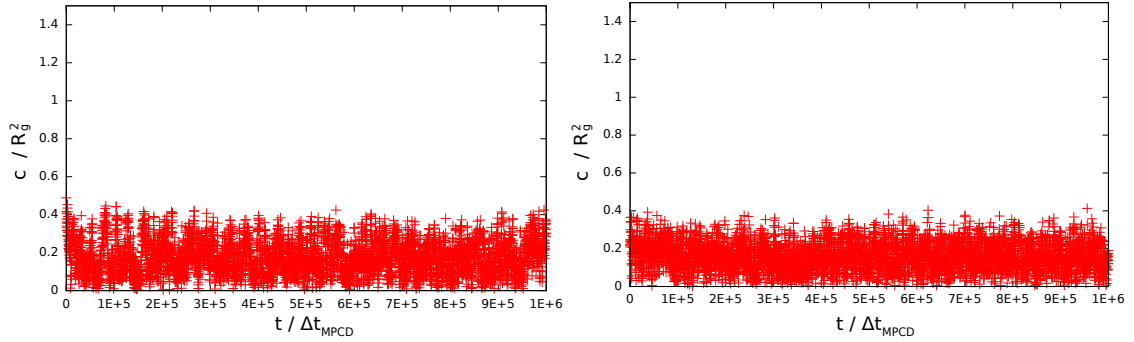


Figure 57: Acylindricity c of a 100-bead polymer ring (left) and a 100-bead ring with a 3_1 trefoil knot (right) in equilibrium.

It can be clearly seen from figures 53-57 that there is a significant difference in the radius of gyration between a simple ring and a knotted ring. One may also observe the smaller fluctuations in the case of the knotted ring for R_g , δ^* and S^* , but no comparably visible change in b or c .

5.2 Simulations Under Shear

In this section, we present results of simulations of both the normal 100-bead ring and the 100-bead 3_1 -knotted ring. Among other results, we provide evidence that the 3_1 -knot prefers to be located on either end of the ring, aligned with the flow axis. Simulations have been carried out for polymers embedded in an MPCD solvent with $N_c = 5$, $a = 1$, $m_f = 1$, $k_B T = 1$, at multiple shear rates and $\Delta t_{MPCD} = 0.1$ for a simulation box of dimensions $(50 \times 50 \times 50)$. The polymers were simulated as flexible, with $m_b = 5$, $\Delta t_{MD} = 0.002$, LJ parameters $\sigma = 1$, $\epsilon = k_B T = 1$ and the FENE potential parameters $R_0 = 1.5\sigma$ and $k = 30k_B T/\sigma^2$ as discussed in section 2.3.3.

5.2.1 Shape Parameters

We present our results for radius of gyration R_g , relative shape anisotropy δ^* , prolateness S^* , asphericity b , acylindricity c , alignment angle χ (eq. (62)) and deformational resistance m_G (eq. (63)). Runs included calculations at several Weissenberg numbers $Wi \in [0.008 : 52]$. Unfortunately, in our code, the shear rate $\dot{\gamma}$ was fixed instead of Wi , and therefore, because τ_s is different for the knotted and the normal ring, values have been taken at different values of Wi . Another issue arose from simulations of the 3_1 -knotted ring at high $Wi \geq 26$: The knot, at that point, was tightened so much that it disentangled itself almost immediately, resulting in a normal ring without the 3_1 trefoil on it. We suggest that in future calculations, longer chains should be used to allow further tightening of the knot, possibly combined with a smaller Δt_{MD} for large Wi .

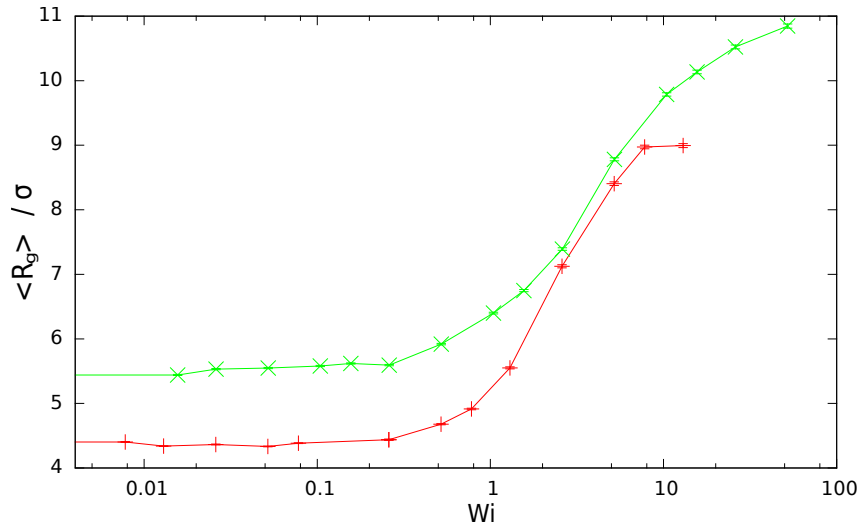


Figure 58: Gyration radius $\langle R_g \rangle$ of a 100-bead ring (green) and a 100-bead 3_1 -knotted ring (red) in dependency of the Weissenberg number Wi . Error bars are given by the standard error, but are so small they are barely visible.

In fig. 58, important to note is the sudden stop in expansion of the 3_1 -knotted ring in comparison to the smooth transition of the normal ring. We suggest the presence of the knot, at high Wi , becomes a significant hindrance for further increase of R_g . Further evidence comes from the fact that at $Wi \approx 13$, the knot was maintained throughout the simulation, whereas for $Wi \approx 26$, the knot was tightened so much that it disentangled itself. The latter is excluded from fig. 58, but obviously agrees with the (green) plot of the normal ring's R_g . We also suggest that the shape transition between polymer ring in sheared and in equilibrium solvent happens quicker and concludes more abruptly in the presence of a knot, with further evidence provided by fig. 59-62.

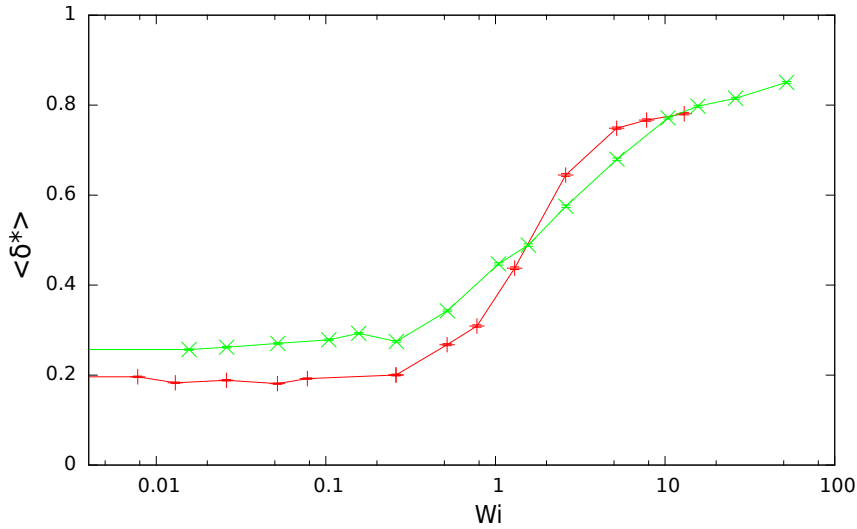


Figure 59: Relative shape anisotropy $\delta^* \in [0; 1]$ of a 100-bead ring (green) and a 100-bead 3_1 -knotted ring (red) in dependency of the Weissenberg number Wi .

Figures 59 (rel. shape anisotropy δ^*) & 60 (prolateness S^*) look very similar and both provide evidence to support the idea that in the presence of a knot, with increasing Wi , the transition between equilibrium and strongly-sheared shape parameter values happens in a smaller range of Wi values.

This is also supported but less visible by figures 61 (asphericity b) & 62 (acylindricity c), where interestingly enough differences in b and c between knotted ring and normal ring seem to get smaller for high enough Wi .

As seen quite clearly in fig. 63, there is behavioral similarity for deformational resistance m_G . However, although the general behavior follows the same pattern (increase of m_G for increasing Wi), it seems the deformational resistance of the knotted ring is, for increasing Wi , significantly lower than that of the ordinary ring polymer. We suggest this might be due to the knot acting as some kind of massive bead, an object more strongly affected by hydrodynamic interactions than the other domains of the knotted ring.

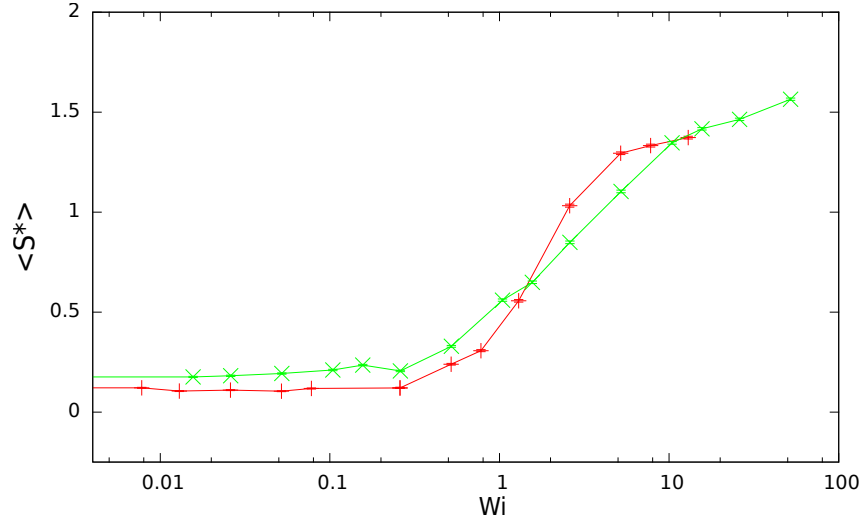


Figure 60: Prolateness $S^* \in [-0.25 : 2]$ of a 100-bead ring (green) and a 100-bead 3_1 -knotted ring (red) in dependency of the Weissenberg number Wi .

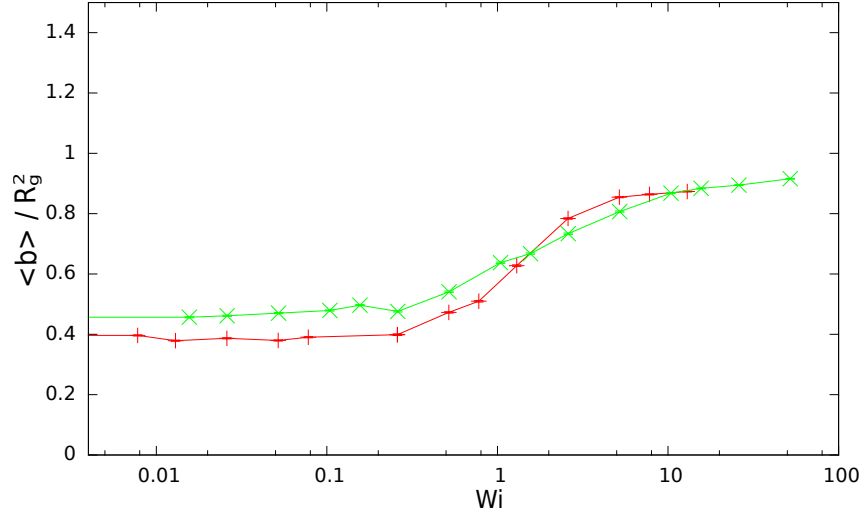


Figure 61: Asphericity $b \geq 0$ of a 100-bead ring (green) and a 100-bead 3_1 -knotted ring (red) in dependency of the Weissenberg number Wi .

Lastly, we present the shear-dependent eigenvalues of the gyration tensor in fig. 64-66.

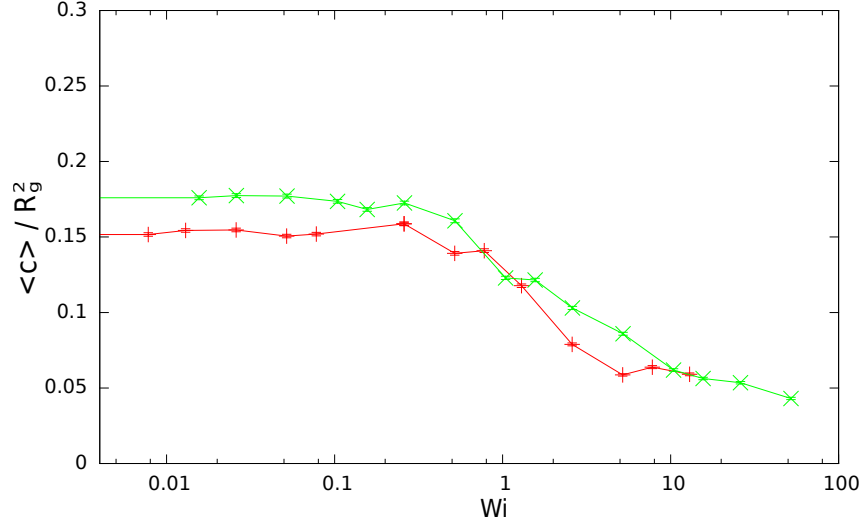


Figure 62: Acylindricity $c \geq 0$ of a 100-bead ring (green) and a 100-bead 3_1 -knotted ring (red) in dependency of the Weissenberg number Wi .

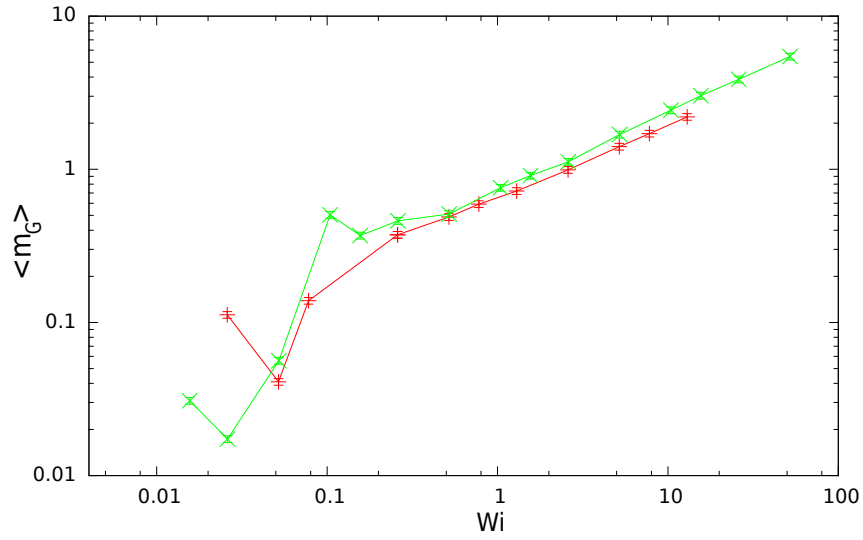


Figure 63: Deformational resistance $\langle m_G \rangle$ of a 100-bead ring (green) and a 100-bead 3_1 -knotted ring (red) in dependency of the Weissenberg number Wi in a log-log plot. At low Wi , strong fluctuations occur. This is most likely due to problems with accuracy when computing m_G at low Wi , because of eq. (63).

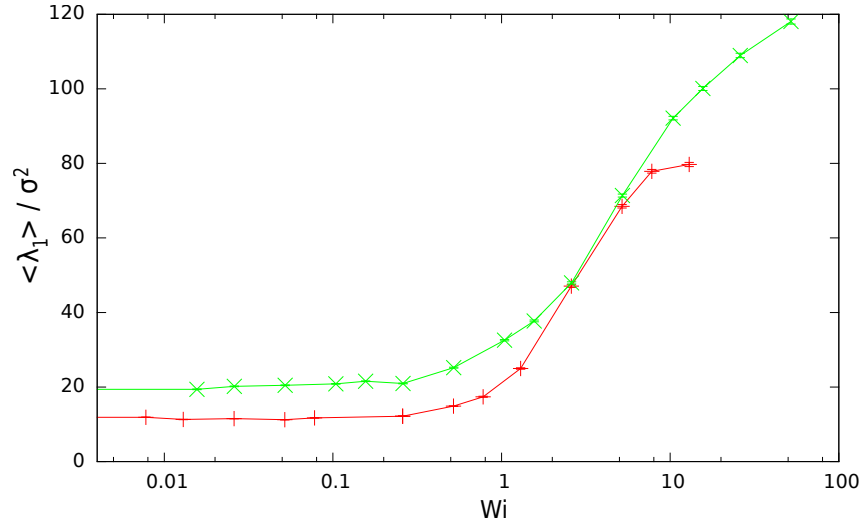


Figure 64: Largest eigenvalue of the gyration tensor of a 100-bead ring (green) and a 100-bead 3_1 -knotted ring (red) in dependency of the Weissenberg number Wi .

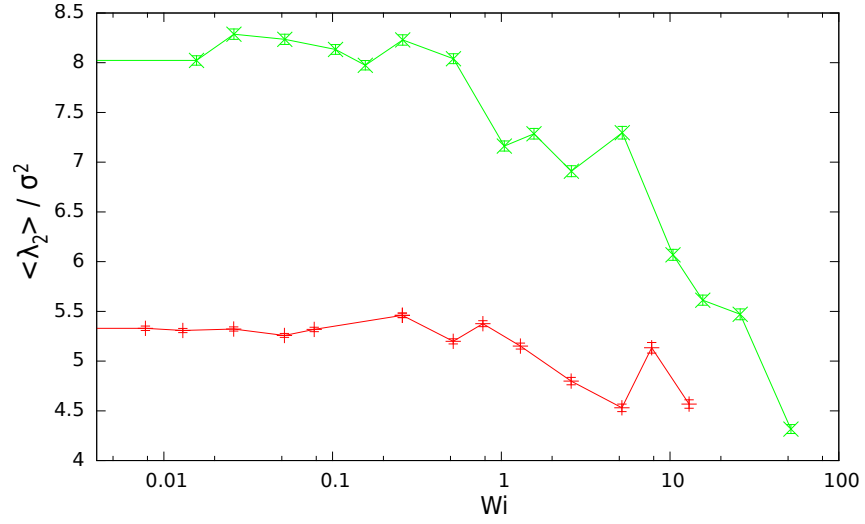


Figure 65: Second-to-largest eigenvalue of the gyration tensor of a 100-bead ring (green) and a 100-bead 3_1 -knotted ring (red) in dependency of the Weissenberg number Wi .

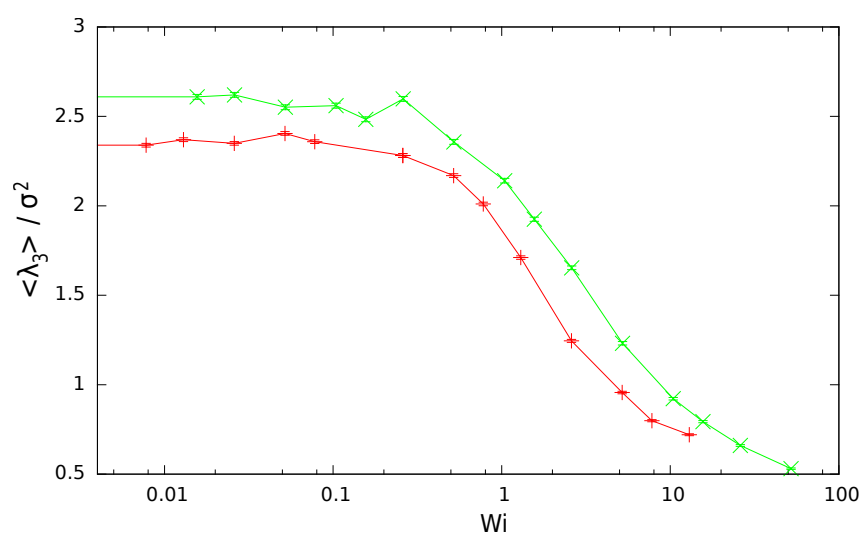


Figure 66: Third and smallest eigenvalue of the gyration tensor of a 100-bead ring (green) and a 100-bead 3_1 -knotted ring (red) in dependency of the Weissenberg number Wi .

5.2.2 Angle Analysis

We present our results on angles between main principal component and flow axis in dependency of Wi . The alignment angle χ is not the most promising parameter at low Wi , where large fluctuations and inaccuracies with the gyration tensor cause a rather inaccurate estimate. We refer to fig. 63 to see a similar behavior for the related quantity m_G .

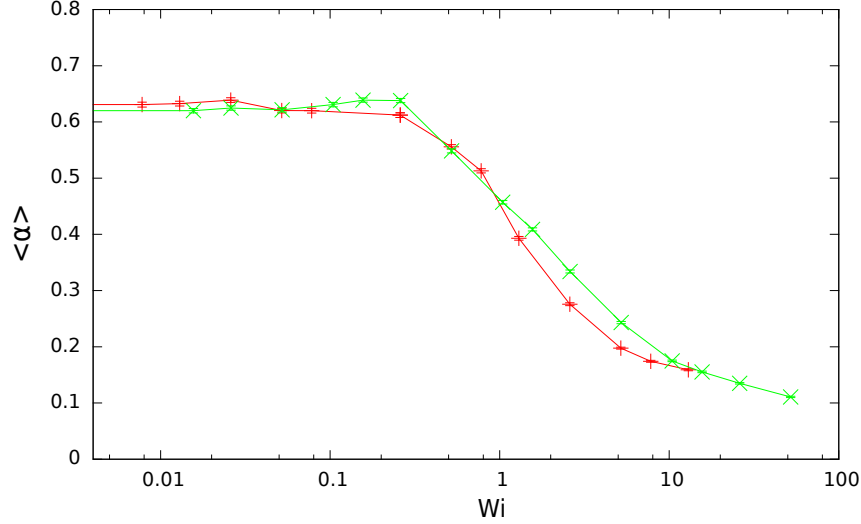


Figure 67: Angle $\langle \alpha \rangle \in [0; \pi/2]$ between the main principal component and the flow axis of a 100-bead ring (green) and a 100-bead 3_1 -knotted ring (red) in dependency of the Weissenberg number Wi .

Fig. 67 suggests a more complete alignment of main principal component and flow axis in the absence of a knot, however, alignment appears to happen at lower Wi in the presence of a knot. We suggest the less complete alignment is caused by the lower deformational resistance and the idea that the number of beads on the moving knot has a significant influence on the orientation of the main principal component. Therefore, a tank-treading or tumbling knotted ring could be expected to influence the orientation of the main principal component more severely than tank-treading or tumbling do for the common, unknotted ring. However, the specifics of tank-treading and tumbling of knotted rings have not been studied in the context of this thesis and will therefore, eventually, have to be discussed elsewhere.

We include fig. 68 to demonstrate that the change in alignment is most prominent for the main principal component (fig. 67), even more so in comparison to the rather small change in the angles between second and third principal components and flow axis, showcased in the two plots of fig. 68.

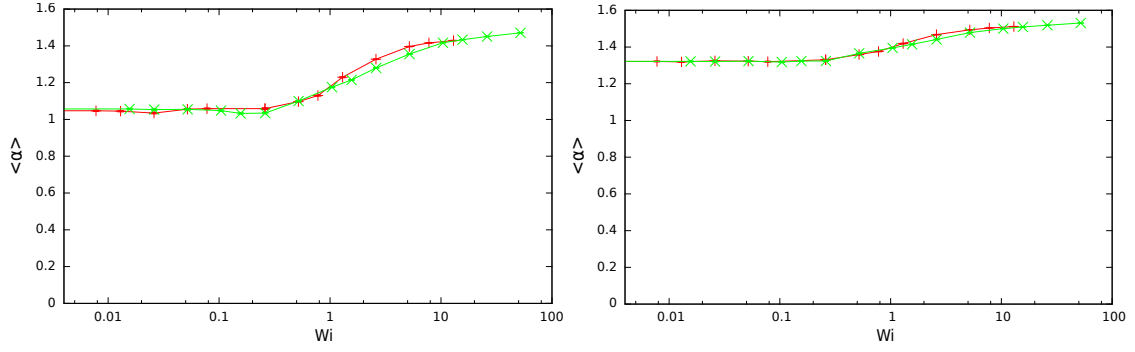


Figure 68: Angle $\langle \alpha \rangle \in [0; \pi/2]$ between second (left) and third (right) principal component and the flow axis of a 100-bead ring (green) and a 100-bead 3_1 -knotted ring (red) in dependency of the Weissenberg number Wi .

5.2.3 Knot-Exclusive Analysis

With all the general analysis out of the way, we now dedicate more thought to the knot itself: Its average number of beads $\langle N_k \rangle$, its radius of gyration $\langle R_g \rangle$, the distance between the center of mass of the polymer and that of the knot itself, and, most importantly, the average angle between the vector from the polymer's center of mass to the knot's center of mass and both the flow axis and the main principal component of the polymer. We then start looking for correlations between these quantities.

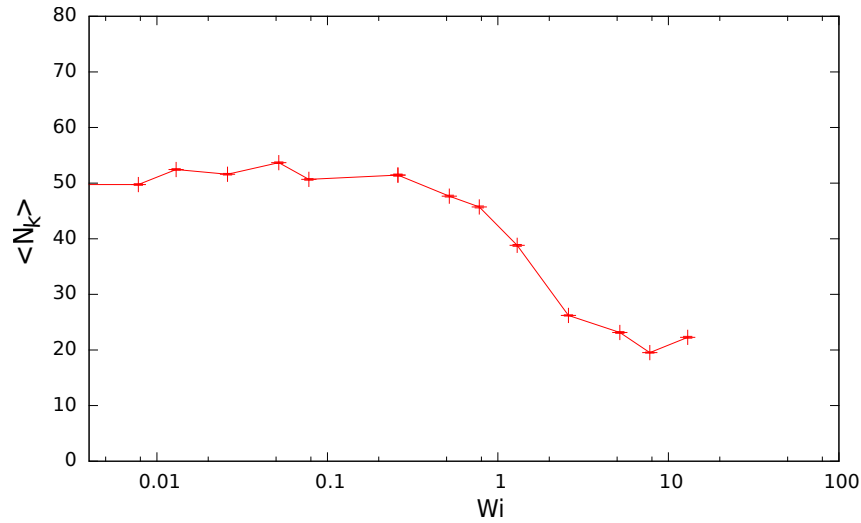


Figure 69: Average number of beads $\langle N_k \rangle$ on the 3_1 trefoil knot of a 100-bead 3_1 -knotted ring in dependency of the Weissenberg number Wi .

From fig. 69 to 71, a few conclusions can be drawn: The average number of beads on the knot, $\langle N_k \rangle$, decreases significantly with increasing Wi . $\langle N_k \rangle$ at equilibrium is more than twice its value at high Wi . R_g shows the same behavior: For higher Wi , R_g gets smaller.

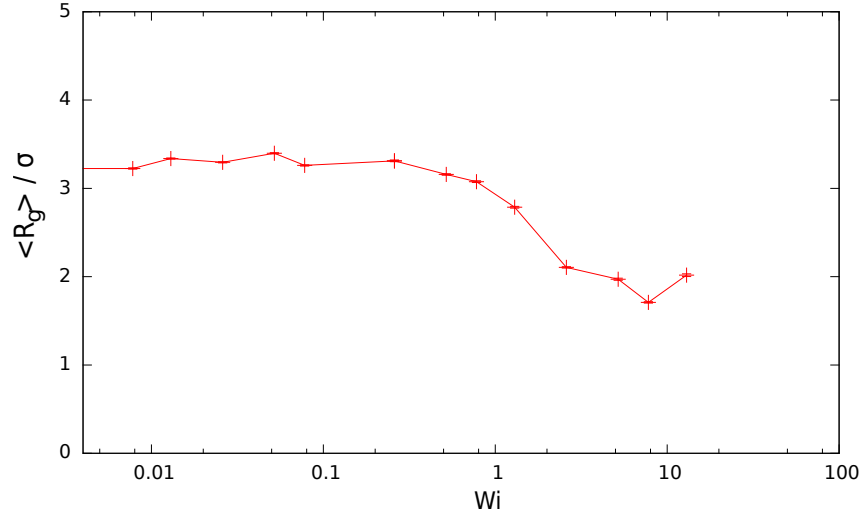


Figure 70: Radius of gyration $\langle R_g \rangle$ of the 3_1 trefoil knot of a 100-bead 3_1 -knotted ring in dependency of the Weissenberg number Wi .

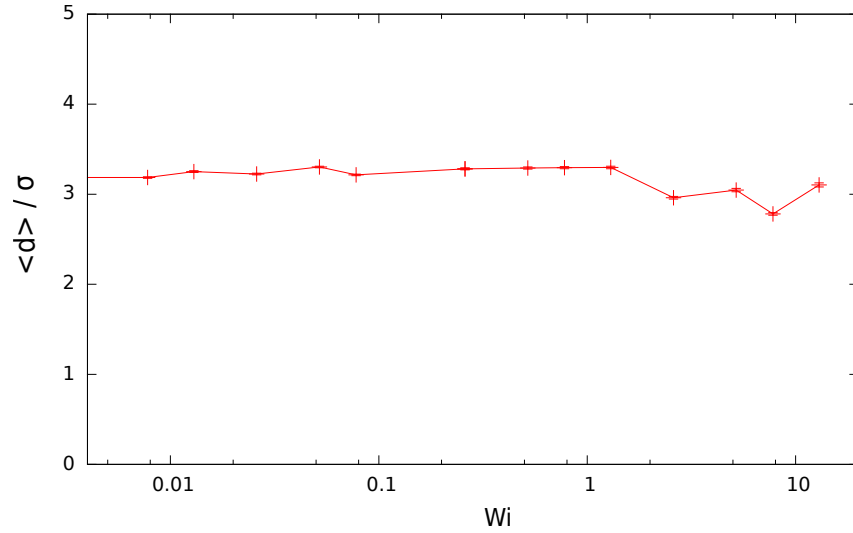


Figure 71: Distance between the center of mass of the entire polymer and the center of mass of the 3_1 trefoil knot for a 100-bead 3_1 -knotted ring in dependency of the Weissenberg number Wi .

This is in agreement with everyday experience - a knot under stress tightens. This appears to be no different for a knot in a sheared solvent. For large values of Wi , the knot tightens and is therefore more localised. However, the distance between the center of mass of the polymer and the center of mass of the knot on it appears to become only slightly smaller under strong shear, and suggest this can be attributed to stronger fluctuations in knot size - either very tight or very delocalised knots. We show later in this section that indeed, at high Wi , knot size jumps between two states (very tight and rather delocalised, fig. 74),

but the average distance between the centers of mass seems only loosely tied to shear.

We shall now take a look at the knot's location on the polymer. We study its location by looking at the average angle $\langle\alpha\rangle$ between the vector from the polymer's center of mass to the knot's center of mass and the main principal component, as well as the second and third principal component.

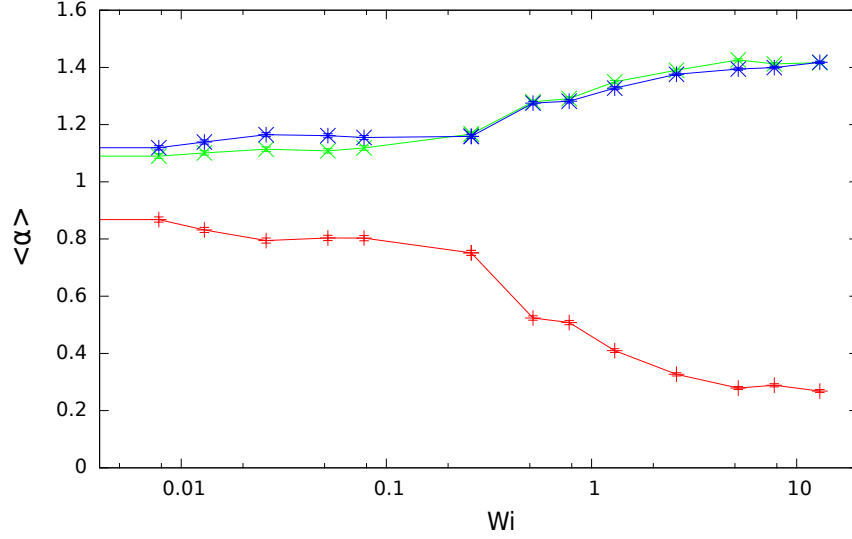


Figure 72: Angle $\langle\alpha\rangle \in [0; 0.5\pi]$ between the vector from the polymer's center of mass to the knot's center of mass and the first (red), second (green) and third (blue) principal component for the 100-bead 3_1 -knotted ring in dependency of the Weissenberg number Wi .

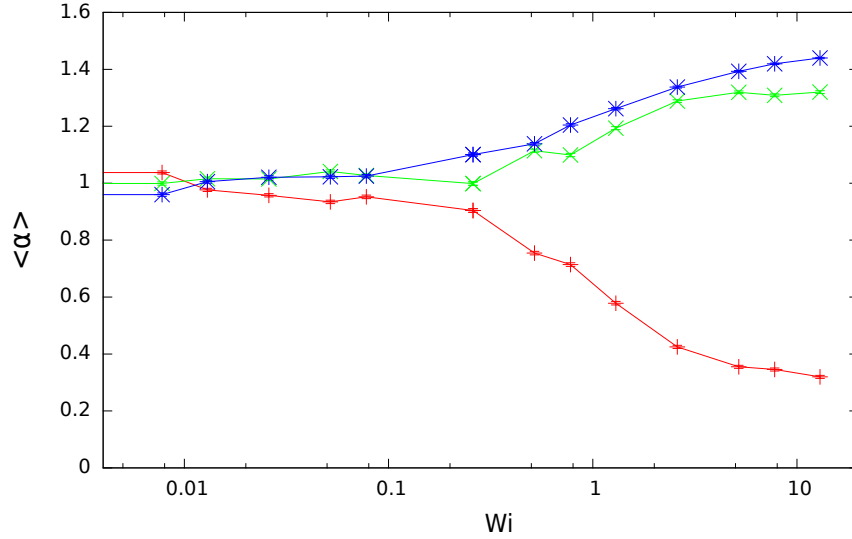


Figure 73: Angle $\langle\alpha\rangle \in [0; 0.5\pi]$ between the vector from the polymer's center of mass to the knot's center of mass and the flow- (red), vorticity- (green) and gradient (blue) axis for the 100-bead 3_1 -knotted ring in dependency of the Weissenberg number Wi .

Figures 72 & 73 provide rather clear evidence that the knot, for high Wi , develops a tendency to be located on either end of the polymer, that is, the vector between the polymer's center of mass and the knot's center of mass develops a tendency to be parallel to the main principal component and the flow axis, rather than orthogonal.

We shall now proceed to look at the number of beads on the knot more closely by examining $N_k(t)$ for several different shear rates (fig. 74).

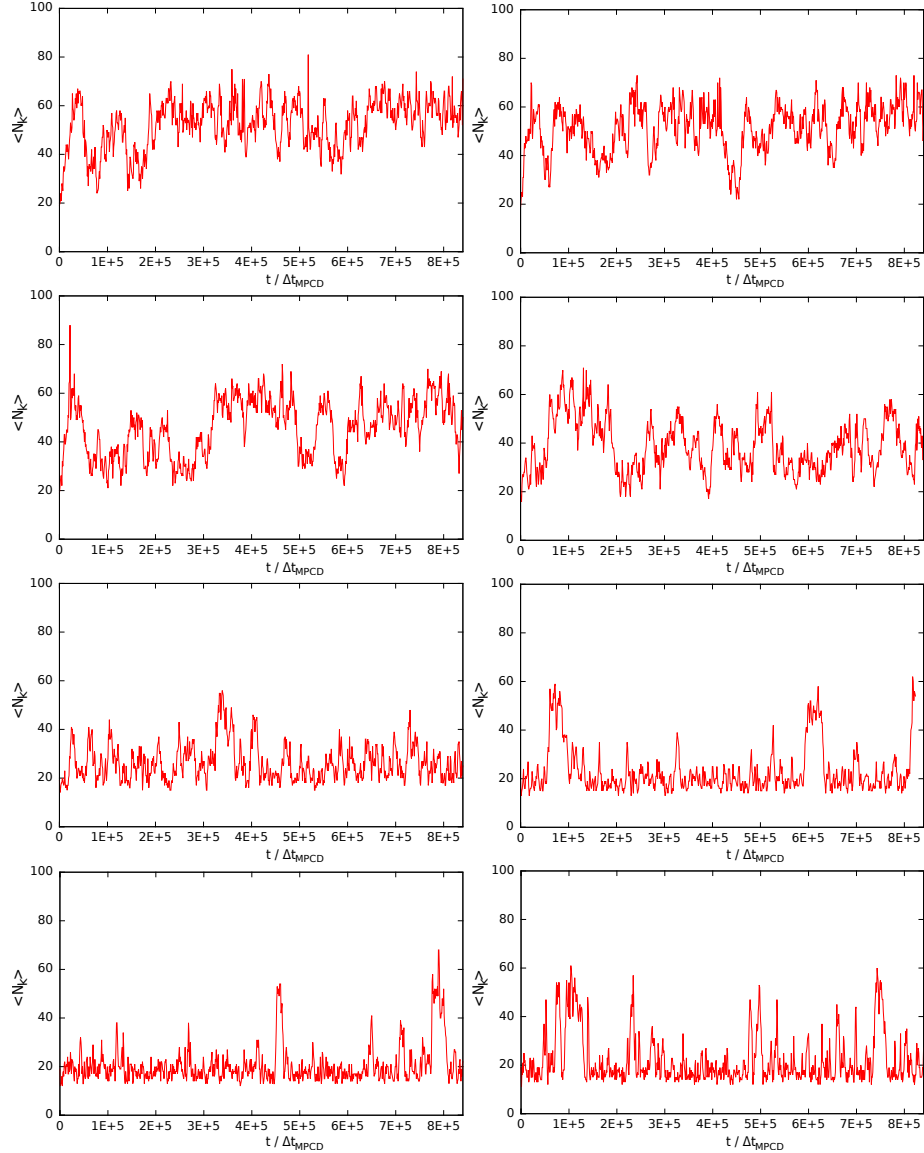


Figure 74: Time-dependent number of beads on the knot $N_k(t)$ over $8.4 \cdot 10^5$ MPCD timesteps for several shear rates. Increasing Wi from left to right, top to bottom: $Wi = 0, 0.26, 0.78, 1.30, 2.60, 5.19, 7.78, 12.96$. At high Wi , N_k essentially starts to jump between two states.

We observe a rather curious behavior: While $N_k(t)$ seems to fluctuate randomly around an average value for low Wi , it develops a tendency for small fluctuations joined by large and overall broader peaks at high Wi . We suggest that a change in size, towards both smaller and bigger N_k , becomes less frequent at high Wi , while the change itself becomes more significant relative to average number of beads N_k . To conclude anything, however, further simulations would have been necessary, possibly at much higher Wi to find more evidence for what is implied by fig. 74.

Now that we have clarified the time-dependency of N_k for individual simulations, we can look at possible correlations between obtained parameters, plotted to fig. 75-83 for several values of Wi . Averages that would have had contributions from less than 30 data points have not been considered.

We shall start with a suspected correlation between $\langle N_k \rangle$ and the angle $\alpha \in [0; \pi/2]$ between the vector from the polymer's center of mass to the knot's center of mass and the first principal component. This is visualised in fig. 75. The on average smaller configurations for higher shear are in agreement with fig. 69, and the same holds true for the smaller angle with increasing shear, as illustrated in fig. 72. There seems to be no clear correlations between N_k and the alignment of the knot with the main principal component, however α is clearly decreasing with increasing Wi , with the knots preferring to be aligned with the flow at high Wi .

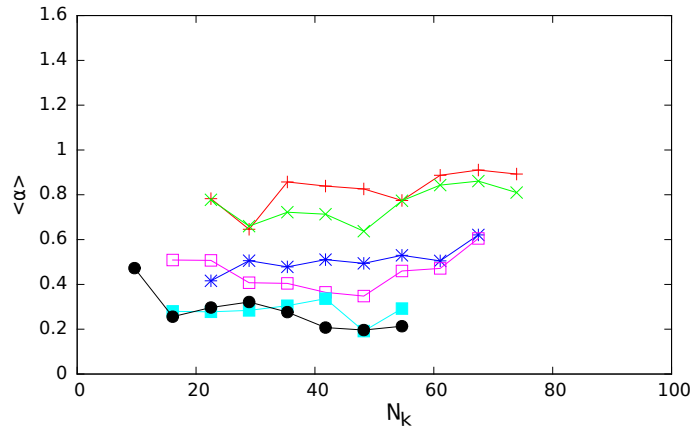


Figure 75: Average angle $\alpha \in [0; 0.5\pi]$ between the vector from the polymer's center of mass to the knot's center of mass and the first principal component in dependency of N_k for several values of Wi : 0 (red), 0.26 (green), 0.78 (blue), 1.30 (pink), 5.19 (turquoise), 12.96 (black).

Continuing with correlations, we look at $\langle N_k \rangle$ and the angle $\alpha \in [0; 0.5\pi]$ between the vector from the polymer's center of mass to the knot's center of mass and the flow axis as depicted in fig. 76. This looks rather similar to fig. 75, and indeed provides further evidence for the implied correlations between high Wi and the knot being more aligned with the flow.

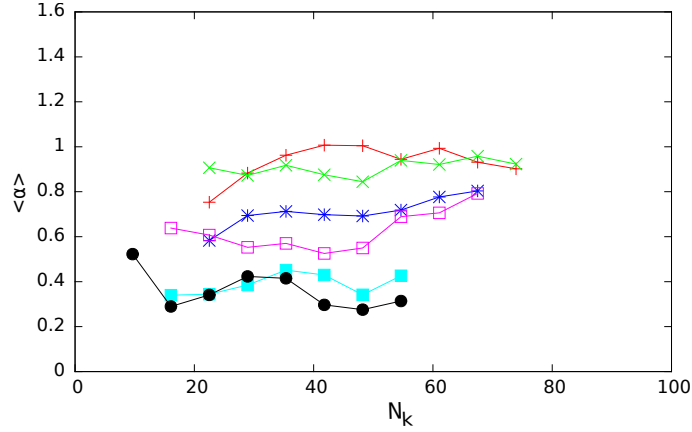


Figure 76: Average angle $\alpha \in [0; 0.5\pi]$ between the vector from the polymer's center of mass to the knot's center of mass and the flow axis in dependency of N_k for several values of Wi : 0 (red), 0.26 (green), 0.78 (blue), 1.30 (pink), 5.19 (turquoise), 12.96 (black).

Next, we plot the distance between the polymer's and the knot's center of mass against N_k , shown in fig. 77. Here, we spot something interesting: For high Wi , there is a clear correlation between distance and size of the knot, with higher N_k being linked to the knot being more distant from the polymer's center of mass. This is especially interesting because at high Wi , the polymers are stretched, and therefore, we expect knots passing from one polymer side to the other to have significantly lower distance to the polymer's center of mass - in short, fig. 77 suggests that a correlation between N_k and the angle to the principal axis exists after all, in a way that favors small knots near the center of the polymer and therefore, accordingly, knots orthogonal to the principal axis tend to be smaller than knots residing on either end of the polymer. In combination with the snapshots presented in section 5.2.4, we suggest that the biggest values of N_k come from the knot residing at either end and becoming extremely elongated due to high Wi (fig. 87), whereas no correlations were clearly identifiable between N_k and the angles to the main principal component. This is also supported by fig. 78, showing very clearly that at high distances, the angle between knot and principal component is typically very low. Since we did not know how much the knot itself would influence the orientation of the principal component, double-checking with fig. 79 confirms a correlation between low angle to high distance at high Wi . Again, we refer to section 5.2.4 for further explanation.

Fig. 80 provides a histogram of the number of configurations in dependency of N_k , presenting further and very clear evidence that small N_k and therefore tighter knots are favoured at high Wi , whereas a broader spectrum of generally wider knots are favoured at low Wi . There is a very interesting behavior to be observed in fig. 80: When increasing Wi , not only does the maximum shift from high N_k to smaller N_k , but before this shift

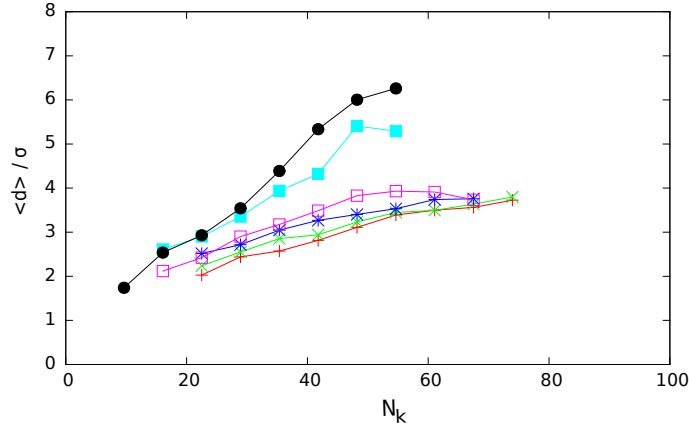


Figure 77: Distance between polymer's center of mass and knot's center of mass in dependency of N_k for several values of Wi : 0 (red), 0.26 (green), 0.78 (blue), 1.30 (pink), 5.19 (turquoise), 12.96 (black). For a very tight knot, the distance is small because the tight knot is, at high Wi , less confined to being aligned with the flow than a large knot. A very large knot, at high Wi , prefers to be further away from the polymer's center of mass, aligned with the flow.

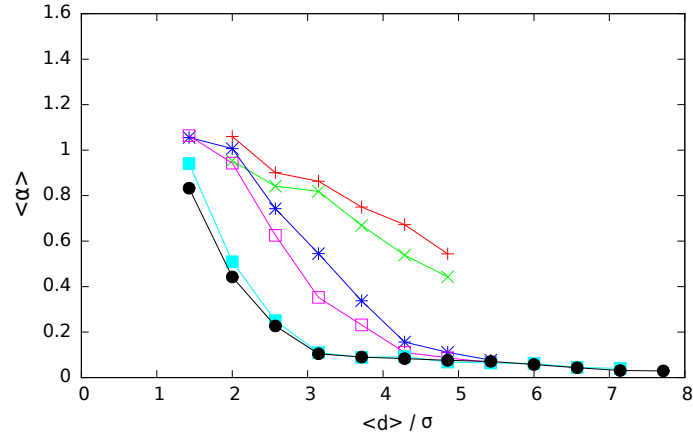


Figure 78: Average angle $\alpha \in [0; 0.5\pi]$ between the vector from the polymer's center of mass to the knot's center of mass and the main principal component in dependency of distance between polymer's center of mass and knot's center of mass for several values of Wi : 0 (red), 0.26 (green), 0.78 (blue), 1.30 (pink), 5.19 (turquoise), 12.96 (black).

happens, we observe two maxima for relatively low, but already perceivable shears (at $Wi = 0.78$ (blue) and 1.30 (pink)). This occurrence may be worth further investigation in future studies.

Fig. 81 shows the histogram for the distance between the knot's center of mass and the polymer's center of mass. What is interesting is that at high Wi , longer distances are registered than at low Wi , adding evidence to our suggestion that the knot is being elongated at either end at high Wi . Also, lower distances are registered more frequently at high Wi . We suggest that this is due to the knot being tightened and performing

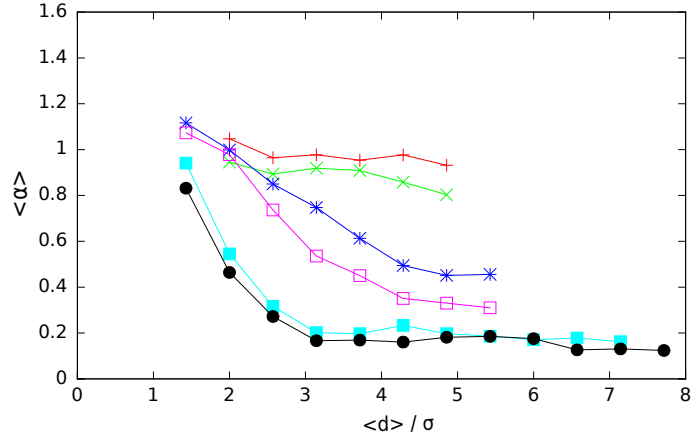


Figure 79: Average angle $\alpha \in [0; 0.5\pi]$ between the vector from the polymer's center of mass to the knot's center of mass and the flow axis in dependency of distance between polymer's center of mass and knot's center of mass for several values of Wi : 0 (red), 0.26 (green), 0.78 (blue), 1.30 (pink), 5.19 (turquoise), 12.96 (black).

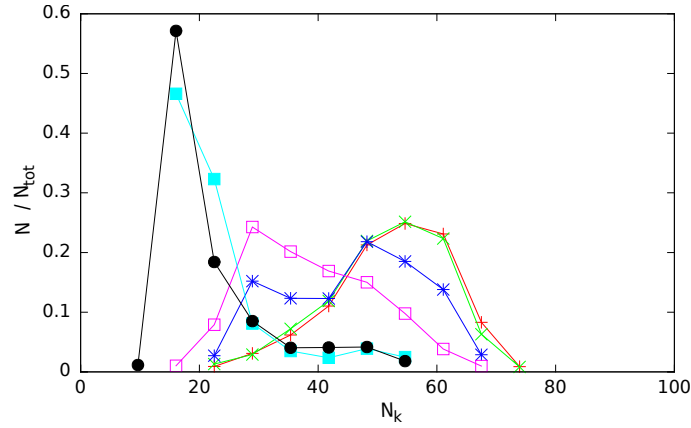


Figure 80: Histogram of number of configurations detected divided by total number of configurations, plotted against N_k for several values of Wi : 0 (red), 0.26 (green), 0.78 (blue), 1.30 (pink), 5.19 (turquoise), 12.96 (black).

tank-treading more frequently. The implications this has for the influence of a knot on tank-treading, however, shall have to be discussed elsewhere.

Another hint that bigger knots reside at either end of the elongated ring comes from fig. 82, where one finds the angle between the first principal component and the flow axis to be slightly correlated to the knot's R_g in the sense that this angle, at low Wi , seems to be bigger at high radius of gyration (with the knot moving freely and, if large, influencing the principal component more strongly) and at high Wi , this tendency is lost (with even large knots not influencing the principal component much, for the knot would be elongated and aligned with the flow, which corresponds to a low angle).

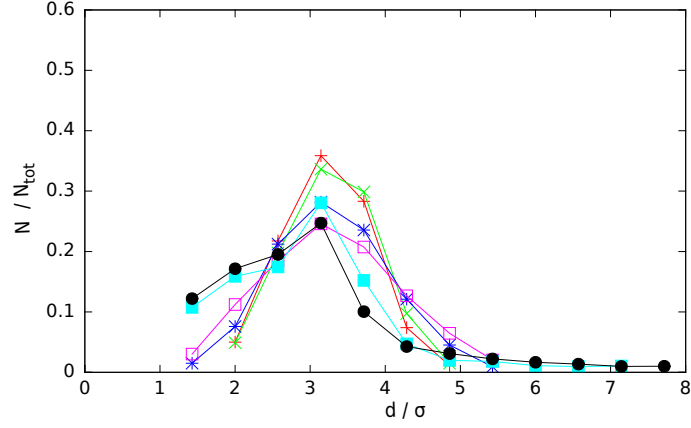


Figure 81: Histogram of number of configurations detected divided by total number of configurations, plotted against distance between polymer's center of mass and knot's center of mass for several values of Wi : 0 (red), 0.26 (green), 0.78 (blue), 1.30 (pink), 5.19 (turquoise), 12.96 (black).

And finally, fig. 83 showcasing the histogram for the radius of gyration is extremely similar to fig. 80, which is not at all surprising. It seems obvious that N_k is heavily correlated to the knot's R_g .

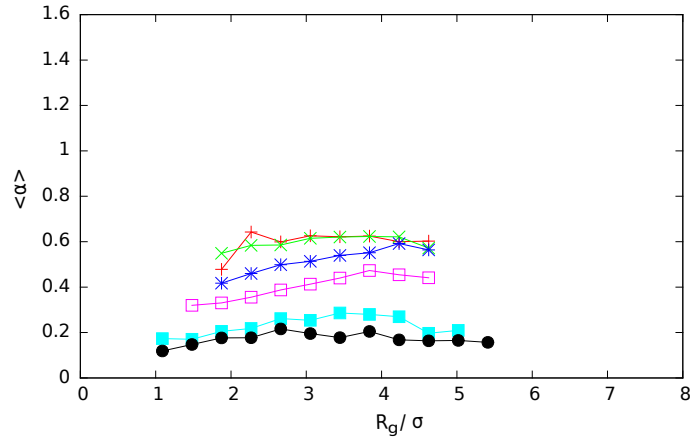


Figure 82: Average angle $\alpha \in [0; 0.5\pi]$ between the main principal component and the flow axis in dependency of the knot's radius of gyration for several values of Wi : 0 (red), 0.26 (green), 0.78 (blue), 1.30 (pink), 5.19 (turquoise), 12.96 (black).

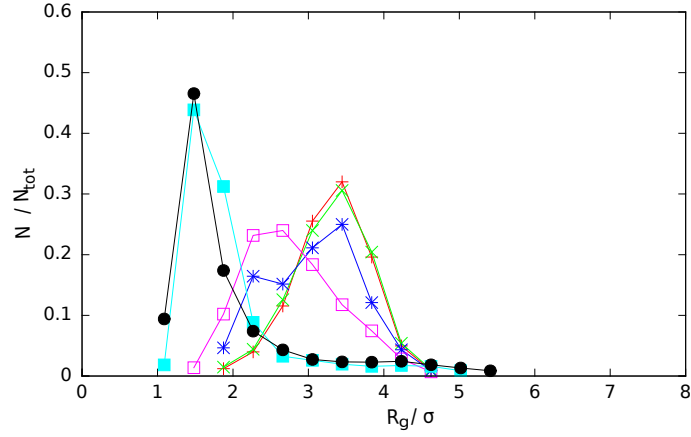


Figure 83: Histogram of number of configurations detected divided by total number of configurations, plotted against the knot's radius of gyration for several values of Wi : 0 (red), 0.26 (green), 0.78 (blue), 1.30 (pink), 5.19 (turquoise), 12.96 (black).

5.2.4 VMD Snapshots

We have taken snapshots of interesting configurations of two simulation runs at high Wi (2.60 and 12.96) with VMD [26] to illustrate further the points and suggestions made in section 5.2.3. Most of the figures in this section should be rather self-explanatory, but descriptions are used to clarify where needed. For all these snapshots, the pink domain marks the detected knot, while the blue domain is the rest of the ring. Note that, since VMD has problems handling bonds between two types of atoms, there is no bond displayed between pink and blue beads, however, that obviously does not mean the bond is not there.

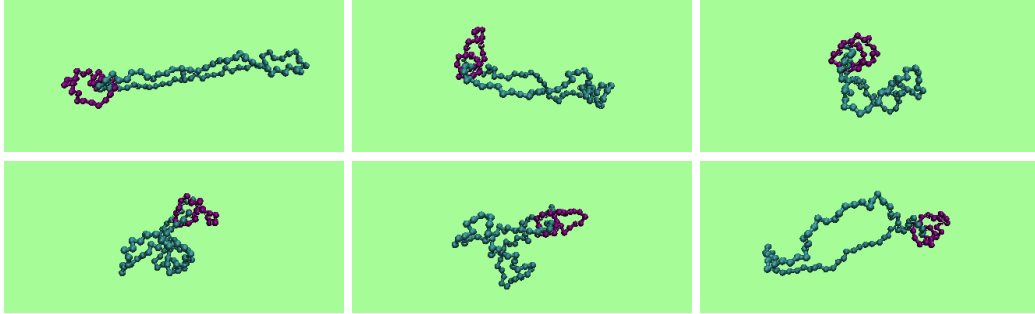


Figure 84: From left to right, top to bottom: Tumbling cycle of a 3_1 -knotted ring at $Wi = 2.60$. In this tumbling cycle, the knot resides aligned with the flow and causes the tumbling by itself.

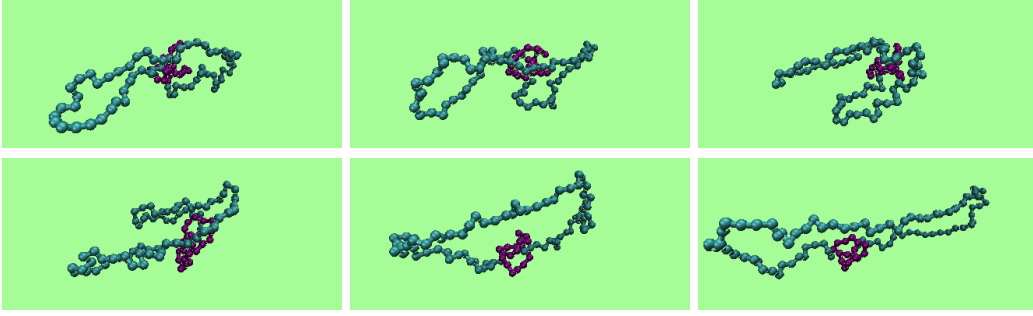


Figure 85: From left to right, top to bottom: Tumbling cycle of a 3_1 -knotted ring at $Wi = 2.60$. In this tumbling cycle, the knot is located somewhere on the ring, but not aligned with the flow. The tumbling is caused by the elongated ends of the polymer, not by the knot. However, the knot acts as a center for the tumbling cycle.

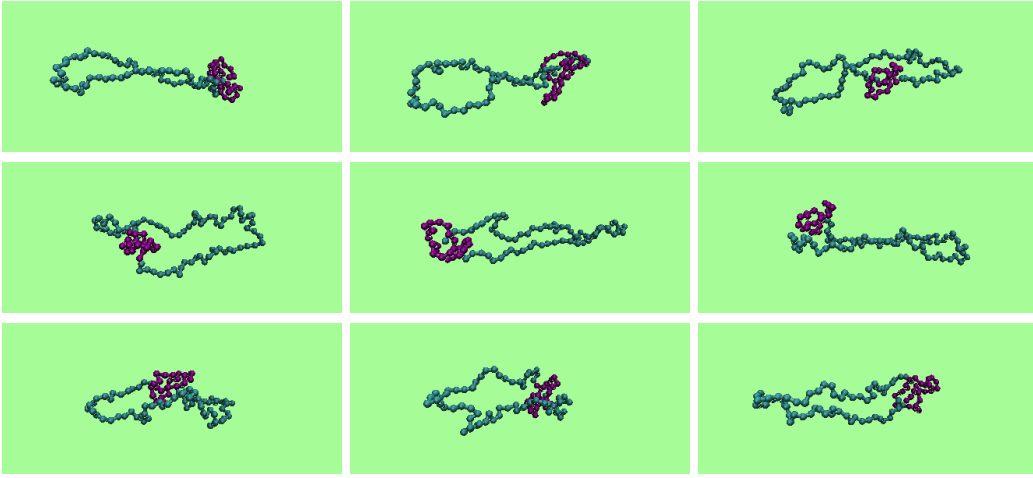


Figure 86: From left to right, top to bottom: Tank-treading cycle of a 3_1 -knotted ring at $Wi = 2.60$. In this tank-treading cycle, instead of a separate segment of beads performing the tank-treading, the motion is clearly visible when looking at the motion of the knot itself, further indicating that the knot acts as a kind of large bead when tight.

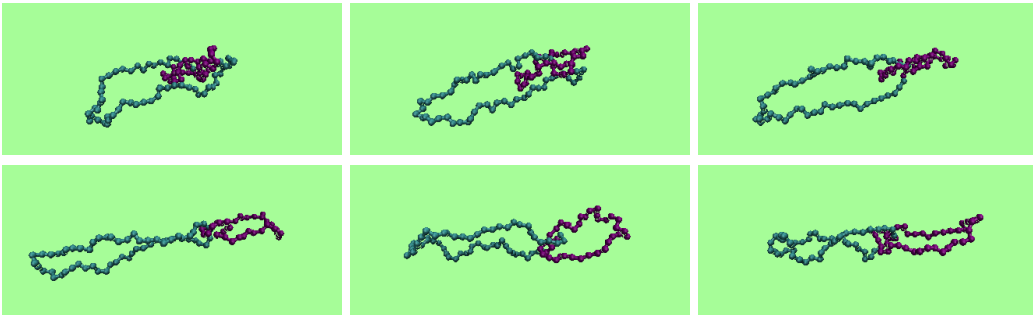


Figure 87: From left to right, top to bottom: Consecutive shots of a large knot forming at high N_k on the 3_1 -knotted ring at $Wi = 2.60$. The knot, if not tight by the time it gets to either end of the polymer, becomes elongated while residing there, aligned with the flow.

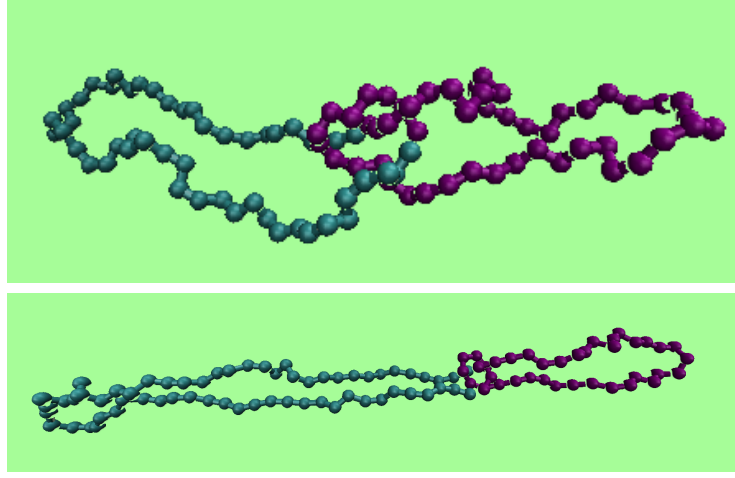


Figure 88: The elongated 3_1 knotted ring at large N_k and knot aligned with flow, taken at $Wi = 2.60$ (top) and $Wi = 12.96$ (bottom). Perspective is adjusted to see the crossing of the knot. The crossing is well-located, while one loop of the knot is stretched due to shear.

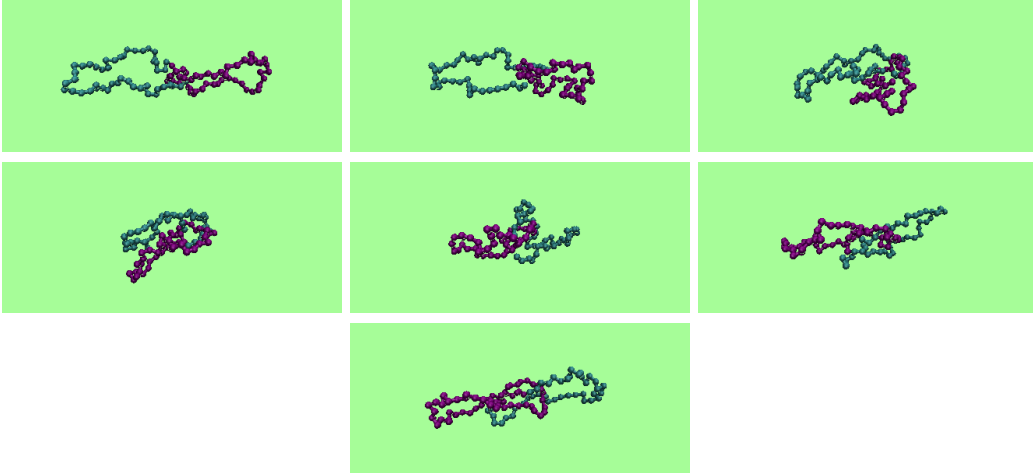


Figure 89: From left to right, top to bottom: Tumbling cycle of a 3_1 -knotted ring at $Wi = 2.60$ and at large N_k . In this tumbling cycle, the knot is elongated and aligned with the flow. This tumbling cycle is a cross between the cycles presented in figures 85 and 84. One end is actually part of the knot. The elongated ends cause the tumbling, and the motion is centered around the well-located crossing residing almost precisely at the polymer's center of mass.

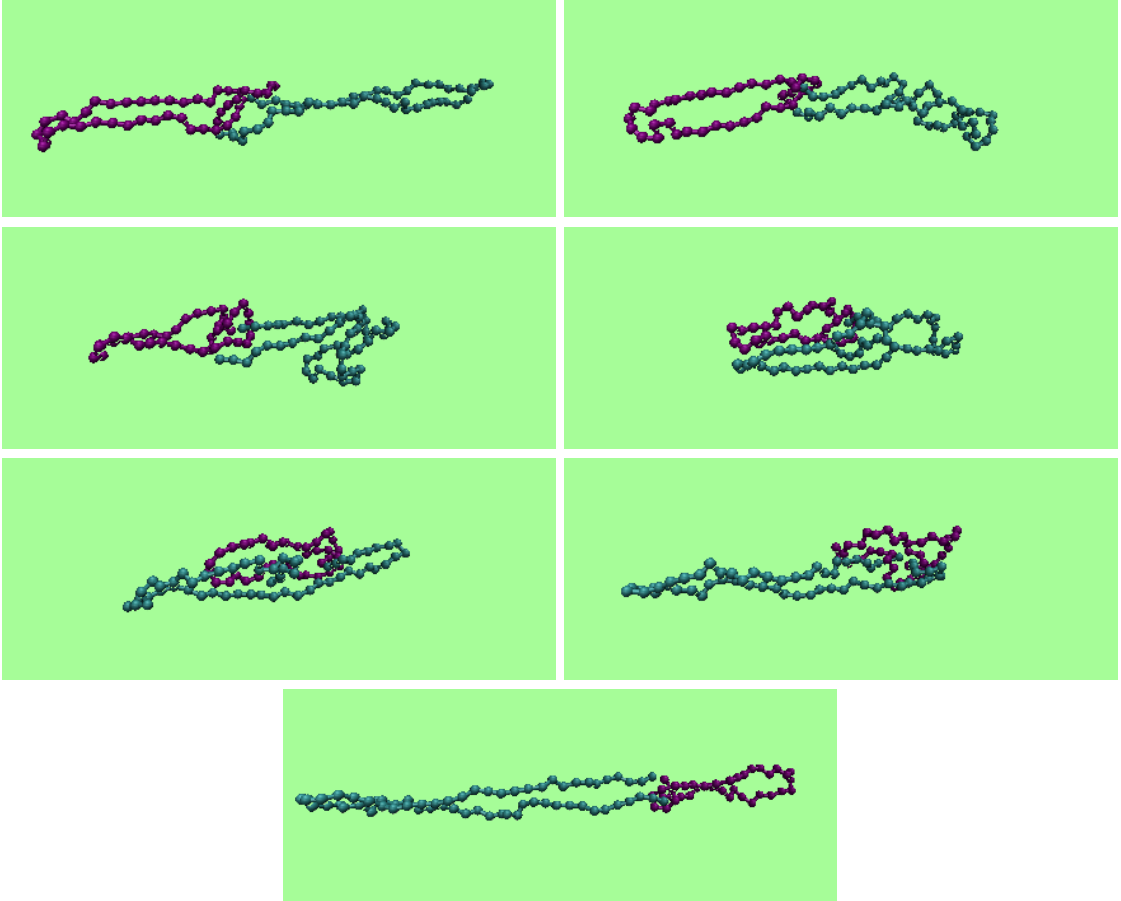


Figure 90: From left to right, top to bottom: Tumbling cycle of a 3_1 -knotted ring at $Wi = 12.96$ and at large N_k . In this tumbling cycle, the knot is elongated and aligned with the flow. The characteristics of this cycle are very similar to the one presented in figure 89, although at significantly higher Wi . Perspective was changed to looking down on the flow-vorticity-plane to get a better look at the still well-located crossing.

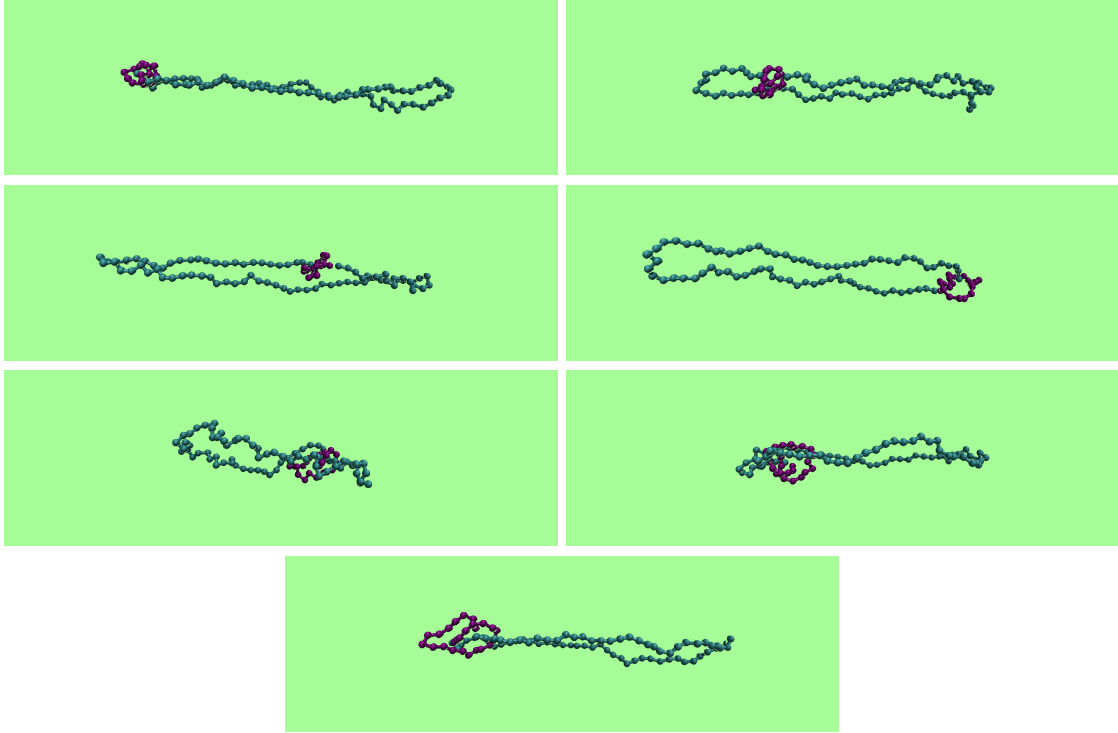


Figure 91: From left to right, top to bottom: Tank-treading cycle of a 3_1 -knotted ring at $Wi = 12.96$. In this tank-treading cycle, the knot is performing the motion by itself, similar to fig. 86. However, at high Wi , the knot is tighter while doing so.

6 Conclusions and Outlook

In this work, we have applied the hybrid approach of Multi-Particle Collision Dynamics (MPCD) to simulate individual polymers of different topology in a solvent under shear. Most importantly, we have compared the shape parameters of an ordinary cyclic polymer to that of a 3_1 -knotted ring and analysed multiple other features of the 3_1 -knotted ring under shear.

We have presented evidence that the radius of gyration of the 3_1 -knotted ring behaves in much the same way but changes more abruptly and reaches its terminal value at lower Wi compared to the ordinary ring, and that the same holds true for relative shape anisotropy δ^* , prolateness S^* , asphericity b and acylindricity c . We have found the deformational resistance m_G to be increasing slower for the 3_1 -knotted ring. (section 5.2.1) Alignment angle χ follows the same pattern for both 3_1 -knotted and normal ring, but is typically lower for the 3_1 -knotted ring. The main principal component aligns quicker with the flow axis in the case of the 3_1 -knotted ring. (section 5.2.2)

Furthermore, we have analysed the properties of the knot itself. The average number of beads on the knot, $\langle N_k \rangle$, decreases with increasing Wi . The average distance between the polymer's center of mass and the knot's center of mass is insignificantly lower at high Wi . However, we have found clear evidence for the knot to prefer being located at either end of the ring at high Wi , aligned with the flow. Implications were found that at high Wi , N_k is typically low, but once peaks occur, a consistently larger N_k is maintained over a longer period of time. Finally, we have presented evidence that at high Wi , large values of N_k are more likely to occur at longer distances from the polymer's center of mass. (section 5.2.3)

Additionally, we have provided snapshots of interesting configurations, such as tumbling and tank-treading cycles of the 3_1 -knotted ring at high Wi , although we have not discussed these motions in detail in this thesis. (section 5.2.4)

All considered, a few open questions remain, which shall undoubtedly be addressed by the scientific community, sooner or later. For one, the time-dependency of N_k for different values of Wi could not be shown to our satisfaction. Secondly, tumbling- and tank-treading motions have not been analysed thoroughly in this thesis, but would certainly justify further investigation because of their importance. In addition to that, simulating 3_1 -knotted rings of $N > 100$ and, generally speaking, at different numbers of beads, might shed more light on $N_k(t)$ and provide results with higher accuracy. Last but not least, we suggest further studies on the influence of knots on rings under shear, such as simulations of 2 or more knots, eventually also not only 3_1 but knots of different types, residing on the same ring, to see how such changes affect the results found in this work.

7 References

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Appendix A: Abstract (English)

The purpose of this Master's Thesis is the calculation of conformations and dynamic modes of polymers of different topologies embedded in a fluid under shear. The simulated fluid is tested for characteristic values. The behavior of linear, circular and, most importantly, 3_1 (trefoil) knotted polymers embedded in the sheared fluid is analysed.

The fluid is simulated in agreement with hydrodynamics, the integration of the polymer's equations of motion obeys the Velocity-Verlet algorithm, which is commonly used for molecular dynamics. For reasons of efficiency, the hybrid approach of Multi-Particle Collision Dynamics (MPCD) is set up, tested and employed to compute the fluid. This method provides an efficient and accurate coupling of the polymer's molecular dynamics to the solvent's hydrodynamics.

The focus lies on the correlation between knot size and angle between knot center of mass and first principal axis relative to the polymer's center of mass, as well as computation of characteristic shape parameters in presence of a knot in comparison to cyclic polymers without knots, each in dependency of Weissenberg number.

We obtain evidence that for the 3_1 -knotted ring at high Weissenberg number, knots develop a tendency to be located at either end of the polymer, aligned with the flow. We also find that the average number of beads on the knot decreases with increasing shear. Additionally, we find evidence that the 3_1 -knotted ring reacts quicker in terms of shape parameters to increasing shear than ordinary rings with the same number of beads.

Appendix B: Abstract (German)

Ziel der Masterarbeit ist die Bestimmung der Konformationen und dynamischen Moden von Polymeren unterschiedlicher Topologie in einem Scherung ausgesetzten Fluid. Das simulierte Fluid wird auf charakteristische Eigenschaften getestet. Das Verhalten linearer, ringförmiger und vor allem 3_1 -(Trefoil-)verknöteter Polymere in einem Scherung ausgesetzten Fluid wird analysiert.

Die Simulation des Fluids erfolgt unter Berücksichtigung der Hydrodynamik, die Integration der Bewegungsgleichungen des Polymers folgt dem für die Molekulardynamik gebräuchlichen Velocity-Verlet-Algorithmus. Zur Berechnung des Fluids wird der Hybridansatz der Multi-Particle Collision Dynamics (MPCD) aufgesetzt, getestet und angewendet. Die Methode bietet eine effiziente und akkurate Kopplung der Polymerdynamik mit der Hydrodynamik des Lösungsmittels.

Das Hauptaugenmerk liegt auf dem Zusammenhang zwischen Knotengröße und Winkel zwischen Knotenmittelpunkt und Hauptorientierungsachse relativ zum Polymerschwerpunkt, sowie auf der Bestimmung charakteristischer Formparameter unter Anwesenheit des Knotens im Vergleich mit Ringpolymeren ohne Knoten, jeweils in Abhängigkeit der Weissenbergzahl.

Unsere Ergebnisse suggerieren, dass Knoten auf dem 3_1 -verknöteten Ring bei hoher Weissenbergzahl eine Tendenz entwickeln, an einem von beiden Enden des Polymers lokalisiert zu sein, parallel zur Flussrichtung. Die mittlere Zahl Beads, welche Teil des Knotens sind, sinkt mit steigender Scherung. Zusätzlich zeigt sich, dass der 3_1 -verknötete Ring im Bezug auf Formparameter schneller auf wachsende Scherung reagiert, als gewöhnliche Ringe mit derselben Anzahl von Beads.