COMPLEX STRESS RELAXATIONS IN SOFT MATTER STUDIED BY COMPUTATIONAL RHEOLOGY

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COMPLEX STRESS RELAXATIONS IN SOFT MATTER STUDIED BY COMPUTATIONAL RHEOLOGY

DISSERTATION

to obtain
the degree of doctor at the University of Twente,
on the authority of the rector magnificus,
prof. dr. T.T.M. Palstra,
on account of the decision of the graduation committee,
to be publicly defended
on Friday 12 April 2019 at 14:45

by

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Typeset in L^AT_EX. Printed by IPSKAMP.

ISBN: 978-90-365-4746-8

DOI: 10.3990/1.9789036547468

URL: <https://doi.org/10.3990/1.9789036547468>

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The work leading to this thesis has received funding from the People Programme (Marie Skłodowska-Curie Actions) of the European Union's Seventh Framework Programme (FP7/2007-2013) under REA grant agreement 607937 – SUPOLEN project.

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Chapter 1

Introduction

1.1 Introduction to Soft Matter Rheology

1.1.1 *What is Soft Matter and why study it?*

Soft Matter is a state of matter which is easily deformed by external stimuli like temperature or mechanical pressure. Their properties are intermediate between those of solids and liquids. Under normal conditions of temperature and pressure, they generally resemble solids, while at the same time are capable of being easily deformed by weak forces. Examples include physical systems like colloidal dispersions, polymers, surfactants and biological materials like tissue. Soft matter is ubiquitous in our daily lives in the form of everyday utilities like toothpaste, cosmetics, gels, foams, detergents, dairy products, etc. In addition, soft matter forms a significant bulk of useful industrial output like pharmaceutical products, lubricants etc. As an example of soft matter in nature, let us consider the constituents of our very bodies, tissues. Biological tissue has evolved over long millennia in its present form due to its ability to withstand stresses, sustain damage and at the same time repair and heal. As a material, biological tissue has this remarkable ability because it can absorb stress by deformation, like a fluid, while at the same time, resist total breakage and ‘spring’ back to its normal form, like a solid. Such ability to adapt to external situations is a hallmark of soft matter and is a reason for its widespread presence both in natural and artificial life.

The unique ability of soft matter to be amenable to weak mechanical deformation while at the same time maintain a semblance of structural integrity is a reason for their widespread usage. Due to the fact that they are solids but can deform, they are also known as complex fluids, since they do not flow easily like simple fluids, but yield under some pressure, unlike simple solids. This classifies them as viscoelastic materials. The rich set of viscoelastic behaviours exhibited by soft matter are a consequence of the complex many-body interactions between their molecular constituents. A complex interplay of varied microscopic factors

operating at the molecular level, coupled with external inputs which may or may not be present, determine their macroscopic properties. Fortunately, the nature of their chemical composition does not matter much as their mechanical properties mostly inherit from the physical interactions between the molecules they are composed of. As such, diverse subtypes of soft matter like polymers, soft deformable colloids, etc. can be studied independent of their chemical constitution, at least when considering their response to external mechanical deformations. Such an abstraction has been found to be very useful so far in studying the mechanical properties of soft matter purely as a function of their physical rather than chemical properties [1, 2, 3, 4, 5, 6].

The typical characteristics of soft matter arise from the fact that most molecular interactions in them are due to weak physical rather than strong chemical covalent bonds. The latter need large amounts of energy to break whereas the former are easily broken and also often reform with the same ease. This molecular behaviour imparts soft materials the necessary flexibility to exhibit their properties. By controlling the nature and strength of these weak interactions, interesting next-generation smart materials like shape-memory polymers [7], self-healing gels [8, 9, 10], nano-devices for targeted drug delivery [11], etc. can be synthesized. These materials will form the backbone of future industrial applications where increasing amounts of stimuli-responsive behaviour will be included into the fabric of the material itself by tailoring the properties of its constituent components. Thus, the mechanical properties of soft matter are not just a subject of academic interest but have great practical utility and this will only increase in the years to come.

1.1.2 *Rheology of Soft Matter: A gentle introduction*

The study of flow properties of soft matter and their response to stress comprises a branch of physics called rheology. Rheology can also be considered to be ‘mechanical spectroscopy’, in analogy with other spectroscopic techniques used to probe matter at molecular scales. On application of a deformation to the sample under study, the material relaxes from this disturbed state by dissipating this applied energy, which can be measured by tracking the stress response of the material as a function of time. This ‘mechanical spectrum’ yields information about the various molecular processes occurring at different time and length scales in the material. In order to achieve a desired set of behaviours, we of course have to quantitatively and qualitatively understand the effect of these molecular properties and interactions at the macroscopic scale. This necessitates the development of theories to describe soft matter rheology [1, 2, 3, 4, 5, 6].

Although having its inception in the atomic hypothesis from Boltzmann and Einstein, soft matter research, at least on timescales of scientific discovery, is fairly recent and continues to grow. As a whole, it is a vibrant topic of contemporary condensed matter research. While the simple liquid and solid phases of matter are rather well understood due to their relatively simple molecular structure and interactions, the intermediate phase region inhab-

ited by soft matter still presents considerable challenges for research. This is because several molecular processes spanning a wide range of time and length scales operate simultaneously in soft matter systems and have to be incorporated into any theoretical treatment. If we take polymers as an example, which are extremely important as they find applications in fields as diverse as rubbers, plastics, paints, food industry, etc., it was only in the latter half of the 20th century that quantitative theories to describe their rheology were given due to the work of Rouse, Edwards, Doi, de Gennes and other workers [12, 13, 14, 15, 16, 17]. This is due to their complicated molecular structure which comprises of long chains of monomers that constantly change their conformations, which becomes even more complex when the chains become very long, resulting in so-called entanglement effects [18, 19, 20] and interactions with several other neighbouring chains, thus making it quite difficult for theorists to provide simple theories for polymer flow. However, considerable progress has been made since the 1960's in providing theories of polymer behaviour due to advances in synthesis and other experimental techniques. For instance, the Nobel Prize in Physics in 1991 was awarded to Pierre-Gilles de Gennes for showing that *'methods developed for studying order phenomena in simple systems can be generalized to more complex forms of matter, in particular to liquid crystals and polymers'*. Even so, as more complicated systems are being synthesized due to increasingly sophisticated synthesis techniques, a pure theoretical and/or experimental approach alone is not sufficient to understand the rheology of this interesting class of matter.

1.1.3 *The need for a computational approach*

Due to the complexity of the theories used to describe soft matter systems which stems from the need to incorporate various time and length scales into the theoretical approach, we need to make use of computer simulations of soft matter models to understand the effect of various molecular processes on their macroscopic flow behaviour. A simulation can basically be described as viewing the 'theory in action' in a computer. Once the mathematical equations describing the dynamics of a soft matter system are known, we can run them on virtual models of the physical system in question and extract static and dynamic properties from the results of the simulation. In a simulation, we can apply external inputs of our choice, add or remove chosen interactions and investigate the entire phase space of possibilities. A great advantage of the computational approach is that the results of the simulation are just enactments of the theory and if the models that are simulated faithfully capture the features of the particular phenomenon being studied, then the real system will behave exactly as predicted. Of course, care must be taken while interpreting the results of the simulations since the models fed to it are abstractions of the real physical system. Still, due to the raw hardware power available today, increasingly sophisticated models can be simulated, making the computational approach a strong pillar of rheological research.

Of the various approaches available to simulate soft-matter, there is the continuum method used in techniques like Computational Fluid Dynamics (CFD), in which the material being

studied is assumed to be a continuum and the velocity and density at each point along the flow are given as a continuous field. Flows of simple fluids like water are simulated by the Navier Stokes Equations in the continuum approach. However, in order to simulate the flows of complex fluids like polymer solutions, additional constitutive relations have to be used to modify the stress tensor term in Navier Stokes to include the complexity arising from more intricate inter-particle interactions at the molecular scale which are not explicitly resolved. Since these methods operate at the continuum, it is a task of some magnitude to incorporate microscopic particle properties since the simulation resolution is several orders of magnitude larger than the actual particle sizes. Thus the continuum method adopts a top-down approach. In order to include more details, a bottom-up approach is taken by particle-based simulation techniques that operate at much finer time and length scales like Molecular Dynamics (MD), Brownian Dynamics (BD), etc. Of course, with the computing speeds available today, the time and length scales that can be simulated with particle-based techniques are much smaller than in CFD, but a rich variety of detail in the form of actual molecular coordinates like in MD or coarse-grained descriptions like in BD can be studied, thereby directly probing interactions at the molecular scale which have an enormous impact on the macroscopic flow properties.

In this thesis we perform simulations of the dynamics of different soft matter systems like telechelic star polymers and soft colloids in order to investigate their stress response. In addition to presenting the results of simulations with Brownian Dynamics (BD), the mesoscopic simulation technique of choice in this thesis, fundamental work has been done on polymer dynamics and the Boltzmann Superposition principle in general, thereby offering greater insight into our understanding of soft matter.

The remainder of the chapter is organized as follows. Starting with a brief overview of the theoretical background of rheology, a section describing the computational techniques used to study the systems in this chapter will follow. The chapter ends with an outline of the thesis.

1.2 Theoretical Background

The response of soft materials to mechanical deformation is a phenomenon of exceptional importance and forms the bedrock of rheological research. When a soft material is deformed, it stores the stress and releases it depending upon several factors such as the molecular shape of its constituents, the spacing between them, temperature, etc. By measuring the response of a system to applied stress, rich information about the different processes spanning ranges of molecular time and length scales can be obtained. Various experimental techniques like linear and non-linear rheology, superposition rheology, etc. exist to determine flow behaviour by investigating the stress response. This section presents a brief outline of the background theory that is used throughout the thesis.

1.2.1 The Stress Relaxation Moduli

The stress response of a viscoelastic material, $\sigma(t)$, at a given time t , to a series of strain rates $\dot{\gamma}$ applied at some time in the past, is a weighted sum of all these past deformations and each strain produces a stress independent of all the others. This is called the Boltzmann Superposition Principle and is expressed mathematically in integral form as:

$$\sigma(t) = \int_{-\infty}^t G(t-t') \dot{\gamma}(t') dt' \quad (1.1)$$

where $G(t)$ is a memory function, which is also the stress response of the system to a unit step strain. $G(t)$, also known as the *stress relaxation modulus* or *shear relaxation modulus* is a function of the molecular properties of the material and is extremely important in determining the equilibrium flow properties of the material under study. With the Green-Kubo relations, the equilibrium $G(t)$ under no-shear conditions is given by:

$$G(t) = \frac{V}{k_B T} \langle \sigma_{\alpha\beta}(t) \sigma_{\alpha\beta}(0) \rangle \quad (1.2)$$

where V is the volume of the material, k_B is Boltzmann's constant, T is the temperature, $\sigma_{\alpha\beta}(t)$ is the $\alpha\beta$ component of the stress tensor at time t and the brackets denote an ensemble average. Eq. 1.2 provides a means of obtaining the relaxation modulus in a simulation under zero external strain.

Under linear rheology, a small amplitude oscillatory strain, $\gamma = A \sin(\omega t)$, is applied to the system. By fitting the resulting sinusoidal stress with two components which are in and out of phase with the oscillatory strain, the storage modulus, $G'(\omega)$, and the loss modulus $G''(\omega)$ are respectively obtained. They are related to the sine and cosine transforms of the $G(t)$ respectively and are given by:

$$G'(\omega) = \omega \int_0^\infty G(t) \sin(\omega t) dt \quad (1.3)$$

$$G''(\omega) = \omega \int_0^\infty G(t) \cos(\omega t) dt \quad (1.4)$$

These moduli are a function of the equilibrium molecular properties of the system. The storage modulus is a measure of the solid-like behaviour of the system and the loss modulus quantifies the liquid-like nature. At small values of the frequency ω , generally the loss modulus dominates, which means that at long times the material flows like a liquid, and vice versa, i.e. at small timescales the material behaves as a solid. A log-log plot of the two moduli versus ω is known as the frequency spectrum and represents the different domains of behavior. The crossovers between the two moduli represent important timescales of stress relaxation in the system.

1.2.2 The Maxwell Model

Since soft materials are viscoelastic in nature, we will describe the method of quantifying such behaviour here. If a strain γ is applied to an elastic solid within the elastic limit, the solid responds with a stress σ proportional to the strain as:

$$\sigma = G\gamma \quad (1.5)$$

where G is a constant of proportionality called the elastic modulus.

On the other hand, if a deformation given by a strain rate $\dot{\gamma}$ is applied to a simple Newtonian liquid, it responds with a stress proportional to this rate:

$$\sigma = \eta\dot{\gamma} \quad (1.6)$$

where η is the viscosity of the liquid. Thus, a liquid response is ‘orthogonal’ to that of a solid and tends to dissipate stress, whereas a solid stores stress. A viscoelastic material has both solid and liquid-like characteristics and can be modeled by a so-called spring-dashpot system, with the spring representing the solid part and the dissipative dashpot forming the liquid part. If a spring and dashpot are put in series, we get the well known ‘Maxwell model’, which is a model representation of the stress response of a material.

Since several molecular processes are generally at play in a typical soft matter system, in standard rheology, a generalized Maxwell model is often used to describe the rheology of the material. For a system with N degrees of freedom, say, by placing N Maxwell elements in parallel, a complex response spectrum with different time-scales τ_i can be fitted. The $G(t)$ in such a case is given by:

$$G(t) = \sum_{i=1}^N G_i e^{-t/\tau_i} \quad (1.7)$$

where G_i is the magnitude contributed by the i ’th molecular process to the overall relaxation. The storage and loss moduli then become:

$$G'(\omega) = \sum_{i=1}^N G_i \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2} \quad (1.8)$$

$$G''(\omega) = \sum_{i=1}^N G_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2} \quad (1.9)$$

At small frequencies, the Maxwell model yields slopes of 2 and 1 respectively for the G' and G'' . Most systems display this relaxation trend showing that terminal behaviour is regularly Maxwellian in soft matter. A departure of these slopes is a sign that either terminal behaviour has not been reached, or that some complex non-linear phenomena are occurring in the system at long timescales. The thesis has ample examples of the latter.

So far we have described the quantities which are important at equilibrium (rest). Having described the basics of the rheological quantities used and concepts explored in the thesis, we next briefly outline the basics of polymer dynamics, since the systems studied in this thesis are composed of polymers.

1.2.3 Polymer Dynamics: Coarse-graining and The Rouse Model

Polymers form an important class of soft matter. They are basically long chain molecules synthesized by joining together elementary building block called monomers. Polymers of different shapes like linear, branched (which includes H-shaped, star-shaped, combs, etc.) or ring-shaped have been synthesized and display vastly different macroscopic flow properties depending on the shape. A polymer, in analogy with a rubber band, can stretch and deform under an external strain. The familiar ‘stretchy’ behaviour of rubber and chewing gum is due to the nature of the polymers they are composed of. Proteins, DNA, and other highly important biomolecules are polymers. All the systems studied in this thesis have polymers as their main component (Chapters 2,3,5,6) or have entities that are composed of polymers (Chapter 4), hence we present an overview of polymer dynamics in this subsection.

Generally, the bead-spring representation is a popular way of modeling polymers, which imparts flexibility to the polymer via springs. A polymer made of n chemical units (monomers) can be considered to be made up of N so-called ‘Kuhn’ segments connected by springs of constant k_s , where $n \gg N$, with each Kuhn segment having no memory of the conformation of its neighbours [3, 4]. By bunching together a certain number of chemical monomers into a bigger blob, details of individual monomer activity are removed as they do not play a big role at larger length and time scales. Such a process of omitting small-scale details to obtain a simpler high-level representation is called ‘coarse-graining’ and has been extensively employed in this thesis.

The most simple bead-spring model of polymer dynamics is the Rouse model. It assumes that the polymers do not have any excluded volume interactions between them, i.e. they are free to cross each other and ignores hydrodynamic interactions. The beads interact with their neighbours by harmonic springs (thereby imparting elasticity), along with a dissipative friction (liquid-like dissipation) and a stochastic random force which is uncorrelated with other degrees of freedom. The basic equation of motion is the overdamped Langevin-equation leading to a Brownian propagator. It is very successful in describing the rheology of melts and concentrated solutions, but does not work for high molecular weight polymers where so-called entanglement effects dominate or in good solvents where hydrodynamics become important.

As an example, consider a linear chain with N beads. The Rouse equations of motion for this chain are a system of coupled stochastic differential equations given by:

$$\frac{d\vec{R}_1}{dt} = \frac{k_s}{\xi}(\vec{R}_2 - \vec{R}_1) + \vec{f}_1(t) \quad (1.10)$$

$$\frac{d\vec{R}_2}{dt} = \frac{k_s}{\xi}(\vec{R}_1 + \vec{R}_3 - 2\vec{R}_2) + \vec{f}_2(t) \quad (1.11)$$

$$\vdots \quad (1.12)$$

$$\frac{d\vec{R}_n}{dt} = \frac{k_s}{\xi}(\vec{R}_{n-1} + \vec{R}_{n+1} - 2\vec{R}_n) + \vec{f}_n(t) \quad (1.13)$$

$$\vdots \quad (1.14)$$

$$\frac{d\vec{R}_N}{dt} = \frac{k_s}{\xi}(\vec{R}_{N-1} - \vec{R}_N) + \vec{f}_N(t) \quad (1.15)$$

where $\{\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N\}$ are the set of co-ordinates of the N beads making up the linear chain. A conformation is a set of these vectors. The polymer constantly changes its conformations as the individual beads move due to random thermal motion by the stochastic Brownian forces $\vec{f}_n(t)$, which obey the fluctuation-dissipation theorem (see Ref. [3]), given by:

$$\langle f_{n\alpha}(t_1) f_{m\beta}(t_2) \rangle = 2 \frac{k_B T}{\xi} \delta(t_1 - t_2) \delta_{n,m} \delta_{\alpha,\beta} \quad (1.16)$$

where the brackets denote an ensemble average, $\delta(t_1 - t_2)$ is the Dirac delta function and $\delta_{n,m}$ is the Kronecker delta. Eq. 1.16 says that the Brownian forces are uncorrelated with each other and with past values in time. ξ is a friction coefficient quantifying the dissipation. The springs connecting the beads are of strength k_s given by:

$$k_s = \frac{3k_B T}{b^2} \quad (1.17)$$

where b is the length of a Kuhn segment. Since there are no energetic interactions in the model, thermal motion tries to maximize the polymer's entropy. Hence the springs connecting the beads together are referred to as 'entropic' springs, since entropy is the main driving factor behind changing the polymer's conformations. We refer the reader to Refs. [3, 4] for the details of the derivation.

We can write the system of equations 1.15 in matrix form as:

$$\frac{dR}{dt} = -wTR + F \quad (1.18)$$

where $R = \{R_{1\alpha}, R_{2\alpha}, \dots, R_{N\alpha}\}$, α is either x,y or z. Similarly, F is a vector containing the components of the brownian forces, $F = \{F_{1\alpha}, F_{2\alpha}, \dots, F_{N\alpha}\}$. If the polymer is represented

as a graph with the beads being the vertices and the springs connecting them the edges, the matrix T , called the Rouse connectivity matrix, is the Laplacian of the graph representing the polymer and depends on its shape. A polymer consisting of N beads leads to a square Rouse matrix of size N , with the diagonal (i, i) entries of T being the degree of each vertex and the off-diagonal (i, j) entries being the negative of the number of springs between the two beads i and j . Examples of such Rouse matrices for linear and star polymers are found in Chapter 2 and Chapter 6 of this thesis respectively.

Multiplying both sides of Eq. 1.18 by the inverse of the diagonalizing orthonormal matrix S , whose columns are the eigenvectors of T , the Rouse equations are decoupled into a set of N independent normal modes $\vec{X}_k(t)$ ([21, 22]), whose dynamics are given by:

$$\frac{d\vec{X}_k}{dt} = -\frac{1}{\tau_k} \vec{X}_k + \vec{F}_k(t) \quad (1.19)$$

where the normal modes X are related to R as $R = SX$. τ_k is the timescale of relaxation of the k 'th mode and $\vec{F}_k(t)$ again obeys the fluctuation dissipation theorem. τ_k is related to the k 'th eigenvalue of T , λ_k , by:

$$\tau_k = \frac{\xi}{k_s \lambda_k} \quad (1.20)$$

The N 'th mode represents the smallest wavelength of oscillation corresponding to a single monomer and decays first, the first mode corresponds to the motion of the whole molecule. Taken together, the Rouse modes decide the manner of relaxation of the polymer after a deformation.

These vibratory ‘breathing’ modes are a function of the architecture of the polymer. A linear polymer thus has very different properties compared to say a star shaped polymer, purely on the basis of its shape. By diagonalizing the Rouse interaction matrix, which is the Laplacian matrix of the graph of the polymer, the normal modes are obtained and the eigenvalues of the same matrix represent the time-scales of relaxation of each of these independent normal modes. The relaxation modulus is given by the form of Eq. 1.7, with the τ_i being replaced by τ_k .

We can further coarse-grain a polymer to represent a single point particle, in which case the effect of the eliminated degrees of freedom have to be included in the model explicitly. The RaPiD model developed by Briels and co-workers [23, 24, 25] provides a very good way of doing this by encapsulating the eliminated degrees of freedom in a set of contact numbers and adds dynamics to these.

1.2.4 Non-linear Rheology

Generally the stress response of a soft material to large deformations is of great interest. When the deformation is large, linear response necessarily does not hold and complex non-

linear phenomena might set in. In non-linear startup experiments, a large deforming steady shear at a particular rate is applied for a certain duration of time and then removed. The stress response immediately after this large deformation is observed with time, which can yield immense information about ‘far-out-of-equilibrium’ phenomena occurring in the material. As mentioned, the stress decay after applying a large deformation helps us calculate the timescales of relaxation of the molecular processes in the material. For instance, if the system is composed of polymers with reversible bonds that are broken during this large deformation, the bonds will try to reestablish after cessation of shear, with a characteristic bond-formation time. In addition, the polymers stretched by flow will try to relax to their equilibrium configurations at a different timescale. By fitting the stress decay with exponentials, we can estimate the number of such relaxation processes and their characteristic times. Generally, the stress decays with time but has also been observed to increase in Chapter 5 of this thesis. Thus non-linear rheology helps us probe complex, non-ordinary relaxations that are highly system-dependent.

It is quite difficult to make theory for systems under large deformations. However, the field of Superposition Rheology aims to apply the technique of linear rheology to out-of-equilibrium systems by applying a second small amplitude sinusoidal probing flow in addition to the strong steady shear. If the probing flow is in the direction of the steady shear, the technique is called parallel superposition [26, 27, 28, 29, 30, 31, 32] and if perpendicular to the steady shear, is referred to as orthogonal superposition [33, 34, 35, 36, 37, 38]. In chapter 3 of this thesis we perform fundamental studies of orthogonal superposition rheology while studying a low-volume fraction system and in chapter 4, we apply it to a similar system but at high concentration.

1.3 Computational Rheology

We have already explained the need for the computational approach in the first subsection. In this section we will briefly describe the simulation method used. It is beyond the scope of this thesis to describe all the details of the simulation, the interested reader is referred to Refs. [39, 40] for more details.

1.3.1 Brownian Dynamics

Simulation techniques range from the particle-based Molecular Dynamics (MD), which operates at the microscopic timescales (pico to nanoseconds) and is applicable to individual molecules or small groups of atoms, to continuum methods like Computational Fluid Dynamics (CFD) which operate at macroscopic length and timescales (milliseconds to seconds) where the material under study is assumed to be a single continuous medium. Between these two lies a range of particle-based techniques that operate on mesoscopic length and time

scales, like Brownian Dynamics (BD), Dissipative Particle Dynamics (DPD) [41], Hydrodynamically Coupled Brownian Dynamics (HCBD) [42], etc. and also an interesting continuum technique called the Lattice Boltzmann method [43, 44, 45, 46]. The mesoscopic particle based methods rely on coarse graining of the particles to reach larger time and length scales than in the microscopic methods at which molecular processes important to rheology of most soft matter systems unfold.

In this thesis, BD is the simulation technique of choice. The name ‘Brownian’ is from Robert Brown, the botanist that first observed the erratic motion of pollen grains suspended in water under a microscope, which was explained by Einstein in one of his seminal *Annus Mirabilis* papers in 1905 [47] as being caused due to the bombardment of the pollen particles by randomly moving water molecules which are much smaller than the pollen themselves. This confirmed the atomic hypothesis, leading to accurate calculations of the Avogadro’s Number etc. Excellent treatments of theory related to BD can be found in the classic references [48, 49, 50, 51, 52]. Since BD is the model for molecular motion at mesoscopic time and length scales, it is only appropriate that we use BD for simulations. In addition, the degree of coarse-graining can be controlled in BD. For example, in the system of star polymers studied in chapter 3 of this study, the entire polymer is represented by one single point in the model and is given by a single vector that changes in time according to forces from its neighbours. Whereas in Chapter 2, a lesser degree of coarse-graining is used where the individual beads along the arms represent an atomic entity.

For a system of particles with position coordinates $\vec{R}_i(t)$, friction coefficient ξ , interacting with a potential Φ , the Brownian propagator is given by:

$$d\vec{r}_i(t) = -\frac{1}{\xi} \frac{\partial \Phi}{\partial \vec{r}_i} dt + \vec{f}_i(t) + \sqrt{\frac{2k_B T}{\xi}} dt d\vec{W}_t \quad (1.21)$$

where $d\vec{W}_t$ is a zero-mean, unit variance Gaussian random vector and $\vec{f}_i(t)$ is a force that may or may not be applied. For example, when a shear rate of $\dot{\gamma}$ is applied in the x-direction with gradient along y, $\vec{f}_i(t) = \dot{\gamma} r_y(i) \vec{e}_x$, where $r_y(i)$ is the y-coordinate of particle i at time t .

The advantage of BD is that the forces on particles arise due to the potential alone. Different potentials exist for soft matter systems like the potential due to Likos and co-workers between star polymers ([53], used heavily in this thesis), the Flory Huggins potential [4], the transient potential used by Briels and co-workers [23, 25, 24] etc. These potentials are derived from microscopic considerations and hence accurately capture the forces between individual particles.

In order to implement a BD simulation, a certain number of particles are initially randomly distributed in a cubic box of volume V . Given a pairwise potential of mean force Φ , the force on each particle is obtained by differentiating Φ (first term in Eq. 1.21). The force on a single particle due to its neighbours is computed pairwise by using a neighbourlist [39, 40].

Periodic boundary conditions are applied by simply moving the particle into the box through the opposite cubic face and by the Lees-Edwards technique in sheared conditions. For a pair of particles i and j , the stress is calculated by:

$$\sigma_{\alpha\beta} = -\frac{1}{V} \sum_{i,j} r_{ij,\alpha} F_{ij,\beta}, \quad (1.22)$$

where the sum runs through all pairs, $r_{ij,\alpha}$ is the α -component of $\vec{r}_i - \vec{r}_j$ and $F_{ij,\beta}$ is the β -component of the force exerted by particle j on particle i .

1.3.2 Simulation code and cluster details

The simulation code was written in FORTRAN. The in-house developed RaPid codebase was used and heavily modified by the author to write the necessary protocols for this thesis. For Chapter 2, LAPACK was used to diagonalize the Rouse matrices for the normal mode simulation method (see chapter 2). The simulations were run on in-house clusters SnowWhite and MrFox, with the former having 18 nodes and the latter with 8 nodes, giving a total of 456 cores. The newest 10 nodes of SnowWhite were installed and maintained by the author.

1.4 Thesis Outline

This chapter gives an introduction to the motivation behind the work, the background theory and simulation methods used in the thesis.

In Chapter 2 we describe the rheology of a telechelic gel-forming star-polymer system with 13 arms and 7 beads along each arm, with an eighth sticker bead at the end with one-sixth the mass of the other beads. Each star polymer was represented by a core and the all the beads of the arms. The cores were moved by the Likos potential and to accelerate the simulations, the normal modes of the arms were updated in time and the forces from the first bead of each arm were collectively added to the core for force-balance. As an important theoretical contribution, we have generalized the Rouse model to be able to incorporate different frictions and/or spring strengths. We show that such a general formulation of the Rouse model also renders the Rouse modes uncorrelated, hence opening up a way to analyze polymers with anisotropic friction distributions with the same methods as for the ordinary Rouse model. The rheology of the uncrosslinked precursor was described by fitting a friction model which grows quadratically outwards from the core to the arm tip. To simulate the telechelic gel, the end beads of the arms were allowed to merge together to form a bead twice as heavy and the rouse modes of the connected arm were then updated. We found that the network crosslink percentage is 25%, i.e. 25% of all arms in the box were involved in forming external bridges between stars. The gelation threshold was at 10-11 %. In addition, the shear relaxation moduli developed a power law tail at 9% crosslinking, whose slope reduced in magnitude

with increasing crosslinking and finally forming a gel-phase at 12 - 14%.

In Chapter 3 we investigate Orthogonal Superposition Rheology of a melt of 13 armed stars interacting via the Likos potential. In equilibrium rheology, the Boltzmann superposition principle gives rise to the equality of the shear relaxation modulus, obtained from oscillatory experiments, and the stress relaxation modulus measured after a step-strain perturbation. We show that the same conclusion does not hold when the system is steadily sheared in a direction perpendicular to the probing flows, and with a gradient parallel to that of the probing deformations, as in orthogonal superposition rheology. In fact, we find that the oscillatory relaxation modulus differs from the step-strain modulus even for the smallest orthogonal shear flows that we could simulate. We do find, however, that the initial or plateau levels of both methods agree, and provide an equation relating the plateau value to the perturbation of the pair-function and also provide a formula to find the same from simulation.

In Chapter 4, we perform BD simulations of OSR upon a concentrated system of star-like micelles with functionality 120 at high volume fractions. The system parameters were taken from an experimental study whose findings we tried to compare with simulations. Two different models were tested out, one where the particles interact only via the Likos potential and the second model incorporates transient forces through the RaPid method. It was seen that above a certain shear rate, both models exhibit shear induced lane formation. The first model leads to eventual establishment of a crystalline phase with the storage and loss moduli becoming parallel to one another (no crossovers) above a specific shear rate while the second model has one crossover at least for all shear rates.

In Chapter 5, we investigated the non-linear rheology of three different associating systems. Stress relaxation upon cessation of shear flow is known to be described by single- or multi-mode monotonic exponential decays. Experimentally, it was found that under some conditions, the relaxation becomes anomalous in the sense that an upturn or increase in the relaxing stress is observed. We show that the effect could phenomenologically be described by a generic model based on an order parameter altered by shear. When bonds re-establish, energy flows from stored to thermal and elastic energy, whereas the latter results in work done on the system. If shear has induced order in the system so that the performed work leads to rearrangements of partly aligned elastic domains, the overall stress increases during the relaxation process.

In Chapter 6, we diagonalize the Rouse interaction matrix for a symmetric star polymer with functionality f and N beads on each arm. Aside from the diffusive mode corresponding to eigenvalue zero, we found that the spectrum consists of two parts: one set of degenerate spectra repeated $f - 1$ times, numbering $N(f - 1)$ and another unique spectrum of N eigenvalues. While the degenerate spectra are the Rouse modes of an N bead chain with one end connected to the origin by a spring, the unique spectrum was found to differ substantially from that predicted by previous studies. Like in the previous studies, the unique spectrum was found to be very closely approximated by that of an N bead linear chain, but only at high functionality, or for small functionalities and large values of N . While previously it was

assumed that the core is the same as the center of mass of the star, this is not the case for stars with low functionality. We show that the difference between the spectrum assumed so far and our derivation of the unique spectrum arises from this physical fact.

Chapter 2

Rouse Model Simulation of Self-Healing Telechelic Star Polymer Gel

The equilibrium mechanical properties of a cross-linked gel of telechelic star polymers are studied by rheology and Brownian dynamics simulations. The Brownian dynamics model consists of cores to which Rouse arms are attached. Forces between the cores are obtained from a potential of mean force model developed by Likos and co-workers. Both experimentally and in the simulations, networks were created by attaching sticker groups to the ends of the arms of the polymers, which were next allowed to form bonds among them in a one to one fashion. Simulations were sped up by solving the Rouse dynamics exactly. Moreover, the Rouse model was extended to allow for different frictions on different beads. In order to describe the rheology of the non-cross-linked polymers, it had to be assumed that bead frictions increase with increasing bead number along the arms. This friction model could be transferred to describe the rheology of the network without any adjustments other than an overall increase of the frictions due to the formation of bonds. The slowing down at intermediate times of the network rheology compared to that of the non-cross-linked polymers is well described by the model. The percentage of stickers involved in forming inter-star bonds in the system was determined to be 25%, both from simulations and from an application of the Green Tobolsky relation to the experimental plateau value of the shear relaxation modulus. Simulations with increasing cross-link percentages revealed that on approaching the gel transition the shear relaxation modulus develops an algebraic tail, which gets frozen at a percentage of maximum cross-linking of about 11%.

2.1 Introduction

Supramolecular polymeric structures are characterized by reversible bond formation which reflects the action of non-covalent bonds such as hydrogen, ionic, or metal-ligand bonds [54, 55, 56, 57, 58, 59]. The interplay of association lifetime with the polymeric timescale dictates the strength and stability of the formed assemblies [60]. The former depends on the fraction, functionality and localization of the bonds, and the latter on the size of polymer segments (between bonds), which may exhibit Rouse-like and disentanglement relaxation. As a result, associating polymeric networks possess intriguing tunable properties such as enhanced elasticity, shape memory, and self-healing [61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 8, 71]. Whereas the dynamics of nonionic polymers of different molecular weights and architectures is reasonably well-understood [72, 73, 74, 75], the situation with associating polymers is more complicated. Clearly, the dynamics of supramolecular networks is highly dependent on bond formation and destruction, polymer dynamics and on the properties of segments between bonds [76, 77]. Starting from the network plateau accounted for by the Green-Tobolsky model [78], the dynamics of associating polymers containing reversible bonds can be described through the breaking and reformation process coupled to chain relaxation by means of the sticky-Rouse [79] or sticky reptation [10] models. The former predicts that with decreasing frequency a transition takes place in the storage modulus G' from Rouse dynamics ($G' \propto \omega^{0.5}$) toward a plateau that reflects the number density of elastically active strands. Eventually, the terminal regime ($G' \propto \omega^2$) is reached when the sticky groups dissociate. The latter model is similar in nature, and predicts that reptation of the chain along its tube is not possible before the stickers disassociate. Briefly, at times longer than the Rouse time of a strand localized between two entanglements and/or stickers τ_e , but shorter than the sticker dissociation time τ , a first plateau modulus (G_1) appears, similar to that observed in permanently crosslinked networks. It includes two contributions, from associations and entanglements: $G_1 = \rho RT(1/M_x + 1/M_e)$, where M_x is the mass between two stickers, and M_e is the entanglement mass. At time $t > \tau$, the stress due to the stickers relaxes, and the modulus drops to the entanglement level $G_2 = \rho RT/M_e$. The second plateau persists until the terminal relaxation time of the reversible network, $\tau_{terminal}$ (say), which is longer than the terminal relaxation time of the respective entangled system without associations. Note that the strength of the physical bonds dictates the dynamics. If they are very strong (as in the present case), the sticker relaxation time τ is prohibitively long to allow for an experimentally accessible terminal relaxation of the network. Hence, the network is not reversible during experimental times, albeit physical.

The above framework, irrespective of the strength of physical bonds, has proven to be highly successful and opened the route for designing and engineering topologically complex macromolecules with selective functionalization, which allows tailoring properties in order to meet specific technological needs and at the same time understanding complex processes occurring in nature [80, 81, 82]. Therefore, several outstanding challenges should be ad-

Figure 2.1: Schematic of the uncrosslinked precursor in panel (a) and the crosslinked network in panel (b). Circles show bonds between stars (inter-star), triangles show bonds between two different arms of the same star (intra-star) and squares show the finger-like stickers closing up amongst themselves to form an intra-arm bond.

addressed in this context. One prominent example is developing quantitative predictions for the coupling of supramolecular interactions and topological effects in polymeric systems with branching architectures [83, 84, 85, 86]. Given this background, coupling highly branched architectures with multifunctional associating groups is expected to yield novel features due to their ability to link more than two chains at a time and their capacity to form stronger assemblies, while making the system dynamics and the associated physics richer, albeit more complex. The various possibilities for junction formation in an associated physical network in such situations is illustrated in Figure 1. The finger-like configuration for the multifunctional associating groups (Fig. 1a) is responsible for linking two or more different stars through one or more associations (inter-star) (circles in Fig. 1b), often with very high activation energy. Concomitantly, two or more arms from the same star can associate (intra-star) (triangles in Fig. 1b) or simply the fingers of the same arm can bridge (intra-arm) (squares in Fig. 1b). These different possibilities may facilitate the reformation of junctions after break-up (temperature or shear-induced) through an inter/intra-star dynamic exchange, which could also promote the self-healing ability of the network [8]. It should be remarked that self-healing can be expected to be more effective in the case of very strong associations. Related aspects of the sulfur-sulfur bond are addressed in the recent literature.[87, 88, 89, 8]

As described above, recent developments in polymer chemistry have enabled the synthesis of well-defined star polymers with multifunctional associating groups, which can serve as models for testing these ideas and their consequences on network dynamics [8, 90]. On the other hand, for the latter, and more generally, a deeper understanding of the macroscopic response of these systems in relation to their internal microstructure, it is often needed to perform simulations [69]. However, before assessing the self-healing properties, it is important to rationalize and control the rheology of this class of telechelic stars. This can be achieved with a combination of well-controlled synthesis, rheological experiments and Brownian Dy-

namics (BD) simulations, which represent the thrust of the present chapter.

The star polymers investigated here consist of a crosslinked ethylene glycol diacrylate (EGDA) core with an average of 13 arms made of poly(*n*-butyl) acrylate attached to it and with three bis(2-methacryloyloxyethyl) disulfide (DSDMA) stickers (fingers) at the tip of each arm. Stickers can bind strongly to those from other arms and thereby form a crosslinked physical network (see Fig. 1). The system is coded as SS3 (disulfide crosslinked with three stickers at the arm tip). The linear viscoelastic response is measured by means of dynamic oscillatory measurements using appropriate protocols to ensure proper equilibration and applying the principle of time-temperature superposition. Simulation studies of crosslinked networks have been reported before [91, 92, 93, 94, 69]. In this chapter we concentrate on the rheological behaviour of this strong physical network, starting from its uncrosslinked precursor, which has no stickers at the arm ends and build up a crosslinked network from this system. The stress relaxation modulus $G(t)$ of the crosslinked network decays much slower than that of its precursor and with increasing crosslink percentage develops a terminal plateau characteristic of gelation. This poses severe problems for BD simulations as the speed of the simulation is set by the timescale of the early decay. Since, however, the arm lengths in our system are smaller than an entanglement length and the system is in a melt state, the standard Rouse model may be assumed to describe the dynamics of the arms and strands between connected cores [3, 4]. This allows us to simulate the latter analytically without any restriction on the timestep by sampling from a Gaussian distribution [95, 96, 97]. As a result, the timestep is now limited by the diffusion of the cores which is much slower than the early decay of the shear relaxation modulus. In addition to this, we present a generalized version of the Rouse model, by proving that the Rouse modes of a polymer are uncorrelated, even when an arbitrary distribution of frictions of the beads is being used. Extensions of the Rouse model to incorporate more than one friction have been suggested before. However, these studies were restricted to systems with just two different friction coefficients[98, 99, 100], or used a random distribution of frictions to incorporate dynamic asymmetry[101, 102, 103]. Here we provide a completely general method, allowing us to sample from a Gaussian distribution even in cases where all the beads have different frictions. In order to establish model parameters associated with the dynamics, we first study the linear rheology of the precursor both by simulations and experiments.

The remainder of this chapter is arranged as follows. We first present the simulation models used to describe the precursor and the network. Next, we present the experimental system, its synthesis and molecular characterization, and give some additional details of the experimental and simulation methods used. We then continue with presenting the results and analysis from the comparison of simulation and experimental data. Finally we summarize the key conclusions and perspectives.

2.2 Simulation Model

In this section we first describe the model that we have used to simulate the rheology of the precursor, a system containing star polymers with functionality f and without connections between the arms on different stars. In the last subsection we indicate what changes we made to simulate the crosslinked systems in which some arms are allowed to connect through interactions at telechelic ends, and by this form bridges from one star to another.

2.2.1 Model Hamiltonian and Propagator

2.2.1.1 Precursor

The most detailed picture of a star-polymer system, relevant for rheology, is the one in which the positions and interactions of all segments are considered as a function of time. At a somewhat coarser level, one might consider all positions and interactions of groups of segments having the size of a Kuhn length. Using a model like this, in principle, would allow the calculation of configurational properties such as, for example, the distribution of the cores in the case of star polymers, and also of rheological properties from time scales of a few tenths of nano-seconds all the way to minutes. Unfortunately with a model like this it would be impossible to reach the large time scales of interest in the present chapter by means of computer simulations. We therefore suggest an even coarser model, thereby obviously losing some accuracy with our predictions.

The Hamiltonian of our model is given by:

$$H_{precursor} = \sum_{I=1}^{N_t-1} \sum_{J=I+1}^{N_t} \phi(r_{IJ}) + \sum_{I=1}^{N_t} \phi_{ROUSE}^I. \quad (2.1)$$

The sum over pairs represents entropic interactions between two stars I and J , with $r_{IJ} = |\vec{r}_I - \vec{r}_J|$ being the distance between their cores and with $\vec{r}_I$ being the position of the core of the I 'th star. N_t is the total number of stars in the system. The pair contributions $\phi(r_{IJ})$ are given by the so-called Likos potential[53]:

$$\begin{aligned} \phi(r_{IJ}) &= \left(\frac{5k_B T}{18} \right) f^{1.5} \left[-\ln \left(\frac{r_{IJ}}{\sigma} \right) + \left(1 + \frac{\sqrt{f}}{2} \right)^{-1} \right] & r_{IJ} \leq \sigma \\ &= \left(\frac{5k_B T}{18} \right) f^{1.5} \left(1 + \frac{\sqrt{f}}{2} \right)^{-1} \left(\frac{\sigma}{r_{IJ}} \right) \exp \left(-\sqrt{f} \left(\frac{r_{IJ} - \sigma}{2\sigma} \right) \right) & r_{IJ} > \sigma \end{aligned} \quad (2.2)$$

where f is the number of arms of the star. The first line in Equation 4.2 describes repulsions at

Figure 2.2: Potential of mean force as a function of dimensionless inter-star distance for two stars with functionality equal to thirteen and forty respectively. The brown line represents the resulting radial distribution function $g(r)$ for a melt of 13 arm stars. The parameter σ is fixed by setting the pressure equal to one atm for the given number density.

distances smaller than σ , while the second line describes the smooth decay of these repulsions to zero at larger distances.

Let us briefly discuss the status of the Likos potential. As mentioned above, ideally we would study the dynamics of all Kuhn segments in the system as governed by the mutual interactions applicable at that level. Having done a simulation like this, one might be interested in the distribution of the cores. In order to find this distribution, P , and the corresponding potential, $-k_B T \ln P$, one would simply average over, *i.e.* ‘integrate out’, all other degrees of freedom. One would end up with the exact distribution, and the exact potential. This potential also governs the exact average forces between cores, and is therefore called the potential of mean force. The Likos potential is a pairwise approximation of this potential[53]. It is the best potential available today to describe the configurations and dynamics of the cores of stars.

Figure (2.2) shows the Likos potential for stars with 13 arms, and for comparison also for stars with 40 arms. With increasing functionality, star polymers become increasingly colloid-like in nature[104], which can be seen by the potential becoming steeper when f increases from 13 to 40. The radial distribution function, simulated with a melt of 13 arm stars interacting via the Likos potential, is also drawn in that figure, and clearly shows how the excluded volume prevents the stars from approaching each other to small distances. We will discuss this picture below.

In order to be able at a later stage to study networks, we need the positions of the stickers. We obtain them by adding chains to the cores, thirteen to each core since this corresponds to the actual experimental system. In order not to influence the distribution of the cores, we choose to add Rouse arms, also called ‘phantom arms’, whose dynamics is governed by the second term in Eq. 2.1, with

$$\phi_{ROUSE}^I = \frac{1}{2} k_s \sum_{a=1}^f \sum_{n=1}^N |\vec{R}_{a,n}^I - \vec{R}_{a,n-1}^I|^2, \quad (2.3)$$

which is nothing but the sum of the free energies stored in the entropic springs connecting consecutive beads along the f arms of the I ’th star. $\vec{R}_{a,n}^I$ denotes the position vector of the n ’th bead along the a ’th arm of the I ’th star and N is the number of Kuhn segments (beads) on each arm, 7 in the case of our precursor. The first bead of each arm a is connected to the central core with position vector $\vec{r}_I = \vec{R}_{a,0}^I$. The spring constant is:

$$k_s = \frac{3k_B T}{b^2}, \quad (2.4)$$

where b is the Kuhn length. The arms are called ‘phantom arms’ because no contributions to the potential energy prevent the arms from crossing each other. It is well known that with relatively short arms, the Rouse model mimics the motion of the Kuhn segments quite well. A somewhat better model might be based on FENE-springs rather than the harmonic springs of the Rouse model, but this would not allow for the speed up of the arm dynamics that we describe below. Besides providing the positions of the stickers, the Rouse arms also reinstate fast stress fluctuations, which had been removed by the procedure to calculate the Likos potential, thereby allowing the calculation of rheological properties at shorter time scales.

During a time-step dt , each bead or core, with position vector $\vec{R}_{a,n}^I$ is displaced according to

$$d\vec{R}_{a,n}^I(t) = -\frac{1}{\xi_n} \frac{\partial H}{\partial \vec{R}_{a,n}^I} dt + \vec{F}_{a,n}^I dt \quad (2.5)$$

where ξ_n is a friction coefficient and $\vec{F}_{a,n}^I$ equals $\sqrt{\frac{2k_B T}{\xi_n dt}} \vec{\Theta}_{a,n}^I$ with $\vec{\Theta}_{a,n}^I$ being a zero mean, unit variance Gaussian vector. Notice that we allow for the possibility that different beads have different friction coefficients, the distribution of these frictions being the same on each arm and each polymer.

2.2.1.2 Network

In the absence of any interactions between the beads in the arms on different stars, the only way their motions can be correlated is through the movements of the cores. In general the frictions on the cores will be much larger than those on the other beads. Therefore, the

displacements of the cores due to interactions with surrounding stars will be very small on time scales that are characteristic for the Rouse dynamics. In that case the internal dynamics of the individual stars and their contributions to rheological properties of interest can be solved analytically, and there is no need to include the Rouse part of the Hamiltonian in a full simulation of the system. This is not true once we have connected a fraction of the arms in order to form a network. In this case, however, we must deal with the fact that the small friction on the beads asks for time steps which are very small to sample all relevant configurations of the cores. In the next subsection we describe how the dynamics of the Rouse part of the Hamiltonian can be simulated efficiently using large time steps, and later indicate changes to be made after bridges have been formed.

The main objective of our investigations is to simulate the stress response of the networks obtained by crosslinking some of the ends of the stars to form bridges from one core to another. In particular we are interested in how the shear relaxation moduli of such systems change with varying crosslink percentages. The network forming star is exactly the same as the precursor except for the presence of an eighth bead representing a sticker group at the end of each arm. After the creation of a network we have, in addition to dangling arms, loops from one core back to itself and bridges from one core to another. In the first case we simply ignore the additional sticker group, while in the other two cases we combine the two sticker groups forming the bond into one bead, leaving us with $2N + 1$ beads of which bead number $N + 1$ represents the two stickers. With these assumptions, the Hamiltonian is given by:

$$H_{network} = \sum_{I=1}^{N_t-1} \sum_{J=I+1}^{N_t} \phi(r_{IJ}) + \sum_{I=1}^{N_t} \phi_{UNCON}^I + \sum_{I=1}^{N_t-1} \sum_{J=I+1}^{N_t} \phi_{CONN}^{IJ} \quad (2.6)$$

with

$$\phi_{UNCON}^I = \frac{1}{2} k_s \sum_{a=1}^{f_{UNCON}^I} \sum_{n=1}^{N_s} |\vec{R}_{a,n}^I - \vec{R}_{a,n-1}^I|^2, \quad (2.7)$$

$$\phi_{CONN}^{IJ} = \frac{1}{2} k_s \sum_{a \in C(I,J)} \sum_{n=1}^{2N+2} |\vec{R}_{a,n}^{IJ} - \vec{R}_{a,n-1}^{IJ}|^2. \quad (2.8)$$

Here, $\phi(r_{IJ})$ is the same potential of mean force (Likos potential) as in the case of the precursor. ϕ_{UNCON}^I is the Rouse potential given in Equation 2.3, where f_{UNCON}^I is the number of arms of star I that are not connected to any other star; in the case of dangling arms $N_s = N$ and in the case of loops $N_s = 2N + 2$, with bead number $N + 1$ representing the two merged stickers as mentioned before. As before $\vec{R}_{a,0}^I = \vec{r}_I$, while also $\vec{R}_{a,2N+2}^I = \vec{r}_I$ in this case. In the second line, ϕ_{CONN}^{IJ} is the Rouse potential for connected arms between stars I and J , where $C(I, J)$ is the set of arms connecting these stars; in this case, the first N beads in the bridges represent the ones contributed by star I with $\vec{R}_{a,0}^{IJ} = \vec{r}_I$, bead number $N + 1$ repre-

sents the two merged stickers, and beads $N + 2$ up to $2N + 1$ represent the beads contributed by star J with $\vec{R}_{a,2N+2}^{IJ} = \vec{r}_J$. In case $C(I, J)$ is empty, the pair IJ does not contribute to ϕ_{CONN}^{IJ} .

Notice that we have left the contribution of the core-core potential of mean force unchanged, still being described by the same Likos potential as we used for the precursor.

2.2.2 The Normal Mode Simulation Method with non-uniform Friction Coefficients

Explicit solutions of the dynamics of many Rouse systems have been published in the literature[3, 4, 95, 96, 97]. The reason that so many individual cases have been treated is that the authors were interested in full analytical solutions that could be explicitly written down. Here, we are satisfied with any procedure that allows for a very quick solution, possibly involving some computationally efficient numerical calculations. Moreover, we want to be able to treat systems in which the friction forces may differ among the various beads in the system. Since solutions of the Rouse dynamics of such general systems do not seem to be easily accessible in the literature, we briefly outline how to update the configuration of Rouse systems with time steps dt of any value. For simplicity we discriminate the various beads by just a single index, writing for the position vectors of the beads $\vec{R}_i$. With this notation the equations of motion read

$$\frac{d\vec{R}_i}{dt} = -\frac{w}{m_i} \sum_j T_{ij} \vec{R}_j + \frac{\vec{F}_i}{\sqrt{m_i}}. \quad (2.9)$$

Here $w = k_s/\xi_0$ is the so called Rouse rate with ξ_0 being some reference friction, and $m_i = \xi_i/\xi_0$. The factor of $1/\sqrt{m_i}$ in the last term has been introduced for notational convenience. The vector $\vec{F}_i$ then represents random displacements resulting from small scale dynamics eliminated from the description. As before it is assumed to be a Gaussian random vector with uncorrelated random components given by $\sqrt{\frac{2k_B T}{\xi_0 dt}} \vec{\Theta}_i$ with $\vec{\Theta}_i$ being a zero mean unit variance random vector. The Rouse matrix $\mathbf{T}$ with elements T_{ij} is the Laplacian matrix of the system describing which pairs of beads are connected to each other through springs with spring constant k_s . By its very definition the Rouse matrix is symmetric. An example of a Rouse matrix for star polymers is given in Liu *et al.*[105] and Zimm and Kilb[106].

A set of linear equations like Eq. 2.9 is most easily solved by diagonalizing the corresponding interaction matrix. In order that the resulting modes, called Rouse modes in the present case, are independent, the stochastic contributions to the Rouse mode dynamics must be uncorrelated. This will automatically be ensured if the transformation matrix that diagonalizes the interaction matrix is orthogonal, which fact is not apparent when the frictions are all different as the factors m_i in the denominators complicate the procedure. Therefore we first symmetrize the interaction matrix by introducing coordinates $\vec{Q}_i$ according to

$\vec{Q}_i = \sqrt{m_i} \vec{R}_i$. The equation of motion then reads

$$\frac{d\vec{Q}_i}{dt} = -w \sum_j T_{ij}^m \vec{Q}_j + \vec{F}_i, \quad (2.10)$$

with $T_{ij}^m = T_{ij}/(\sqrt{m_i m_j})$, which is still symmetric and therefore has an orthogonal diagonalizing matrix. Note that this procedure also works when the springs are all different. In this case, the differing spring constants must be moved into the Rouse matrix $\mathbf{T}$, which, however, still is symmetric.

We now proceed in the usual way, defining

$$\vec{X}_k = \sum_{i=1}^N \vec{Q}_i S_{ik}, \quad (2.11)$$

with $\mathbf{S} = (S_{ik})$ being the orthogonal matrix that diagonalizes the Rouse matrix, *i.e.* $\mathbf{S}^T \mathbf{T}^m \mathbf{S} = \mathbf{\Lambda}$. An important point is that $\mathbf{S}$ can be calculated once and for all at the start of the simulation. Eq. 2.11 can easily be inverted to obtain $\vec{Q}_i = \sum_{k=1}^N S_{ik} \vec{X}_k$, so one can switch between using Rouse mode vectors $\vec{X}_k$ and bead position vectors $\vec{R}_i$. The Rouse mode vectors at any time may now be obtained according to

$$\vec{X}_k(t) = \vec{X}_k(0) e^{-t/\tau_k} + \int_0^t e^{-(t-t')/\tau_k} \vec{G}_k(t') dt' \quad (2.12)$$

$$\vec{G}_k(t) = \sum_{i=1}^N \vec{F}_i(t) S_{ik}. \quad (2.13)$$

Here $\tau_k = \frac{w}{\lambda_k} = \frac{\xi_0}{k_s \lambda_k}$ is the characteristic time of mode k , while λ_k is the k^{th} eigenvalue in matrix $\mathbf{\Lambda}$ defined above. $\vec{G}_k(t)$ is a sum of Gaussian vectors and therefore is itself a Gaussian vector. Similarly, the integral in Eq. 2.12 is a Gaussian vector with mean zero and variance $\sigma_k(t)^2$, which can easily be obtained from the properties of $\vec{F}_i$. The updates for the Rouse vector $\vec{X}_k$ then becomes

$$\vec{X}_k(t + dt) = \vec{X}_k(t) e^{-dt/\tau_k} + \sigma_k(dt) \vec{\Theta}_k \quad (2.14)$$

$$\sigma_k(dt) = \sqrt{\frac{k_B T}{\xi_0} \tau_k (1 - e^{-2dt/\tau_k})}. \quad (2.15)$$

These equations solve the Rouse dynamics exactly, so dt may take any value. Our time step is now not limited anymore by the fast dynamics of the Rouse system and may therefore be adjusted to the dynamics of the cores. Once the eigenvalues of the Rouse matrix are known, the contribution of the Rouse dynamics to the shear relaxation modulus may easily

be calculated (see Eq. 2.20 below).

We verified our code by comparing simulation and theoretical results for various time steps and friction models. Moreover, we verified that the radial distribution function of the cores is not influenced by the introduction of the arms.

2.2.3 Arms and Bridges

As mentioned before, because of the slowness of the motion of the cores, the internal Rouse dynamics of the individual stars may be calculated independently of the motion of the cores during time step dt set by the core dynamics. Assuming, as we do, that the friction on the cores is much larger than that on the other beads, one may expect that a star may be considered as consisting of a fixed core with f arms attached to it. This is corroborated by the following observations concerning the spectrum of the internal modes. Besides the diffusive mode with eigenvalue equal to zero, there are Nf internal modes (see Chapter 6 for details). N of these give rise to a unique spectrum while the remaining ones give rise to $f - 1$ degenerate spectra, each consisting of N eigenvalues. So, in total there are $N + (f - 1)N = fN$ internal modes and one translational mode. The degenerate spectra are each exactly equal to the spectrum of one arm attached to a fixed core. With increasing values of the core friction, the eigenvalues of the unique spectrum gradually change in order to finally become equal to those of the degenerate spectrum which remained unchanged all the time.

We conclude that the spectrum of a star with high enough functionality consists of f degenerate spectra, all equal to that of one arm with N beads attached to a fixed core (see Fig 2.3a). Since $G(t)$ is only dependent on the eigenvalues and not on the eigenvectors, we may replace the full Rouse dynamics with that of stars consisting of fixed cores with f independent arms attached to them. The precise way to handle this case is given further down in this subsection.

We now describe the propagator for networks. In the case of bridges and loops, the equation of motion reads

$$\frac{d\vec{Q}_n}{dt} = -w \sum_m T_{nm}^m \vec{Q}_m + \frac{w}{\sqrt{m_n}} (\delta_{n,1} \vec{r}_I + \delta_{n,2N+1} \vec{r}_J) + \vec{F}_n, \quad (2.16)$$

where $\delta_{n,N}$ is the Kronecker delta, being zero except if $n = N$, in which case it equals one. The additional terms are due to the connection of beads number one and $2N + 1$ to cores I and J respectively. The Rouse matrix $\mathbf{T}$ with elements $T_{mn} = \sqrt{m_m m_n} T_{mn}^m$ is shown below, and has size of 15×15 . The analytical solution of the Rouse modes now becomes:

$$\vec{X}_k(t) = \vec{X}_k(0) e^{-t/\tau_k} + \left(\frac{S_{1,k}}{\sqrt{m_1}} \vec{r}_I + \frac{S_{2N+1,k}}{\sqrt{m_{2N+1}}} \vec{r}_J \right) \frac{1}{\lambda_k} \left(1 - e^{-t/\tau_k} \right) + \int_0^t e^{-(t-t')/\tau_k} \vec{G}_k(t') dt'. \quad (2.17)$$

In the second case, *i.e.* when the $(2N + 1)$ -long chain is looping from core I back to core I ,

Figure 2.3: a) Schematic drawing of an arm modeled as a Rouse chain attached to a core at one end; only three beads are shown for clarity b) Picture of two arms bridging two cores. Each of the two arms has been provided with a sticker group at its end, which subsequently have formed a short range bond resulting in one additional red bead representing the merged mass of the two sticker groups.

one just has to put $\vec{r}_J = \vec{r}_I$. In the case of a dangling arm attached to core I , one simply puts $\vec{r}_J = \vec{0}$ and replaces the Rouse matrix by the one given, whose size now is 7×7 .

$$\mathbf{T}_{7 \times 7} = \begin{bmatrix} 2 & -1 & 0 & \cdots & 0 \\ -1 & 2 & -1 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & \cdots & -1 & 2 & -1 \\ 0 & \cdots & 0 & -1 & 1 \end{bmatrix}$$

$$\mathbf{T}_{15 \times 15} = \begin{bmatrix} 2 & -1 & 0 & \cdots & 0 \\ -1 & 2 & -1 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & \cdots & -1 & 2 & -1 \\ 0 & \cdots & 0 & -1 & 2 \end{bmatrix}$$

The stochastic term in Eq. 2.17 is obtained as before.

We finally summarize the sequence of updates during a time step in the case of networks. First, all cores are moved according to Brownian dynamics with forces derived from the Likos potential. Next, all beads in dangling arms are updated according to the equations also used in the case of the precursor. Finally, all loops and bridges are updated according to the methods of the present section.

It is worth mentioning one consequence of the use of phantom arms that will not be shared by the real system. Creating crosslinks in an experimental system will most probably severely slow down the dynamics of the cores. This will also hold true for any simulation

model in which the beads experience mutual repulsive interactions besides the spring interactions present in the Rouse model, or in which other means have been introduced to avoid crossings of chains [107, 108]. In the present model this can only be achieved by adjusting the frictions on the beads and the cores. Besides this, the finite extensibility of the bridges between the cores will limit the volume that the cores can explore. This is not the case with our phantom bridges, since the Gaussian springs between the beads can in principle be stretched beyond any limit, although with increasingly lower probability. This can be prevented by using finitely extensible bonds, but then the possibility to use large time steps as described above will be lost.

2.3 Materials and Methods

2.3.1 Synthesis and Characterization

The synthesis of the precursor and the gel are described by Kamada *et al.* [90] In this reference, the authors synthesized and measured the sizes of stars consisting of ca 23 arms containing ca 63 PnBA units each, attached to a crosslinked EGDA core.

The present system was synthesized according to the same procedure, except that as initiator methyl 2-bromopropionate was used instead of ethyl 2-bromopropionate. The first step consists of synthesizing an EGDA microgel, whose molecular mass was estimated to be about 6600 g/mol., leading to a diameter of about 1.4 nm. This is the ‘chemical core’ to which the arms are attached in the second step. Using light scattering experiments, the average molecular mass of the stars was measured. We estimated that on average each star contained 13 arms of mass 16662 g/mol. each, equivalent to ca 130 PnBA units. This is the system that we refer to as the precursor. It is important to realize, that the ‘chemical core’ referred to here is not the ‘core’ that we mentioned when describing the model (Section 2.2.1.1). The latter will be further discussed below in relation to the rheology of the precursor, and shown to have a diameter of about 6 nm (Section 2.4.1)

Next, the system was crosslinked to form a *gel* by adding sticker groups of DSDMA, to the end of each arm, and allowing the stickers to equilibrate. In principle, each arm was provided with one group of three stickers. As a result of simultaneous growth and gelation of the system the distribution of the stickers over the arms may not be very sharp, there may be arms with more than 3 stickers and arms with no stickers. More details are presented in the Supporting Information that goes with this chapter.

2.3.2 Molecular and simulation parameters

In order to determine parameters in Hamiltonian Eq. 2.1, we have proceeded as follows. First, the functionality f , was put equal to its average value of 13. For the precursor, this is a harmless assumption, since the Rouse dynamics of a star is to a very good approximation

equal to that of f individual arms attached to a fixed point. Besides this, we also removed any polydispersity of the length of the arms. We will argue in section 2.4.1 that the dynamics of the precursor will be influenced by this assumption only to a small degree, not affecting the study of the network. With these assumptions, from the molecular weight per arm M_{arm} and the total mass density we obtained the number density of stars ρ . Next we need a method to determine the Likos parameter σ in Eq. 4.2. Since we are dealing with a polymer melt we know that the calculated number density applies to a system at a pressure of 1 atm. Given that the Rouse arms do not contribute to the pressure we performed several simulations with the correct number density and temperature, and varied the value of σ until we obtained a pressure of 1 atm. This resulted in $\sigma = 6.1$ nm.

Although the above monodispersity assumptions have little or no influence on the modeling of the precursor, they may have a larger influence on describing the dynamics of the network. An appropriate way to prepare networks would be to generate a precursor system by sampling from some appropriate distribution of functionalities and arm lengths, next allow for crosslinking as described below, and finally average calculated shear relaxation moduli over many such boxes until reasonable statistics would be obtained. As we will see below, it takes at least ten runs per monodisperse system to obtain reasonable statistics, which makes an ensemble average as just mentioned computationally prohibitive. We therefore decided to stick to the monodisperse system already used for the precursor. Moreover, we assume that on average one sticker group per arm will be active.

We now turn to the parameters in the Rouse part of the potential. The spring constant can be calculated when the Kuhn length is known. We used a Kuhn length b of 4 nm as cited for poly-nBA by Pahnke *et. al*[109]. This yields a spring constant $k_s = 6.67 \times 10^{-4} \text{ Nm}^{-1}$. The final remaining unknown is the number of Kuhn segments, or beads, per arm N . To obtain this number, we first estimate the average end-end length R_{arm} of a polymer arm. Since the Likos potential is basically the entropy loss of two stars when they overlap, it must have decayed to zero when the distance between them is roughly twice the average end-end length of an arm. By looking at the potential in Fig. 3.1, we see that above $R_C = 3.5\sigma$ the potential has decayed to an insignificant value, from which it follows that $3.5\sigma = 2R_{arm} = 2\sqrt{N}b$. This leads to $R_{arm} = 10.6$ nm and $N = 7$. $R_c = 3.5\sigma$ has been used as a cutoff radius for the Likos potential.

Obviously, the procedure that we have applied to obtain R_{arm} and N depends quite a bit on the chosen value of R_c . Reasonable choices of R_c lead to numbers of beads per arm ranging from six to eight. Moreover, we want to mention that a Kuhn length of 4 nm seems to be quite large, but that none of the qualitative results below will change if a smaller Kuhn length is used. The only difference will be that the agreement between experimental and simulated shear relaxation moduli will be extended to somewhat smaller times.

All simulation parameters mentioned so far are given in Table 2.1, together with two friction parameters appearing in the propagators. The friction parameters have been adjusted to obtain the best possible agreement between theoretical and experimental shear relaxation

Parameter		Value
Butyl Acrylate	M_w	128.17 g mol ⁻¹
DSDMA	M_w	290.4 g mol ⁻¹
Mass per arm	M_{arm}	16662 g mol ⁻¹
Functionality	f	13
Kuhn length	b	4 nm
Mass density	ρ_{mass}	1.06 g cm ⁻³
Temperature precursor	T_{prec}	258 K
Temperature gel	T_{netw}	273 K
Number Density	ρ	2.959×10^{24} m ⁻³
Number of stars	N_t	300
Box length	L_{box}	46.7 nm
Likos parameter	σ	6.1 nm
Cutoff Radius	R_C	21.2 nm
Number of beads per arm	N	7
Spring coefficient	k_{spring}	6.67×10^{-4} Nm ⁻¹
Core Friction	ξ_C	7.60×10^{-3} kg s ⁻¹
Reference bead Friction	ξ_0	9.45×10^{-8} kg s ⁻¹

Table 2.1: System Parameters

moduli. One of them is ξ_C , the friction on the cores. Below it will turn out to be equal to 7.6×10^{-3} kg/s. The other is ξ_0 , occurring in the Rouse mode dynamics through $w = k_s/\xi_0$, which will turn out to be 9.45×10^{-8} kg/s. Various ways to define the m_n will be discussed later. From its molecular mass, we determine that the DSDMA sticker group is approximately one sixth of the mass of each Kuhn bead in the arms [90]. As mentioned before, when creating loops and bridges, we lump together the two sticker groups that form the bond into one bead, leading to chains of $2N + 1$ beads, with the middle bead having a friction equal to one third of a normal bead at that position.

Assuming that the cores should not move by more than a twentieth of the radius of the stars we find that the time step dt should at most be equal to $(R_{arm}/20)^2 \xi_C / k_B T$, which is equal to 0.5s. This is roughly confirmed from calculations of the mean square displacements shown in Fig. 2.4, where it is seen that dt must be less than one tenth of a second to capture sub-diffusive behavior.

Figure 2.4: Mean square displacements of the core for various timesteps. The dashed line, corresponding to a timestep of 1s, does not reproduce the correct diffusive behavior, and thus is too large to obtain reliable results. The maximum timestep used in this study is 10 ms.

Figure 2.5: Schematic of two sticker groups binding. The central red bead in the right part represents the merger of the groups to form one bead of twice the mass.

2.3.3 Creation of Networks

Our main interest in this chapter is the relation between the degree of crosslinking in the network and its rheological properties. To quantify crosslinking we introduce a parameter p_{ext} , defined as the number of stickers involved in external bonds divided by the total number of stickers and next multiplied by one hundred. This is the same as the total number of external bonds divided by the total number of possible bonds, also multiplied by one hundred. For short we will call it the percentage of external bonds. In a similar way we define the percentage of loops and the percentage of dangling chains, the latter being just the percentage of all stickers that are not involved in any bond. Since the contribution of a loop to the shear relaxation modulus is not very different from that of (two) dangling chains, at least compared to the changes that will occur on creating bridges, from now on we will not discriminate between the two and restrict ourselves to systems that have prescribed values for p_{ext} . For stars with very long arms this may not hold true anymore, but then also modeling the arms by Rouse chains will become invalid.

In order to generate crosslinked networks, we attached an additional 8'th bead with one sixth the friction of a regular bead to the end of each arm of the precursor, the factor of one sixth being roughly estimated on the basis of the relative sizes of the sticker with respect to the Kuhn length. Next the system was equilibrated in the usual way. After this preliminary run, the sticking procedure was started. To this end we ran the system with a time step of 1 ms, and included a sticking step after every one hundred steps. During the sticking step, for every sticker, we scanned a spherical volume of radius one tenth of a Kuhn length and formed a bond to the nearest neighbor in this volume. The run was stopped as soon as a prescribed value for p_{ext} was obtained. In our case, one tenth of a Kuhn length corresponds to a few Å. Moreover, the sticking probability in this case is rather small, so the total run-time for creating a box lasted long enough for the cores to diffuse over about one diameter.

In order to further reduce the statistical noise in our final results, ten boxes were created for each value of p_{ext} and the final shear relaxation moduli were obtained by averaging over these ten boxes. Moreover in each case three runs were performed with time steps of 0.1 ms, 1 ms and 10 ms respectively, in order to resolve all time scales from the smallest, allowed by the coarseness of the model, to the longest, needed to reach the plateau values of the shear relaxation moduli.

2.3.4 Methods

2.3.4.1 Rheological experiments:

The linear viscoelastic responses were probed by small-strain amplitude oscillatory shear measurements with an ARES-2KFRTN1 strain-controlled rheometer equipped with a force rebalance transducer (TA Instruments, USA). The TTS principle was applied to build master curves at the reference temperature of $T_{ref} = T_g + 44^\circ \text{ C}$ for all the samples, where T_g

is the glass transition temperature of the sample considered. The reference temperatures for the precursor and the network were chosen in order to compare both sets of data at the same distance from their respective T_g (please see SI of our publication in *Macromolecules*, available online). For the precursor this amounts to $T_{ref} = -15^\circ \text{C}$, and for the network to $T_{ref} = 0^\circ \text{C}$. 8 mm Invar parallel plates with low expansion coefficient were used and reproducibility of the measurements was checked by going down in temperature by a step of 10°C as a first measurement and up to check the reproducibility of the data at 2 or 3 temperatures.

2.3.4.2 Simulation:

Simulated stresses were obtained according to

$$\sigma_{xy}(t) = -\frac{1}{V} \sum_j \sum_i (r_{ix}(t) - r_{jx}(t)) F_{ij,y}(t) \quad (2.18)$$

where $F_{ij,y}(t)$ is the y-component of the force exerted by particle j at position $\vec{r}_j$ on particle i at position $\vec{r}_i$. By particle we mean either core or bead. The shear relaxation modulus $G(t)$ was calculated according to

$$G(t) = \frac{V}{k_B T} \langle \sigma_{xy}(t) \sigma_{xy}(0) \rangle \quad (2.19)$$

Applying these equations to the Rouse model leads to the well known result

$$G(t) = \nu k_B T \sum_{k=1}^{N_s} e^{-6 \frac{k_B T \lambda_k}{\xi_0 b^2} t} \quad (2.20)$$

where λ_k is the k 'th eigenvalue of the Rouse matrix. Here N_s stands for the number of Kuhn segments being considered; for dangling arms this is N , and for bridges $2N + 1$.

2.4 Results

In Figure 2.6a we present the storage and loss moduli $G'(\omega)$ and $G''(\omega)$ obtained with the strain-controlled rheometer mentioned before, both for the precursor and for the network. Using the method of Schwarzl [110] we transformed these data into ‘experimental’ shear relaxation moduli shown in Figure 2.6b. We refer the reader to the Supporting Information (available online) for the raw data and some additional discussion concerning the application of the Time Temperature Superposition principle. At intermediate and lower frequencies TTS becomes increasingly difficult, especially in associating systems and may fail eventually[84].

Based on extensive experience with similar systems, we have concluded that the Schwarzl method[110] is superior to the other methods available. This is confirmed in a paper by Emri

Figure 2.6: Panel (a) shows the shear relaxation moduli obtained from experiment both for the precursor and for the crosslinked network. The terminal plateau at low frequencies is an indication of gelation. Two different y axes are used to clearly distinguish between the two sets of moduli. Panel (b) shows the corresponding $G(t)$ for both the network and precursor. The time domain moduli are easier to work with for simulations.

et al.[111], who especially address this issue.

2.4.1 Rheology of the precursor

We first discuss the results for the precursor.

As already mentioned before, the motion of the cores is much slower than that of the Rouse beads, so the early decay of the shear relaxation modulus is totally determined by the Rouse dynamics. Moreover, at early times, the contribution of the core-core interactions to the shear relaxation modulus is negligibly small compared to those of the Rouse modes. We therefore neglect at this stage the contribution of the core-core interactions to the stress and completely concentrate on the Rouse dynamics. As we have already determined the bead density, the plateau value of the Rouse contribution is fixed, and we should only decide about the best possible friction model and corresponding parameters. As a first try we used a simple iso-frictional model. The best result was obtained using a friction value of $\xi = 1.89 \times 10^{-6} \text{ kg s}^{-1}$ (for all beads). The corresponding shear relaxation modulus is shown in Fig. 2.7a and 2.7b as a red curve, together with the experimental curve. It is clear that the agreement is reasonably good, but not perfect. In particular the slope of the theoretical curve is different from that of the experimental curve.

In view of the polydispersity of the experimental system (Section 2.3.1 and Supporting Information), we tried to ameliorate the quality of the Rouse model prediction by including

polydispersity. As already mentioned we only needed to calculate the contribution to the shear relaxation modulus of individual arms of various lengths, average the result over a reasonable distribution of arm lengths and multiply by thirteen (the nominal number of arms per star). We used discrete Gaussian distributions with given standard deviations. To be more explicit, we calculated the Rouse prediction for arms attached to a fixed point with the arm-length running from 4 to 11 Kuhn beads, took relative weights for each arm-length from a Gaussian distribution with mean of 7 Kuhn beads and the given standard deviation, and averaged over the chosen weights; this result was finally multiplied by thirteen. The result is shown in Fig. 2.7a for two values of the standard deviation. With all standard deviations ≥ 5 we found the same result. It is seen from this plot that including polydispersity does extend the relaxation to somewhat larger time scales, for obvious reasons, but does not change the slope of the curve (in log-log representation). We therefore decided to stick to monodisperse arm lengths and focus on frictions in order to obtain a better model.

Since it is conceivable that frictions on different beads along the arms may differ substantially, we investigated if better agreement can be obtained using models with non-uniform frictions. In order to clearly see the influence of the various friction models, we decided to keep the total friction on each arm constant, *i.e.* we chose all models such that $\sum_{i=1}^7 \xi_i = 13.23 \times 10^{-6} \text{ kg s}^{-1}$.

First we applied a model with frictions increasing or decreasing linearly with bead number. The model with frictions increasing towards the free end slightly improved the results. We next tried several other models and found good results with a model in which the bead friction grows quadratically with the bead number: $\xi_i = \xi_0 \times i^2$. The only unknown, ξ_0 , follows from the constraint of constant total friction introduced earlier; its value is given in Table 2.1. The results are depicted in Fig. 2.7b, along with those of a model for which $\xi_i = \xi'_0 \times i^{-2}$ for comparison. Clearly the model with quadratically outwards growing frictions does a very good job, while the one with quadratically inwards growing frictions obviously does not describe the data as well. Even though this result may be a bit counter intuitive we continue with this friction model, leaving a more detailed analysis with different models for future research.

Up to now, we have only been concerned with the Rouse dynamics of the model that determines the early decay of the shear relaxation modulus. We now add the contributions from the core-core interactions and vary the value of the core friction ξ_C to obtain the best agreement between theory and experiment. The final result is presented Fig. 2.8, for which $\xi_C = 7.60 \times 10^{-3} \text{ kg s}^{-1}$. We notice that the agreement is good, given the fact that apart from the two frictions, shifting the two contributions along the horizontal axis, all parameters were obtained from considerations totally independent of the rheological data.

Whereas the agreement is good enough for our purposes (given the simplicity of the model and the approximations used), one might argue that the final shear relaxation modulus appears to relax in a one-step, rather than a two-step process, as also suggested by the experiment. In this context, we recall that the Kuhn length of 4.0 nm, as inferred from data in

Figure 2.7: a) Effect of polydispersity on stress relaxation. Arms sampled from a gaussian distribution with standard deviation 1 (dashed line) and standard deviation 5 (dash-dotted line) relax later than the solid line. Also shown is the quadratic-out result (dots, same as dash dotted line in the Panel b). b) Quadratic friction model with friction increasing quadratically towards the core (dashed line) or outwards (dash-dotted line).

Figure 2.8: The best fit (dashed line) to the precursor experimental $G(t)$ (symbols). The contribution of the potential of mean force is shown separately (dash-dotted line). In the simulation model the bead friction increases quadratically along the arms of the star.

the literature seems to be quite large. However, if we consider a model with a Kuhn length half of that, we end up with more Kuhn beads (28). As a result, the shear relaxation function starts at a larger value at time zero and extends slightly to longer times. The latter can be made more pronounced by using a polydisperse model which includes arm lengths up to 45 beads. This partially fills the gap between the time scales of the Rouse modes and the core dynamics, thereby smoothing out the two-step character mentioned above. Since our main goal is to provide a sound distribution of stickers before starting the relaxation process, we did not investigate these possibilities further. This is worth investigating in the future.

Before finishing this section, let us discuss the meaning of ‘core’ a bit further. By ‘core’ we do not just mean the chemical unit that has been used to attach the arms to (see Section 2.3.1). After attaching the arms, the central region of the star will be rather crowded. In a realistic model, based on Kuhn beads including mutual repulsions, this means that it will be difficult for two stars to approach each other closer than a certain distance. This distance may be considered to be the core diameter and has to be calculated. From the radial distribution function in Fig. 3.1 we find that no stars come closer than 0.5σ , so we could define the diameter to be 0.5σ . This of course seems like a gross underestimation. A better choice obviously is to notice that according to Boltzmann statistics, stars will hardly ever come closer to each other than distances for which the mutual interaction energy is less than, let’s say, $10 k_B T$. This leads to a diameter of about one σ , and a corresponding volume fraction of about 0.39. Consequently the cores still have plenty of space to move. The same conclusion follows from the fact that the value of the first peak of the scattering function (structure factor), which is not shown, equals 1.33, well below the value of 2.85 where, according to the Hansen Verlet rule, [112] the system crystallizes. The picture now is that of a collection of cores in a sea of arms. The sea of arms in a real system is a rather complicated, dense fluctuating liquid. It will cause a large, probably distance dependent, friction on the cores, leading to rather slow motions and corresponding stress relaxation of the cores. The slowness of the cores is just a reflection of the complicated motion of the arms that is not fully captured by the Rouse model.

It may be useful to notice that although the contribution of the core to the stress relaxation is the slowest in the system, its stress value is the smallest, and hence its contribution to the viscosity is rather modest. As a result, one may conclude that the viscosity of the star systems is dominated by the lengths of the arms, rather independent of the functionality. This result has been confirmed for entangled stars with experiments and tube model theory but only for functionalities not exceeding 32 [113, 114, 115].

2.4.2 The Network

After having studied the precursor, we added a sticker to the arms of the stars, making them telechelic, and proceeded to generate a network [90]. We measured the rheological response of the resulting network with our strain controlled rheometer. The results are shown in Fig.

Figure 2.9: Mean square displacement (MSD) of the cores with increasing crosslink percentage. The MSD decreases with increasing p_{ext} , showing that the cores find it increasingly difficult to move with higher degrees of crosslinking. This slowing is due to the tethering effect of the bridge chains between cores.

2.6a. As with the precursor, we transformed the data into $G(t)$ by means of the method of Schwarzl [110]. The resulting ‘experimental’ $G(t)$ is shown in Fig. 2.6b together with the one of the precursor. The first thing to notice is that both curves agree at times below about 10^{-5} s, after which they begin to differ substantially. For times larger than 10^3 s the modulus of the network reaches a plateau value, caused by the network structure.

Before continuing with a discussion of the rheological results, let us quickly sketch how the motion of the cores is influenced by the introduction of bridges. In Fig 2.9, we have plotted the mean square displacements of the cores in networks for various values of p_{ext} . It is clearly seen that in the network the mean square displacements of the cores level off beyond times of about 100 seconds, depending somewhat on the degree of crosslinking. It is clearly seen that the cores explore a volume with a diameter of about one or two times the radius of a star, even for crosslink percentages of 60 to 80 percent. So, at lower crosslink percentages, it may be expected that all cores, including those in star clusters, have the freedom to move over about one diameter.

It is not fully clear what causes the slowing down of the network in the intermediate region, indicated by the difference of the slopes of the two curves. One might argue that crosslinking the stars has resulted in topologies of the arms in which some of them are constrained to slide along others in order to relax stresses whose removal requires larger displacements of the beads then needed to relax short range stresses. Another point of view might be that there is a distribution of clusters (of connected stars), each contributing with their own

Figure 2.10: a) Stress relaxation moduli for various crosslink percentages. The terminal plateau, which first appears at 15%, keeps increasing with increasing degrees of crosslinking. The model with 25% of maximum crosslinking describes the experimental modulus best. b) Stress relaxation modulus for 25% of maximum crosslinking along with two curves, one standard deviation above (dash line) and one below (dash dotted line) average. Each of the latter two is represented twice, once for a run with a short time step, and once for a run with a larger time step. Besides these, in both figures the experimental curve is shown.

characteristic relaxation times, which increase with increasing cluster sizes.

An important aim of our simulations is to shed light on these matters. Moreover we wish to establish the degree of crosslinking in the system.

In order to allow for reasonable statistics with the simulated results, we prepared ten boxes of crosslinked systems for a range of crosslink percentages p_{ext} . Since the bond-energy of a sulfur-sulfur bond[116, 117, 118] is about $250 \text{ kJmol}^{-1}/R \approx 30000 \text{ K}$, where R is the gas constant, the life time of a bond is extremely long, and fluctuations caused by association and dissociation can safely be ignored. Since the network response spans several decades in time, we ran each of these boxes for three different timesteps of 0.1, 1, and 10 milliseconds and then merged the resulting shear relaxation moduli into one smooth curve. The results of all these calculations are shown in Fig. 2.10a, together with the experimental curve. As is clear from this picture, the simulated results meet the experimental data very well when a crosslinking percentage of 25 % is assumed. In Fig. 2.10b we present the simulated $G(t)$ again, but now together with $G(t) \pm \sigma_{st}(t)$, where $\sigma_{st}(t)$ is the standard deviation of the average obtained with the ten simulation boxes. Comparing Fig. 2.10a with Fig. 2.10b it seems safe to say that the actual crosslink percentage is $25 \pm 10\%$.

There is a second way to estimate the actual p_{ext} . With increasing crosslinking, the terminal plateau seems to converge to a value of about 70 kPa for a fully crosslinked network

(confirmed by simulations with larger p_{ext} , not shown to save the picture from becoming unreadable). This result is in agreement with an estimate suggested by van Ruymbeke *et.al* [85]. According to these authors the maximum crosslink percentage is given by $\nu_{max} = \rho_m N_{Av} / 2M_a$, where ρ_m is the mass density of stars, N_{Av} is the Avogadro number, and $M_a = 16.6$ kg/mol the mass of one arm (including the sticker). With the Green-Tobolsky relation $G_{max} = \nu_{max} k_B T$ one again obtains $G_{max} = 70$ kPa. Now, with an experimental plateau value of about 14 kPa and the proportionality of the plateau value to the crosslink percentage, we conclude that the degree of crosslinking is about 20 percent, in reasonable agreement with the previous estimate.

It is worth reflecting as to why the percentage of all possible crosslinks that finally materialize is so low. As is clear from the binding energy of a disulfur bond, 30000 K, this cannot be due to reversible association and dissociation of the bonds. From the description of the synthesis, however, it is clear that some arms may have no sticker groups while others may have more than one. Also, two out of three fingers at the end of an arm can become inactive by intra-sticker association. This will influence the efficiency with which crosslinks can be formed. Similarly, during the crosslinking process sticker groups must diffuse over substantial distances to find possible partners. This becomes increasingly more difficult with increasing degree of crosslinking already established, so stickers may finally get kinetically trapped in regions with few or no free partners. This also means that after annealing at elevated temperatures the percentage of crosslinking may slightly have gone up. Note that this is contrary to the effect of temperature with lower association energies, when a reversible association dissociation equilibrium is established.

We now turn our attention to the intermediate time scales between 10^{-5} s and 10^2 s. In order to obtain good agreement between our simulated results and the experimental data at times shorter than 10^{-5} s, we have multiplied all frictions by a constant factor of 2.65, no other modifications being applied. From this we draw two conclusions: First, the fact that the friction of the beads in the network is much larger than those in the precursor agrees with our earlier hypothesis that crosslinking the system results in topologies with enhanced friction when chains move in order to relax their stresses. This, of course, is not reproduced by phantom chains, and therefore had to be introduced by hand. Second, the fact that no further changes of relative frictions are needed confirms that the remaining slowing down, indicated by the smaller frequency slope of moduli for the network than for the precursor, is indeed reproduced by our phantom chains. It must therefore be a result of the distribution of cluster sizes occurring in the crosslinked system, as suggested before.

Stresses in the network again consist of two components, one due to entropic interactions between stars, described by the potential of mean force, and the other due to Rouse springs. The first contribution is small in magnitude but plays an important role in keeping the stars apart, and its relaxation is roughly identical to that of the precursor shown in Figure 2.8 for all the different crosslink percentages. Only for crosslink percentages of 60 percent or more the relaxation becomes slightly slower than that of the precursor. Given their non-negligible

Figure 2.11: Rouse contribution to stress relaxations for networks of increasing degree of crosslinking. All curves enter a ‘Rouse’ plateau at about 0.3 seconds. With crosslink percentages of 15% and onwards they develop a second plateau, which increases and merges with the first plateau with increasing crosslinking. $G(t)$ for 10% of full crosslinking clearly has a power law tail. Circles are obtained with runs of timestep 0.1 ms and solid lines with a timestep of 10 ms.

size, it may be a bit surprising that the Likos forces do not contribute to the final plateau. The reason for this is that their actual volume fraction is rather small. The connection to other cores through rather flexible Rouse arms is also not very restrictive topologically. Therefore, as we have seen above, the cores have plenty of space to wiggle around, thereby reducing their contribution to the stress correlation. Of course, since the cores are now part of a physical network, they cannot diffuse over all space anymore, but the remaining space is sufficient to allow for core-core stress relaxation, without the need (or possibility) to hop from one cage to another. These considerations do not mean that the cores do not contribute to the final plateau. Being part of the network, and as such experiencing forces generated by the Rouse part of the Hamiltonian, Eq. 2.7, the cores do contribute to the stresses and stress relaxations of the network. This is the part that we call ‘the Rouse part’ of the stress relaxation.

The Rouse part, dominating in all cases and shown in Figure 2.11 for the largest timestep of 10 milliseconds has some interesting characteristics. For all crosslink percentages, there is an onset of a second plateau at 0.3 seconds. For 5 and 10% pre-gel states, this plateau eventually decays. The magnitude of the plateau increases with crosslink percentages and eventually segues into the terminal plateau when gelation occurs at about 15% in the figure. For percentages higher than 30, there is one single plateau due to the whole system being interconnected.

We now analyze the onset of gelation as much as is allowed by the statistics of our data.

Figure 2.12: a) Appearance of a power law tail in $G(t)$'s for 9%, 10% and 10.5% of maximum crosslinking; the dashed straight lines represent the suggested power laws. b) Power law exponents α of the terminal parts of $G(t)$ as a function of percentage of maximum crosslinking (squares), and fit revealing the gelation point at 10.55% of maximum crosslink percentage (solid line).

Increasing the crosslink percentage starting with 5.5%, below which the terminal part of $G(t)$ decays exponentially to zero, $G(t)$ develops a tail, which roughly may be described by a power law $G(t) \propto t^{-\alpha}$. In Fig. 2.12a we present these tails together with the suggested power law descriptions for crosslink percentages ranging from 9% to 10.5%. At 11%, $G(t)$, instead of decaying, enters a terminal plateau region, described by $\alpha = 0$. Beyond this point the system finds itself in the gel state. For higher percentages, the value of the terminal modulus increases as reported earlier. The exponents of the power law, α , are plotted in figure 2.12b. Included in this figure is a fit of the data according to $\alpha(p_{ext}) = A(p_G - p_{ext})^\beta$, which yielded $A = 0.5283$, $p_G = 10.55\%$ and the exponent $\beta = 0.3895$. We conclude that the gelation occurs at about $p_G = 10.55\%$. It is tempting to call β a critical exponent associated with the gel transition, even when this may not be fully justified, since there is no variable in the system which is thermodynamically conjugate to p_{ext} . Notice that the various p_{ext} were obtained by just freezing them in.

It is clear that the onset of gelation may be attributed to the appearance of a so-called ‘giant component’, which is one very large cluster that connects or spans the whole system. In order to explore this point, we made histograms of the distribution of cluster sizes in the system.

Figure 2.13a shows the distributions of the cluster sizes, in terms of the fraction of stars $P(N)$ that find themselves in clusters of size N (not the bead number here), which is repre-

Figure 2.13: a) Distribution of cluster sizes for 9, 10 and 11% of maximum crosslinking. The rightmost bar in the middle and bottom panes after the x-axis break represents the size of the largest cluster. At 10% of maximum crosslinking about 25% of all stars in the sample are in this big cluster, which number increases to 50% at 11% of maximum crosslinking. b) Fraction of the largest cluster in the sample as a function of percentage of maximum crosslinking. The tangent at the inflection point intersects the line $y = 1$ at 12.5% of maximum crosslinking.

sented along the x-axis. First, consider the top panel of figure 2.13a which shows the cluster size distribution at 9% of maximum crosslinking. Most stars in the system are unconnected, represented by the bar at 1 on the extreme left. The largest cluster at the extreme right has 24 stars. From the figure we read $P(24) = 0.16$, from which we conclude that there are $0.16 \times 300/24 = 2$ clusters of size 24. At 10%, shown in the middle panel, the biggest cluster increases in size, to include 72 stars. The corresponding bar is the rightmost one, after the axis break. From the figure we read $P(72) = 0.24$, so there is only one single largest cluster in this case, which takes about 25% of all stars in the box. There is still a substantial fraction of unconnected stars and clusters of varying sizes up to a maximum of 25. However, with just a 1% increase of the crosslink percentage, at 11%, the situation is quite different. From the bottom panel of figure 2.13a, we notice a substantial change of the structural properties of the system. The rightmost bar is now dominant, and represents a single giant cluster of 172 stars, which is a little over 50% of the total number of stars in the system. The proportion of unconnected stars has reduced a lot, and the sizes of the small clusters now range only up to nine. The big component has come to existence by eating the small clusters. As the sticking percentage is increased, this cluster continues to grow, as shown in Figure 2.13b, where the fraction of stars in the largest cluster is plotted as a function of the crosslink percentage. First of all, this analysis shows that gelation is strongly related to the growth of the largest cluster in the system, as expected. Secondly, the largest cluster does not yet span the whole system

at the crosslink percentage where according to rheology gelation takes place. One procedure to extract a p_G from this data might be to draw the tangent line to the curve at the inflection point, and read the value of p_{ext} where this line crosses unity. This procedure leads to a value of $p_G = 11 - 12\%$, in rough agreement with the rheology based value.

This analysis shows the connection between the statistics of the clusters, and the onset of the power law tail in the $G(t)$. It is clear from Fig. 2.12a, that at 10% of full crosslinking, a power law tail in $G(t)$ has developed. At the same time, we see the appearance of a large cluster represented by the rightmost bar in the middle panel of Fig. 2.13a. This was a feature that was observed in all 10 simulation boxes. With increasing p_{ext} both the size of the large cluster increases, and the power law decay slows down. We checked that p_G obtained with the structural analysis is equal in boxes with 300 stars and boxes with 1000 stars.

2.5 Summary and Conclusions

In this chapter, we have studied the rheological and gelation properties of a star polymer melt consisting of telechelic stars with thirteen arms of seven Kuhn segments each, both using experimental and simulation methods. First we studied the non crosslinked precursor, and next crosslinked networks of various degrees of crosslinking. The agreement between theory and experiment is very good. This allowed us to analyze the origin of the gel transition in some detail, using our simulation techniques.

As usual with soft matter systems, the information about molecular properties of the various constituents of the system is rather limited. For example knowing the hydrodynamic radius of the molecule is of little help when it comes to decide about the structure of the molecule in the melt. Here we decided to use a thermodynamically consistent model in which the stars are treated as point particles dressed with phantom, or Rouse chains. Forces between the point particles are governed by the potential of mean force, which we modeled with a function that has extensively been used by Likos and co-workers. Adjusting the only unknown parameter in this function until the pressure of the system was equal to one atmosphere, we managed to fully determine the potential of mean force. Since only the Kuhn length was known, but not the mass of the corresponding segment, we estimated the length of the arms by simply choosing a cut-off for the potential of mean force and equating this to twice the length of an arm. The results in this chapter seem to fully justify this procedure. Even so, the suggested procedure is not uniquely defined, and in other cases may even not be applicable at all. In those cases independent information, like for example from SAXS or other scattering experiments will be of great help.

The remaining parameters in the model are the friction coefficients for the cores and for the Rouse beads. These were adjusted to obtain agreement between theory and experiment for the precursor system. In order to obtain good agreement it turned out to be necessary to assume that the frictions on the beads depend on their position along the arms. It turned

out that a model in which the friction increases quadratically with the bead number along the arm, starting with one for the bead connected to the core, does a perfect job. We derived the exact Rouse dynamics for cases with variable frictions in order to be able to use large time steps needed to reach the extremely long decay times of the shear relaxation moduli, also in the case of crosslinked networks.

We created and simulated crosslinked networks with various degrees of crosslinking. Without any further parameter tweaking, *i.e.* just using the parameters obtained for the precursor, we found that simulations with twenty five percent of all the arms involved in crosslinks to other stars yield shear relaxation moduli in very good agreement with the experimental results. We analyzed the long time tails of the shear relaxation moduli for systems approaching the gel transition, and found algebraic decays with exponents decaying to zero as also observed with thermodynamic properties of systems near second order phase transitions. We confirmed that the gel transition is strongly related to the growth of the largest cluster in the system.

Chapter 3

Orthogonal Superposition Rheology by Brownian Dynamics

The most general linear equation describing the stress response at time t to a time-dependent shearing perturbation may be written as the integral over the past history t' of a time dependent relaxation modulus, depending on $t - t'$, multiplied by the perturbing shear rate at time t' . This is according to the Boltzmann superposition principle, which says that the stress response of a system to a time dependent shearing deformation may be written as the sum of responses to a sequence of step-strain perturbations in the past. In equilibrium rheology, the Boltzmann superposition principle gives rise to the equality of the shear relaxation modulus, obtained from oscillatory experiments, and the stress relaxation modulus measured after a step-strain perturbation. In this chapter we describe the results of Brownian dynamics simulations of a simple soft matter system showing that the same conclusion does not hold when the system is steadily sheared in a direction perpendicular to the probing flows, and with a gradient parallel to that of the probing deformations, as in orthogonal superposition rheology. In fact, we find that the oscillatory relaxation modulus differs from the step-strain modulus even for the smallest orthogonal shear flows that we could simulate. We do find, however, that the initial or plateau levels of both methods agree, and provide an equation relating the plateau value to the perturbation of the pair-function.

3.1 Introduction

The non-linear flow properties of complex fluids like polymers, colloidal suspensions, surfactants etc are not fully understood and are the subject of much discussion. One of the techniques of mechanical spectroscopy used to study such non-equilibrium phenomena, Superposition Rheology, has emerged in recent years as a very useful tool to probe soft matter

systems far from equilibrium [26, 33, 37, 119, 120, 121, 122, 123, 124, 125]. In superposition techniques, two different shear flows are superimposed simultaneously on the sample under study. One of them is a steady shear that disturbs and defines the sample far from equilibrium and the second is a small oscillation superimposed on the first, probing the sample. The first will be called ‘the disturbing flow’ and the second ‘the probing flow’. The probing flow is either in the direction of the disturbing flow, in which case the method is called Parallel Superposition Rheology (PSR) [26, 27, 28, 29, 30, 31, 32], or orthogonal to it, when it is called Orthogonal Superposition Rheology (OSR) [33, 34, 35, 36]. PSR experiments are easier to perform than OSR experiments, hence there are a substantial number of studies dedicated to PSR so far [126, 127, 28, 29, 30, 31, 128, 129, 130, 131]. Constitutive equations used to define system properties both under PSR and OSR conditions, however, have been found to be much more difficult to apply to PSR data than to OSR data [33, 132, 133]. This is because the small amplitude shear used to probe the material has the same symmetry as the disturbing flow that defines the material. Hence, in this study we will concentrate on OSR only, aiming for some understanding of the out-of-equilibrium material properties in a way similar to that achieved with linear visco-elastic properties.

With the construction of OSR apparatus by Vermant and others, providing reliable and reproducible data [134, 38, 33], several experiments have been done on a variety of soft matter systems. Most of these experiments have been analyzed using Yamamoto’s phenomenological expressions [34, 135, 136, 137, 133]. Yamamoto defines a generalized response spectrum $H(\tau, \dot{\gamma})$ which depends on shear rate $\dot{\gamma}$ but is otherwise related to the storage and loss moduli in the same way as in linear viscoelasticity near equilibrium. Among other things this implies the validity of the Kramers-Kronig relations [138] as already noticed by Vermant *et. al.* [33] and Dhont and Wagner [37]. Other models have been suggested, like the K-BKZ based constitutive model by Tanner and Williams which expresses the storage and loss moduli in terms of some time dependent elastic energy, and the Wagner model which gives slightly different relations for the relaxation moduli from those of Yamamoto. In addition, there is a mode coupling theory based analysis [139, 140, 141], relating structure and rheology. Hence, there are a wide variety of constitutive models available in the literature that provide different kinds of interpretations of OSR data.

As emphasized above and explained in Section 3.2 below, the equations proposed by Yamamoto show a large resemblance to those used to analyze linear viscoelastic experiments near equilibrium. The main difference is that response spectrum $H(\tau, \dot{\gamma})$ depends on the imposed stationary shear rate $\dot{\gamma}$. A natural question then is how much of the conceptual framework of linear viscoelasticity near equilibrium may be transferred to OSR applied to systems brought far out of equilibrium by the stationary applied shear flow. One may ask if the usual Green-Kubo relations are still valid, or if the relationship between various different experimental techniques, like for example between step strain and oscillatory experiments, are still valid. The emphasis here must in principle be on ‘far out of equilibrium’, because with small values of $\dot{\gamma}$ of the disturbing flow the experiments degenerates into the superposi-

tion of two independent, mutually orthogonal linear experiments near equilibrium, in which case linear viscoelastic analysis applies. It is the main goal of this work to shed some light on the answers to these questions. The obvious method of choice in this case will be particle based simulations, since they provide the most detailed information, and allow for the most detailed analysis. Since OSR is of most interest to soft matter physicists, we choose to model a system of star polymers, characteristic both for polymer behavior and colloidal behavior [104]. We use a single particle model in which the particles interact through a potential developed by Likos and coworkers [53], and are propagated through Brownian dynamics.

To the best of our knowledge no study similar to the one reported here has been published till now. Somewhat related work has been done by Jacob *et. al.* [35], but there the emphasis was on supporting experimental findings instead of interrogating fundamental assumptions about OSR. Besides this, stresses were not calculated directly, but were inferred from mean square displacements invoking the generalized Stokes-Einstein relation [142], which in itself is not fully undisputed.

This chapter is structured as follows. In Section 3.2 we present a bit of the theoretical background of the Yamamoto model and explain the context of the questions that we want to address. In section 3.3 we describe the system and the methods that we used for the simulation. In section 3.4 we present the results of our simulations. In the last section we summarize our findings. In the Appendix we present some derivations of theoretical expressions that are needed to analyze and discuss our results.

3.2 Theory

We apply a perturbing shear flow in the x-direction with gradient in the y-direction, and an oscillatory probing shear flow in the z-direction with gradient in the y-direction. Measurements are performed once all transients are over and the flow velocities are given by

$$\begin{aligned} u_x(t) &= \dot{\gamma}y \\ u_y(t) &= 0 \\ u_z(t) &= \gamma_{\perp}\omega\cos(\omega t)y, \end{aligned} \tag{3.1}$$

where $\dot{\gamma}$ is the imposed perturbing shear rate and $\gamma_{\perp}$ the amplitude of the probing flow. According to Yamamoto the stress component $\sigma_{yz}(t; \dot{\gamma})$ in this case is given by

$$\sigma_{yz}(t; \dot{\gamma}) = \gamma_{\perp} [G'_{\perp}(\omega; \dot{\gamma})\sin(\omega t) + G''_{\perp}(\omega; \dot{\gamma})\cos(\omega t)], \tag{3.2}$$

with

$$\begin{aligned} G'_{\perp}(\omega; \dot{\gamma}) &= \int_{-\infty}^{\infty} H(\tau, \dot{\gamma}) \frac{(\omega\tau)^2}{1 + (\omega\tau)^2} d\ln\tau \\ G''_{\perp}(\omega; \dot{\gamma}) &= \int_{-\infty}^{\infty} H(\tau, \dot{\gamma}) \frac{\omega\tau}{1 + (\omega\tau)^2} d\ln\tau. \end{aligned} \quad (3.3)$$

$H(\tau, \dot{\gamma})$ is the aforementioned response spectrum, which in this case may depend on $\dot{\gamma}$. It is not difficult to show that these equations are equivalent to

$$\sigma_{yz}(t; \dot{\gamma}) = \int_{-\infty}^t G_{\perp}(t - t', \dot{\gamma}) \dot{\gamma}_{\perp}(t') dt', \quad (3.4)$$

with $\dot{\gamma}_{\perp}(t) = \gamma_{\perp} \omega \cos(\omega t)$, and

$$G_{\perp}(t - t', \dot{\gamma}) = \int_{-\infty}^{\infty} H(\tau, \dot{\gamma}) e^{-(t-t')/\tau} d\ln\tau, \quad (3.5)$$

and that under weak conditions on the response spectrum the Kramers-Kronig relations must hold.

Of course Eq. 3.4 is the usual expression used in linear rheology near equilibrium to define the shear relaxation modulus. Near equilibrium we put $\dot{\gamma} = 0$, and we omit the superfluous subscript $\perp$. Eq. 3.4 becomes $\sigma_{yz}(t) = \int_{-\infty}^t G(t - t') \dot{\gamma}_{yz}(t') dt'$, which is the most general linear expression possible in agreement with causality. Near equilibrium, we are formally allowed to substitute $\dot{\gamma}_{yz}(t) = \gamma \delta(t)$ in this equation, equivalent to applying a strain step of size γ at time zero, and obtain a stress $G(t)$ at later times. This fact gives a meaning to $G(t)$ independent from its definition through oscillatory experiments. We consider this to be the true content of Boltzmann's superposition principle [143], which states that the stress is the sum of the responses to delta pulses in the past. We can go even further and derive from this the famous Green-Kubo expression for the shear relaxation modulus: $G(t) = \beta V \langle \sigma_{yz}(t) \sigma_{yz}(0) \rangle$, with V being the volume of the system, β being $(k_B T)^{-1}$ with k_B being the Boltzmann constant, and the angular brackets denoting an equilibrium average. Finally, by applying an oscillatory strain and calculating the work performed to keep the oscillation going on, we easily find that the dissipated work is proportional to the loss modulus $G''(\omega) = \int_0^{\infty} G(t) \omega \cos(\omega t) dt$ [144, 145].

The similarity between Eq. 3.4 and the equations governing equilibrium rheology has led Vermant *et al.* [33] to state that $G'_{\perp}$ and $G''_{\perp}$ seem to retain their physical meaning of storage and loss modulus. Since the work done during one cycle of the orthogonal probing is proportional to the total stress and the latter is just the sum of the unchanged stress caused by the perturbing flow and the one caused by the probing flow, $G''_{\perp}$ indeed must be the additional work to be performed to keep the oscillation going on top of the perturbing flow. We therefore

will call $G'_\perp$ and $G''_\perp$ the storage and loss moduli. In this chapter we investigate if the other two relationships mentioned above are valid. So we will test if $G_\perp(t, \dot{\gamma})$ is equal to the stress measured after applying unit step strain orthogonal to a perturbing flow, and if a generalized Green-Kubo relation still holds.

We want to emphasize that the model of Yamamoto presented here has only served as a framework to clearly state our objectives. The results that we will present only depend on the microscopic particle model, and in particular are independent of any rheological model used to describe the results.

The equations for the storage and loss moduli in parallel superposition contain an additional term that depends on the derivative of the spectrum with respect to shear rate. We do not see a way to derive an equation analogous to Equation 4 in this case. Therefore, we do not have available a parallel oscillatory modulus that can be compared with the parallel step strain modulus. Hence we do not consider PSR in this chapter.

3.3 System and Methods

In this section we describe the system that we have simulated and some of the methods that we have used to calculate the various properties presented in this chapter.

3.3.1 System

As mentioned before, it is our aim in this chapter to investigate the consequences of an imposed shear flow on rheological probing techniques orthogonal to that shear flow. We want to restrict ourselves to the influence of the bare shearing flow. Therefore, we have chosen a very simple soft matter system in which the imposed flow has no influence on the internal properties of the particles, nor on their mutual interactions. We will briefly comment on possible changes to our findings caused by the latter in section 3.5. Since, moreover, we did not want to run into specific problems that go with high volume fractions and the glassy state, we have chosen as our system a melt of thirteen armed stars at a pressure of one atmosphere. So, the system consists of particles, which interact through an effective potential advocated by Likos and co-workers [104] :

$$\begin{aligned} \phi(r_{ij}) &= \left(\frac{5k_B T}{18} \right) f^{1.5} \left[-\ln \left(\frac{r_{ij}}{\sigma_L} \right) + \left(1 + \frac{\sqrt{f}}{2} \right)^{-1} \right] & r_{ij} \leq \sigma_L \\ &= \left(\frac{5k_B T}{18} \right) f^{1.5} \left(1 + \frac{\sqrt{f}}{2} \right)^{-1} \left(\frac{\sigma_L}{r_{ij}} \right) \exp \left(-\sqrt{f} \left(\frac{r_{ij} - \sigma_L}{2\sigma_L} \right) \right) & r_{ij} > \sigma_L, \end{aligned} \quad (3.6)$$

Figure 3.1: Potential of mean force as a function of dimensionless inter-star distance for two stars with a functionality of thirteen. The solid line represents the resulting radial distribution function $g(r)$ in a melt. The dotted line is the potential scaled to fit on the graph. The parameter σ_L is fixed by setting the pressure equal to one atm for the given number density.

where r_{ij} is the distance between particles i and j , *i.e.* $r_{ij} = |\vec{r}_i - \vec{r}_j|$ with $\vec{r}_i$ being the position vector of the i 'th particle. The first line in Equation 3.6 describes repulsions at distances smaller than σ_L , while the second line describes the smooth decay of the entropic repulsions to zero at larger distances. f is the functionality of the stars, *i.e.* their number of arms. In the present application $f = 13$. σ_L sets the length scale of the model.

In order to have some appreciation of the system, in Fig. (3.1) we present the Likos potential for stars with 13 arms, together with the radial distribution function for a system with a number density of 0.672 particles per cubic σ_L and a temperature of 273 Kelvin; the potential was set equal to zero at distances beyond $R_C = 3.48\sigma_L$. Taking the value of r_{ij} where the radial distribution goes through one for the first time as the diameter of the particle, we find a diameter of one σ_L and next a volume fraction of 0.35. If, on the other hand, we take the value of r_{ij} at the first peak of $g(r_{ij})$ to be the diameter, we obtain a diameter of $1.2\sigma_L$ and a volume fraction of 0.61. A hard sphere representation of the present model would probably have a diameter and corresponding volume fraction between these two extremes.

In the remaining part of this chapter all quantities will be presented in SI. Therefore, in Table 3.1 we have collected all parameter values in SI, together with some other information defining the simulation. The value of σ_L was adjusted to obtain a pressure of one atmosphere with the given number density.

Parameter		Value
Temperature	T	273 K
Pressure	P	2.82 atm
Number Density	ρ	$2.959 \times 10^{24} \text{ m}^{-3}$
Box length	L_{box}	70 nm
Number of particles	N_t	1015
Functionality	f	13
Distance parameter	σ_L	6.1 nm
Cutoff Radius	R_C	21.2 nm
Friction Coefficient	ξ	$8 \times 10^{-3} \text{ kg s}^{-1}$

Table 3.1: System Parameters

3.3.2 Orthogonal Superposition propagator

Since we only describe the motion of the centers of mass of the stars using the potential of mean force, this means that we have eliminated all the degrees of freedom that go with the arms from our simulation. In order to obtain the correct dynamics for the centers of mass, we must supply friction forces to them and use a stochastic propagator. With the rather large frictions applying in the present case, we may move forward the particles by the Brownian Dynamics propagator. Forces are derived from the total potential

$$\Phi(r^{3N}) = \sum_{\langle ij \rangle} \phi(r_{ij}). \quad (3.7)$$

The sum $\langle ij \rangle$ runs through all pairs of particles.

In order to implement orthogonal superposition flow as defined in Eq. 3.1, we make use of the following equations of motion:

$$dx_i = -\frac{1}{\xi} \frac{\partial \Phi}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial x_i} dt + u_{\alpha_i, x} dt + f_{i, x} \quad (3.8)$$

$$dy_i = -\frac{1}{\xi} \frac{\partial \Phi}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial y_i} dt + f_{i, y} \quad (3.9)$$

$$dz_i = -\frac{1}{\xi} \frac{\partial \Phi}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial z_i} dt + u_{\alpha_i, z} dt + f_{i, z}. \quad (3.10)$$

Here dx_i is the increment of x_i during the time interval of length dt , ξ is a friction coefficient and $f_{i, x}$, $f_{i, y}$ and $f_{i, z}$ are the components of the Brownian stochastic displacements. The latter obey the fluctuation dissipation theorem

$$\langle f_{i, \alpha} f_{j, \beta} \rangle = \frac{2k_B T}{\xi} \delta_{\alpha, \beta} \delta_{i, j} dt, \quad (3.11)$$

where k_B is the Boltzmann constant and T is the temperature. $\delta_{\alpha,\beta}$ is the Kronecker delta, which is equal to zero unless $\alpha = \beta$, when it is equal to one. The friction coefficient was taken from a previous paper on the same system [146] (the star system in Chapter 2).

The velocities $u_{\alpha_i,x}$ and $u_{\alpha_i,z}$ are the average flow velocities in the x- and z-direction, at the position of particle i . In order to measure these velocities, we divide the system into 10 slabs along the y-direction and calculate the average velocities $\langle \dot{x}_i(t) \rangle_\alpha$ and $\langle \dot{z}_i(t) \rangle_\alpha$ in each slab α at each time-step. Here $\dot{z}_i = dz_i/dt$ etc. The flow velocities are then updated for every slab according to

$$\begin{aligned} u_{\alpha,x}(t+dt) &= \langle \dot{x}_i(t) \rangle_\alpha \left(1 - e^{-dt/\tau_f}\right) + u_{\alpha,x}(t)e^{-dt/\tau_f} \\ u_{\alpha,z}(t+dt) &= \langle \dot{z}_i(t) \rangle_\alpha \left(1 - e^{-dt/\tau_f}\right) + u_{\alpha,z}(t)e^{-dt/\tau_f}. \end{aligned} \quad (3.12)$$

Here, τ_f characterizes how far in the future the present average velocities co-determine the flow velocities, in order to smooth the otherwise wildly fluctuating flow velocities. τ_f should be chosen large enough to effectively time-smooth the measured flow fields, but small enough not to influence the physics.

The actual flow field that develops in the system is imposed through Lees-Edwards boundary conditions, which are applied at the two bounding planes of the box perpendicular to the gradient direction. In the present application, the gradient direction is the same for the steady defining flow and for the oscillatory probing flow. In an OSR simulation, *i.e.* when both flows are present, a particle leaving the box through the upper y-plane comes back into the system through the lower y-plane with a displacement in the x-direction of $-\dot{\gamma}Ht$ (modulo one) and in the z-direction of $-\gamma_\perp \sin(\omega t)H$; H is the height of the box in the y-direction. Similar operations are applied when a particle leaves the box through the lower y-plane and enters through the upper y-plane, but now with reversed signs. Furthermore, the average velocities in the lowest slab are not measured locally, but are put equal to those in the uppermost slab reduced by $\dot{\gamma}H$ in the x-direction and by $\gamma_\perp \omega \cos(\omega t)H$ in the z-direction.

3.3.3 Storage and loss moduli

As emphasized before, we consider the system as being defined by a shear flow along the x-direction with gradient along the y-direction, and being probed by an oscillatory flow in the z-direction with gradient along the y-direction. Unless some nonlinear processes occur in the system we expect a linear response to the perturbing flow. This means that for sufficiently small values of $\gamma_\perp$ Eq. 3.2 should hold. Here $G'_\perp(\omega; \dot{\gamma})$ is the stress per unit strain amplitude that is in phase with the strain, and $G''_\perp(\omega; \dot{\gamma})$ is the stress per unit strain amplitude that is out of phase with the strain. A different way of writing this equation is

$$\sigma_{yz}(t; \dot{\gamma}) = G'_\perp(\omega; \dot{\gamma})\gamma_\perp(\omega, t) + G''_\perp(\omega; \dot{\gamma})\frac{1}{\omega}\dot{\gamma}_\perp(\omega, t). \quad (3.13)$$

We have calculated the storage and loss moduli by running an OSR simulation as described in Section 3.3.2, and next fitted the σ_{yz} to Eq. 3.13. In order to obtain a full spectrum, this had to be repeated for different frequencies. Stresses were calculated according to

$$\sigma_{\alpha\beta} = -\frac{1}{V} \sum_{i,j} r_{ij,\alpha} F_{ij,\beta}, \quad (3.14)$$

where the sum runs through all pairs, $r_{ij,\alpha}$ is the α -component of $\vec{r}_i - \vec{r}_j$ and $F_{ij,\beta}$ is the β -component of the force exerted by particle j on particle i .

For a given frequency ω , the time-step dt must be chosen small enough to decently sample the oscillating signal, *i.e.* to have enough points within one cycle. In all runs we made sure that there were at least 20 points per cycle. On the other hand we need enough cycles to be able to fit the results to Eq. 3.13. In all simulations we have aimed for at least 100 cycles per run. At low frequencies, the stress response is generally noisy, so a larger amplitude $\gamma_{\perp}$ was used to obtain a good signal-to-noise ratio. The maximum value of $\gamma_{\perp}$ was restricted to 5%. At intermediate frequencies (greater than the crossover frequency) the signal was quite smooth and fitting was considerably easier. For the higher shear rates it is important that the characteristic time τ_f used in Eq. 3.12 is small enough to not poison the signal. For consistency we have used $\tau_f = dt$ throughout the chapter. In Fig.3.2 we present three examples of fits of Eq. 3.13 to the measured stresses. Further results are presented and discussed in section 3.4.1.

3.3.4 Step-strain experiments

Once the storage and loss moduli have been obtained, $G_{\perp}(t; \dot{\gamma})$ can be calculated by Fourier transformation [110]. As mentioned before, one of our aims in this chapter is to investigate if $G_{\perp}(t; \dot{\gamma})$ is equal to the stress relaxation after a unit step strain perturbation in the direction orthogonal to the steady shear rate, defined as

$$G_{\perp}^s(t; \dot{\gamma}) = \lim_{\gamma \rightarrow 0} \frac{1}{\gamma} \sigma_{yz}(t, \gamma; \dot{\gamma}). \quad (3.15)$$

Here γ is the imposed strain step at time zero, and $\sigma_{yz}(t, \gamma; \dot{\gamma})$ is the resulting stress at later times t .

In order to calculate $\sigma_{yz}(t, \gamma; \dot{\gamma})$ first ten boxes were run for 5 million steps for every shear rate investigated. Next, for every shear rate, each of the ten boxes was run for an additional ten million steps from which 200 frames were stored at regular intervals. So, we had prepared 2000 boxes for every shear rate. Next, for each of the step strain values γ investigated, in all boxes all z-coordinates $r_{z,i}$ were replaced by $r_{z,i} + \gamma r_{y,i}$, using periodic boundary conditions of course. Finally all boxes were run for another 10000 steps, enough for all stresses to relax to zero, and $\sigma_{yz}(t, \gamma; \dot{\gamma})$ was measured. In all cases the time step was 0.001 seconds.

Figure 3.2: Sinusoidal fits (red) for the simulated stress (green) after application of different oscillatory perpendicular strains to various steadily sheared boxes. The top panel is for a shear rate of 0.1 s^{-1} at a frequency of 500 rad/s . The middle panel is for a shear rate of 1 s^{-1} at a frequency of 0.1 rad/s . The bottom panel is for a shear rate of 2.5 s^{-1} at a frequency of 50 rad/s . The applied sinusoidal strain, $\gamma_{\perp} \sin(\omega t)$, scaled to become comparable to the stress, is shown in blue. In the top and bottom panels stresses and strains are almost in phase with each other; in the middle panel they are out of phase. In the top panel, the difference between the actual values and the fit is hardly visible. In the middle panel the stress signal is very noisy, but still can be fitted without big problems. The bottom panel shows that with a high shear rate of 2.5 s^{-1} the fitting is difficult due to a low frequency oscillation that occurs at medium and high frequencies. With even higher shear rates this poses a severe problem that prevents such systems from being studied.

3.4 Results

In this section we present the results of our Brownian Dynamics simulations of orthogonal superposition experiments for a system of particles interacting via the Likos potential, and compare them with a variety of results obtained from different calculations.

3.4.1 Storage and loss moduli from OSR

In Fig. 3.3 we present the $G'_{\perp}(\omega; \dot{\gamma})$ and $G''_{\perp}(\omega; \dot{\gamma})$ obtained from the OSR simulations for different shear rates. The data for $G''_{\perp}$ are very noisy at the higher frequencies in all cases. For the lower shear rates, the data for $G'_{\perp}$ are somewhat noisy at the lower frequencies. In fact for the non-sheared system the storage and loss moduli can better be obtained from Fourier transformations of the relaxation modulus. One clearly notices that the moduli of sheared systems increasingly shift to higher frequencies with increasing shear rates. Also a clear decrease of the plateau modulus ($G'_{\perp}$ at high frequencies) with increasing shear rates is evident, indicating an increased fluidization of the sample with increasing steady shear rates.

We want to emphasize that our data in all cases could be well-described by Eq. 3.13. This implies that the response of the sheared system to the orthogonal probing is linear. In particular, no additional non-linear contributions are needed to describe the data. If we next assume that the orthogonal storage and loss moduli are the sine and cosine transform of a time-domain function, then we can work our way back to Eq. 3.4. This implies that Eq. 3.4 holds for an oscillatory shear rate, *i.e.* for $\dot{\gamma}_{\perp}(t) = \gamma_{\perp} \omega \cos(\omega t)$. This does not mean that Eq. 3.4 necessarily also holds for other shear rates.

In Fig. 3.4 we have collected all $G_{\perp}(t; \dot{\gamma})$ obtained by Fourier transformation according to the method of Schwarzl [110]. Again we notice a decrease of the plateau values ($G_{\perp}$ at small times) with increasing steady shear rates. Another interesting characteristic is that the long time behavior of $G_{\perp}$ changes from exponential decay to algebraic decay. As a rough indication we have fitted an algebraic decay, $G_{\perp}(t; \dot{\gamma}) \propto t^{-1.5}$, in the case of a shear rate of 2.5 s^{-1} .

Since the storage and loss moduli are the objects that have been obtained directly from the simulation, while the relaxation modulus was obtained from these by a Fourier transform, the former are statistically better defined than the latter. We therefore fitted algebraic expressions to the low frequency part of the storage modulus $G'_{\perp}(\omega; \dot{\gamma}) \propto \omega^{\alpha}$, as shown in Fig. 3.5. The exponent α depends on the imposed shear rate, as shown in Fig. 3.6. Clearly α changes from a value of 2 for zero shear rate to 1.5 for an imposed shear rate of 2.5 s^{-1} . The drawn line in this plot, given by $\alpha = 2 - 0.3497 \cdot (\dot{\gamma})^{0.2055}$, only serves as a guide to the eye. Even so, however, the plot seems to indicate that $\dot{\gamma} = 0$ is a singular point.

Figure 3.3: Storage and loss moduli for steadily sheared systems. $G'_\perp(\omega; \dot{\gamma})$ is shown in black and the $G''_\perp(\omega; \dot{\gamma})$ in red. a) Steady shear rates of 0.0 s^{-1} (circles), 0.1 s^{-1} (triangles) and 0.5 s^{-1} (asterisks). While the curves of 0.1 s^{-1} are almost indistinguishable from the zero shear response, those of 0.5 s^{-1} are slightly shifted to higher frequencies. A slight decrease of plateau modulus for 0.5 s^{-1} can be seen. b) Steady shear rates of 0.0 s^{-1} (circles), 1.0 s^{-1} (triangles) and 2.5 s^{-1} (asterisks). Shifts along the frequency axis and decreases of plateau values are more pronounced.

Figure 3.4: $G_\perp(t; \dot{\gamma})$ for different shear rates obtained by the method of Schwarzl applied the OSR moduli shown in Figure 3.3. The plateau moduli decrease and the terminal decay becomes algebraic with increasing shear. For the largest shear rate the terminal algebraic decay is shown by a dotted line with a slope of 1.5.

Figure 3.5: The figure shows the low frequency part of the storage moduli $G'_L(\omega; \dot{\gamma})$ fitted with dashed lines for different shear rates in order to obtain the terminal slope α . For visual reasons, the moduli have been shifted vertically with respect to the zero-shear curve (black) by dividing the original $G'_L(\omega; \dot{\gamma})$ by a factor of 5, 10, 10, 20 and 25 Pa for $\dot{\gamma} = 0.01, 0.1, 0.5, 1.0$ and 2.5 s^{-1} respectively in order to clearly separate them.

Figure 3.6: The slopes α obtained in 3.5 shown as a function of shear rate $\dot{\gamma}$. The values range from a maximum of 1.978 for $\dot{\gamma} = 0$ to 1.566 for $\dot{\gamma} = 2.5$. The drawn-line fit is given by $\alpha = 2 - 0.3497 \cdot (\dot{\gamma})^{0.2055}$.

Figure 3.7: Normalized stress relaxation functions $\sigma_{yz}(t, \gamma; \dot{\gamma})/\sigma_{yz}(0, \gamma; \dot{\gamma})$ for $\dot{\gamma} = 2.5 \text{ s}^{-1}$, after step-strains of 0.2, 0.4, 0.6 and 0.8, all of which collapse onto the same master curve. The behavior is similar for all other shear rates considered.

3.4.2 Step-strain simulations

We now discuss the results of our step strain simulations.

3.4.2.1 Time dependence

In this subsection we concentrate on the time dependence of the stress relaxation after a strain step. Therefore all relaxation curves are normalized by their value at time zero. Plateau values will be discussed in the next subsection.

In Fig. 3.7 we present the normalized relaxation function $\sigma_{yz}(t, \gamma; \dot{\gamma})/\sigma_{yz}(0, \gamma; \dot{\gamma})$ for a steady shear rate of 2.5 s^{-1} , and for four values of the strain step γ ranging from 0.2 to 0.8. Surprisingly all curves are identical to within the statistics that we obtained with our procedure, and are therefore equal to $G_{\perp}^s(t; \dot{\gamma})/G_{\perp}^s(0; \dot{\gamma})$. The same holds for all other steady strain rates that we applied, *i.e.* normalized relaxation curves for different values of the strain step γ only differ by their height. When discussing normalized relaxation curves we have always averaged over the curves obtained with the four different strain steps.

In Fig 3.8 we present the normalized step-strain relaxation curves $G_{\perp}^s(t; \dot{\gamma})$ for all different values of the steady shear rates that we have studied, together with the corresponding normalized $G_{\perp}(t; \dot{\gamma})$. It is clearly seen that the change of the characteristic decay times with increasing shear rates are very similar for both cases, but that the long time decays develop differently. For zero shear $G_{\perp}(t; 0) = G_{\perp}^s(t; 0)$ to a good approximation. With increasing shear rate $G_{\perp}^s(t; \dot{\gamma})$ continues to decay exponentially, whereas $G_{\perp}(t; \dot{\gamma})$ gradually develops an algebraic tail as discussed in Section 3.4.1.

Figure 3.8: The average normalized step-strain relaxation curves $G_{\perp}^s(t; \dot{\gamma})$ (solid lines) for all steady shear rates along with the normalized $G_{\perp}(t; \dot{\gamma})$ (dashed lines). With increasing shear rate $G_{\perp}^s(t; \dot{\gamma})$ continues to decay exponentially, whereas $G_{\perp}(t; \dot{\gamma})$ gradually develops an algebraic tail.

Figure 3.9: The relaxation moduli obtained for a shear rate of 2.5 s^{-1} for both boundary driven and force-driven methods (symbols) and the step strain (solid line with no symbols). The results from both methods are in good agreement, and differ significantly from those obtained with the step strain simulations. This shows that the onset of power-law behavior with increasing shear rates at low frequencies is not a consequence of the implementation method.

Figure 3.10: Stress per unit step-strain, $\sigma_{\perp}(\gamma; \dot{\gamma})/\gamma$, for different values of the step magnitude γ (symbols) and the theoretical fits for them shown by dashed lines. The curves from top to bottom are for shear rates 0, 0.5, 1.0, 1.5 and 2.5 s^{-1} . The drawn lines through the symbols are a guide to the eye. Close agreement with theory is clearly seen.

One of the differences between the two experiments is that the displacements in z-direction are not strictly linear with height y in the oscillatory simulation, whereas they are linear by definition in the initial frames of the step strain simulations. This is a result of the use of a ‘boundary driven method’ in the OSR simulations, in which the linear profile has to develop by itself. We therefore ran a simulation in which the flow fields are applied more directly. This we did by replacing $u_{\alpha i, x}$ by $\dot{\gamma} y_i$ and $u_{\alpha i, z}$ by $\omega \gamma_{\perp} \cos(\omega t) y_i$ in the propagator Eq. 3.10. We call this method the ‘force driven method’. In Fig.3.9 we have plotted the storage and loss moduli for the case with $\dot{\gamma} = 2.5 \text{ s}^{-1}$, both for the boundary driven case and for the force driven method, together with those obtained from the step strain simulation. To within the statistics of our results one may say that the difference between boundary driven results and force driven results is smaller than the differences between both of them and the step strain results.

We conclude that, for stationary sheared systems, the relaxation spectrum probed by small oscillatory perturbations is different from that obtained with step strain simulations.

3.4.2.2 Plateau values

We now consider the time zero values of the relaxation moduli, *i.e.* the normalization constants $\sigma_{yz}(0, \gamma; \dot{\gamma})$ used in the previous subsection. For ease of notation, we define $\sigma_{\perp}(\gamma; \dot{\gamma}) = \sigma_{yz}(0, \gamma; \dot{\gamma})$ and refer to them as peak values.

Since the stress immediately after a strain step is a non-dynamical property, we can easily

Figure 3.11: Panel (a) shows the first coefficient $\sigma_{\perp}^{(1)}(\dot{\gamma})$ as a function of shear rate calculated by two different methods: simulation of expression 3.17 (circles) and by using the spherical part of the radial distribution function $g^{(0)}(r; \dot{\gamma})$ (squares), 3.18. These are compared with the plateau modulus from OSR (triangles). For all shear rates the coefficient calculated from simulation is very close to the plateau values. When using $g^{(0)}(r; \dot{\gamma})$, the first coefficient differs substantially from OSR plateau values at large imposed shear rates, while at smaller shear rates both results converge to each other. Panel (b) shows the third coefficient calculated from the expression and from $g^{(0)}(r; \dot{\gamma})$.

derive theoretical expressions for it. In Section 3.6.1 we will show that we may write

$$\sigma_{\perp}(\gamma; \dot{\gamma}) = \sigma_{\perp}^{(1)}(\dot{\gamma})\gamma + \frac{\sigma_{\perp}^{(3)}(\dot{\gamma})}{6}\gamma^3 + \dots \quad (3.16)$$

with

$$\sigma_{\perp}^{(1)}(\dot{\gamma}) = \frac{1}{V} \sum_{i < j} \left\langle \left(z_{ij}^2 \frac{\phi''}{r_{ij}^2} y_{ij}^2 - z_{ij}^2 \frac{\phi'}{r_{ij}^3} y_{ij}^2 + \frac{\phi'}{r_{ij}} y_{ij}^2 \right) \right\rangle_{\dot{\gamma}} \quad (3.17)$$

and a similar expression for $\sigma_{\perp}^{(3)}(\dot{\gamma})$. The primes in Eq. 3.17 denote differentiations and $x_{ij} = x_i - x_j$ etc. The angular brackets $\langle \rangle_{\dot{\gamma}}$ denote an average over the configurations sampled from a steadily sheared run. For obvious reasons, terms with even powers of γ are absent (see Section 3.6.1). Comparison of Eqs 3.15 and 3.17 shows that $G_{\perp}^s(0; \dot{\gamma}) = \sigma_{\perp}^{(1)}(\dot{\gamma})$. We refer to $\sigma_{\perp}^{(1)}(\dot{\gamma})$ as the step strain plateau value, since it is equal to the constant value to which the storage modulus corresponding to $G_{\perp}^s(t; \dot{\gamma})$ converges for large frequencies.

In Fig. 3.10 we present $\sigma_{\perp}(\gamma; \dot{\gamma})/\gamma$ (symbols) for various values of the strain step, and compare them with the theoretical results (dashed lines). The figure clearly confirms the theory. Remaining small differences could be a result of finite size effects which are different

Figure 3.12: The spherical part of the radial distribution function, $g^{(0)}(r; \dot{\gamma})$, for different shear rates. The first peak reduces in magnitude, showing the effect of increasing shear on removing correlations between particle positions.

for the simulated plateau values and the calculated ones.

In Figs 3.11a and 3.11b we present $\sigma_{\perp}^{(1)}(\dot{\gamma})$ (circles) and $\sigma_{\perp}^{(3)}(\dot{\gamma})$ (circles) as a function of the shear rate of the imposed stationary flow. Included in Fig. 3.11a are also $G_{\perp}(0; \dot{\gamma})$ (triangles) obtained from the oscillatory simulations. These values clearly agree with those from the step strain simulations. So, although moduli obtained from oscillatory experiments do not agree with those obtained from step strain experiments in their long time behavior, they do have the same short time values.

Now, let us shortly discuss what information is to be found in $\sigma^{(1)}(\dot{\gamma})$ and $\sigma^{(3)}(\dot{\gamma})$. From Eq. 3.17 we notice that $\sigma^{(1)}(\dot{\gamma})$ is a sum over pair-terms, each averaged over the configurations obtained from a sheared simulation. As such it may be considered to be a way of probing the perturbation of the pair distribution function by the applied stationary flow. We therefore write Eq. 3.17 as

$$\sigma_{\perp}^{(1)}(\dot{\gamma}) = \frac{\rho^2}{2} \int d^3r g(\vec{r}; \dot{\gamma}) \left(z^2 \frac{\phi''}{r^2} y^2 - z^2 \frac{\phi'}{r^3} y^2 + \frac{\phi'}{r} y^2 \right), \quad (3.18)$$

where $g(\vec{r}; \dot{\gamma})$ is the perturbed pair distribution function. Note that we have assumed a homogeneous and isotropic density of particles ρ . A similar equation holds for $\sigma_{\perp}^{(3)}(\dot{\gamma})$. For

non-zero shear rates we write approximately

$$\begin{aligned}
 g(\vec{r}; \dot{\gamma}) &= g^{(0)}(r; \dot{\gamma}) + g^{(1)}(r; \dot{\gamma}) \frac{xy}{r^2} \dot{\gamma} \\
 &+ \left[g^{(2,1)}(r; \dot{\gamma}) \frac{x^2 y^2}{r^4} + g^{(2,2)}(r; \dot{\gamma}) \frac{x^2 + y^2}{r^2} \right] \dot{\gamma}^2 + \dots
 \end{aligned} \tag{3.19}$$

In this equation we have accounted for the symmetry imposed by the shear flow. The coefficients $g^{(0)}(r; \dot{\gamma})$ etc. may still depend on $\dot{\gamma}$. In particular we leave open if they are analytic or singular functions of the shear rate. In Fig. 3.12 we depict the spherical part $g^{(0)}(r; \dot{\gamma})$ of the perturbed pair function. It is clearly seen that also the spherical part of the distribution function is severely changed by the stationary shear flow. Restricting ourselves to just this contribution to the pair function we obtained the results denoted ‘ $g(r)$ ’ (squares) in Figs 3.11a and 3.11b. For shear rates below $0.5s^{-1}$ the $\sigma_{\perp}^{(1)}(\dot{\gamma})$ within this approximation are rather close to the actual values. At larger shear rates, the difference between the actual coefficients and those obtained with the spherical pair function indicates that the contribution of the non-spherical terms must be substantial. Including the next term of the pair distribution function, the one proportional to $\dot{\gamma}$, will make no difference. This can be inferred from the fact that including this term gives rise to an additional sum of terms in the integrand which are all proportional to odd powers of x and y , which will all become zero after an integration over all space. A similar argument shows that the next terms, proportional to $\dot{\gamma}^2$, do contribute to the integrals. Since possible density gradients may further complicate the picture, we do not investigate this here, referring for a more detailed discussion to reference [147]. A phenomenological analysis of the role of configurations, based on the Giesekus model, has been presented in Ref [148].

Before ending this section, let us conclude from results in this section and those of Section 3.4.2.1 that for the sheared systems, relaxation moduli obtained from oscillatory simulations are largely equal to those obtained from step strain simulations, but that their moduli differ in late time behavior. The strong version of the Boltzmann principle, as we defined it in the Introduction, is therefore not valid. It even seems that in this respect the zero shear case is a singular case, as strongly suggested by the results in Fig. 3.6.

3.4.3 Violation of Green-Kubo

Under zero-shear conditions, the shear relaxation modulus is proportional to the time correlation function of any off-diagonal component of the stress tensor. Naively, one might argue that the imposed stationary shear flow serves only to define the system, and that the Green-Kubo relations should still hold, with the exception that time correlation functions should be calculated in the sheared ensemble. We therefore ask: is $G_{\perp}(t; \dot{\gamma})$ given by

$$G_{\perp}^{GK}(t; \dot{\gamma}) = \frac{V}{k_B T} \langle \sigma_{yz}(t) \sigma_{yz}(0) \rangle_{\dot{\gamma}} \tag{3.20}$$

Figure 3.13: Shear relaxation moduli from the Green-Kubo relation, Equation 3.20, $G_{\perp}^{GK}(t; \dot{\gamma})$ (solid lines), for three shear rates of 0.5, 1.0 and 2.5 s^{-1} . Moduli calculated from OSR results, $G_{\perp}(t; \dot{\gamma})$, are shown as dashed lines. The zero-shear relaxation modulus is shown as a dash-dotted line for reference. Clearly the GK moduli are very different from the ‘real’ moduli $G_{\perp}(t; \dot{\gamma})$. Not only do they have a higher plateau value which, contrary to those of $G_{\perp}(t; \dot{\gamma})$, increases with shear rate, but they also decay much later than their counterparts and in a qualitatively different manner.

On the other hand, one of the easiest ways to derive the Green-Kubo relations at zero shear is through the analysis of step strain experiments, which for completeness we show in Section 3.6.2. Now that we have seen that under shear, orthogonal step strain and oscillatory experiments yield different relaxation moduli, one may expect that also Green-Kubo does not apply.

In Fig. 3.13 we present $G_{\perp}^{GK}(t; \dot{\gamma})$ calculated using Eq. 3.20. In order to obtain good statistics, 30 pre-equilibrated boxes were run for 10 million steps each, and the stress correlations from them were averaged to yield the results. It is clearly seen in Fig. 3.13 that the Green-Kubo moduli do not agree with the OSR moduli. While the initial values are decreasing for the OSR results, they are increasing for the GK results. The dynamics is somewhat similar in the sense that both moduli decay earlier with increasing shear rates, but the GK moduli do not develop the characteristic algebraic tails as the OSR moduli do. We checked that the normalised GK moduli are also different from the normalized step strain moduli. Only in the non-sheared system do all moduli, *i.e.* the OSR moduli, the GK moduli and the step strain moduli, agree.

3.5 Summary and discussion

We have investigated, by means of Brownian dynamics simulations, the applicability of Boltzmann's superposition principle to orthogonal superposition rheology. We prepared our systems by shearing them along the x-axis, with gradient along the y-axis, and maintained this shear during all subsequent 'experiments'. We interrogated these systems by measuring the response to the application of small probing perturbations orthogonal to the applied steady shear. The probing perturbations were either a small step strain perturbation or an oscillating perturbation, both in the z-direction with gradient along the y-axis. These perturbations give rise to the following responses

$$\begin{aligned}\sigma_{yz} &= \gamma G_{\perp}^s(t; \dot{\gamma}) \\ \sigma_{yz} &= \int_{-\infty}^t G_{\perp}(t - t'; \dot{\gamma}) \dot{\gamma}_{\perp}(t') dt',\end{aligned}\tag{3.21}$$

with γ being the value of the strain step, and $\dot{\gamma}_{\perp}(t)$ the time dependent orthogonal shear rate. Both shear moduli $G_{\perp}^s$ and $G_{\perp}$ depend parametrically on the applied steady shear rate $\dot{\gamma}$. At zero shear rate, *i.e.* when $\dot{\gamma} = 0$, both shear moduli are equal. We have found in this chapter that this is not true anymore for non-zero shear rates.

Although the initial values of both moduli are the same, and their decay times are roughly the same, their late time dependencies are different. While $G_{\perp}$ develops an algebraic tail with increasing steady shear rates, the step strain modulus $G_{\perp}^s$ does not do so. We quantified these findings by calculating the exponents α of the low frequency algebraic increase of the storage modulus, $G'_{\perp}(\omega; \dot{\gamma}) \propto \omega^{\alpha}$, as a function of the imposed steady shear rate. It turns out that α continuously approaches its zero shear rate value of 2, when shear rates become very small, but that the corresponding curve is singular, *i.e.* has no derivative, at zero shear rate. This is an indication that even at the smallest shear rates orthogonal probing cannot be considered to be a linear probing of a linearly perturbed system. Apparently the different 'symmetries' of a small *steady* shear and an *oscillatory* orthogonal shear with small amplitude do not just give rise a stress response whose components can be calculated from equilibrium properties. Obviously, combining two steady shear flows can be turned into a simple shear flow by rotating the coordinate system. It will be interesting to investigate the same problem for two oscillatory flows.

Besides their differences, $G_{\perp}^s$ and $G_{\perp}$ also have similarities. Both of them accelerate, *i.e.* decay at increasingly smaller times with increasing shear rates, to roughly the same extent. For the step-strain experiments this may be a result of shear induced diffusion [149]. When orthogonal to the imposed shear flow, an oscillatory flow is applied this severely influences the shear induced diffusion processes, probably giving rise to additional diffusion modes. The latter may be the cause of the algebraic decay.

As mentioned in the main text, the initial values $G_{\perp}^s(0; \dot{\gamma})$ and $G_{\perp}(0; \dot{\gamma})$ do coincide. We

have presented a simple equation allowing to calculate the dependence of these quantities on the imposed steady shear rate. It is interesting that, for small imposed shear rates, the numerical evaluation of this equation only requires the spherical part of the pair correlation function as a function of the imposed shear rate. This means that the vertical shift factor in a time-shear rate superposition presentation, analogous to a time-temperature superposition presentation, of the data can be simply related to the perturbation of the spherical part of the pair correlation function caused by an imposed steady shear flow. For interesting phenomenological relations concerning this type of superposition, see Ref. [150].

Let us finish with a few comments concerning the molecular model that we have used in this chapter. We have explicitly not taken into account many aspects that are characteristic for soft matter systems. Near equilibrium, usually a wide range of time scales related to internal dynamics is visible in rheological spectra, among which are Rouse and reptation dynamics in general, or arm retraction moves as in star polymers [19, 20]. With larger shear rates, on a very coarse level, particles may be considered to interact through mean forces augmented with transient forces [24, 151]. As it has been used so far, that model will be insufficient in many cases since it does not take into account the deformation of the individual particles caused by the imposed shear flow. A consequence of this would be that the potential interactions become anisotropic, and that the frictions in Eqs 3.10 should be different for motions in different directions [152]. It is difficult to predict what the influence of these responses of the particles to the imposed shear flow would be, but one may speculate that they help to delay the onset of the algebraic tails found in this chapter to larger shear rates. This seems to be corroborated by results presented in Ref [125].

3.6 Appendix

3.6.1 Taylor expansion of the virial stress after a strain step

In this Appendix we will show that the virial stress $\sigma_{\perp}(\gamma; \dot{\gamma})$ at time $t = 0^+$ after a strain step, may be written as a power expansion in γ of the form:

$$\sigma_{\perp}(\gamma; \dot{\gamma}) = \sum_{n=0}^{\infty} \frac{\sigma_{\perp}^{(n)}(\dot{\gamma})}{n!} \gamma^n. \quad (3.22)$$

Since the stress must change sign when γ changes sign, only odd powers of γ will have non-zero coefficients.

To determine the coefficients $\sigma_{\perp}^{(n)}(\dot{\gamma})$, we simply mimic the step strain experiment, by sampling from an ensemble of systems applicable at the given shear rate $\dot{\gamma}$, performing a strain step of size γ , and measuring the stress immediately after the step. Since the strain step

changes $\vec{r}_i$ into $\vec{r}_i + \gamma y_i \hat{e}_z$, the relevant stress component may be written as

$$\sigma_{\perp}(\gamma; \dot{\gamma}) = \frac{1}{V} \sum_{i < j} \left\langle y_{ij} \frac{\phi'(r_{ij} + \Delta_{ij})}{r_{ij} + \Delta_{ij}} (z_{ij} + \gamma y_{ij}) \right\rangle_{\dot{\gamma}}. \quad (3.23)$$

In this equation we have used the virial expression for stress given in Equation 3.14 while the angular brackets $\langle \rangle_{\dot{\gamma}}$ indicate an average over the ensemble applicable when the stationary shear rate equals $\dot{\gamma}$. The difference Δ_{ij} is given by:

$$\Delta_{ij} = \frac{z_{ij} y_{ij}}{r_{ij}} \gamma + \frac{1}{2} \left(\frac{y_{ij}^2}{r_{ij}} - \frac{z_{ij}^2 y_{ij}^2}{r_{ij}^3} \right) \gamma^2 + \frac{1}{2} \left(\frac{z_{ij}^3 y_{ij}^3}{r_{ij}^5} - \frac{z_{ij} y_{ij}^3}{r_{ij}^3} \right) \gamma^3 \quad (3.24)$$

where we have expanded upto the third order in γ . The second and third powers of Δ_{ij} are given by:

$$\Delta_{ij}^2 = \frac{z_{ij}^2 y_{ij}^2}{r_{ij}^2} \gamma^2 + \left(\frac{z_{ij} y_{ij}^3}{r_{ij}^2} - \frac{z_{ij}^3 y_{ij}^3}{r_{ij}^4} \right) \gamma^3 \quad (3.25)$$

$$\Delta_{ij}^3 = \frac{z_{ij}^3 y_{ij}^3}{r_{ij}^3} \gamma^3 \quad (3.26)$$

where again we have retained only terms upto the third order in γ .

Expanding the pair interaction potential to third order in Δ_{ij} , we find

$$\sigma_{\perp}(\gamma; \dot{\gamma}) = \frac{1}{V} \sum_{i < j} \left\langle \left(\phi' + \phi'' \Delta_{ij} + \frac{\phi'''}{2} \Delta_{ij}^2 + \frac{\phi''''}{6} \Delta_{ij}^3 \right) \left(1 + \frac{\Delta_{ij}}{r_{ij}} \right)^{-1} \left(\frac{z_{ij} y_{ij}}{r_{ij}} + \frac{\gamma y_{ij}^2}{r_{ij}} \right) \right\rangle_{\dot{\gamma}} \quad (3.27)$$

The number of primes with the potential ϕ represents the order of the derivative. Expanding the middle factor and next all powers of Δ_{ij} we obtain the following expressions

$$\sigma_{\perp}^{(1)}(\dot{\gamma}) = \frac{1}{V} \sum_{i < j} \left\langle \left(\frac{\phi'' z_{ij}^2 y_{ij}^2}{r_{ij}^2} - \frac{\phi' z_{ij}^2 y_{ij}^2}{r_{ij}^3} + \frac{\phi' y_{ij}^2}{r_{ij}} \right) \right\rangle_{\dot{\gamma}} \quad (3.28)$$

$$\begin{aligned} \sigma_{\perp}^{(3)}(\dot{\gamma}) &= \frac{1}{V} \sum_{i < j} \left\langle \left(\frac{z_{ij}^4 y_{ij}^4}{r_{ij}^4} \phi'''' + \frac{6 z_{ij}^2 y_{ij}^4}{r_{ij}^3} \phi''' - \frac{6 z_{ij}^4 y_{ij}^4}{r_{ij}^5} \phi''' \right) \right\rangle_{\dot{\gamma}} \\ &+ \frac{1}{V} \sum_{i < j} \left\langle \left(\frac{15 z_{ij}^4 y_{ij}^4}{r_{ij}^6} \phi'' - \frac{18 z_{ij}^2 y_{ij}^4}{r_{ij}^4} \phi'' + \frac{3 y_{ij}^4}{r_{ij}^2} \phi'' \right) \right\rangle_{\dot{\gamma}} \\ &+ \frac{1}{V} \sum_{i < j} \left\langle \left(\frac{18 z_{ij}^2 y_{ij}^4}{r_{ij}^5} \phi' - \frac{15 z_{ij}^4 y_{ij}^4}{r_{ij}^7} \phi' - \frac{3 y_{ij}^4}{r_{ij}^3} \phi' \right) \right\rangle_{\dot{\gamma}} \end{aligned} \quad (3.29)$$

Both coefficients are averages over configurations of a sheared ensemble of sums of terms, each of which is proportional to even powers of y_{ij} and z_{ij} .

Coefficients with even superscripts are averages over configurations of a sheared ensemble of sums of terms, each of which is proportional to odd powers of y_{ij} and z_{ij} . Replacing the averaging $1/V \sum_{i < j} \langle \rangle_{\dot{\gamma}}$ by $\rho^2/2 \int d^3r g(\vec{r}; \dot{\gamma})$ and noticing that $g(\vec{r}; \dot{\gamma})$ contains only terms proportional to powers of x and y , we find that all terms are proportional to an odd power of z and will become zero after integration over all space. This constitutes a mathematical proof of the physically obvious fact that terms proportional to even powers of γ do not contribute in Eq. [3.22].

The remaining non-zero terms are all of the type

$$\int dr F(r) \oint dS z^\alpha y^\beta = I_{\alpha,\beta} \int dr F(r), \quad (3.30)$$

where $\oint dS$ denotes an integral over the unit sphere. The only integrals $I_{\alpha,\beta}$ that we needed are $I_{2,0} = 4\pi/3$, $I_{2,2} = 4\pi/15$, $I_{4,0} = 4\pi/5$, $I_{4,2} = 4\pi/35$, and $I_{4,4} = 4\pi/105$. The remaining integrals over r were done numerically.

3.6.2 Derivation of Green-Kubo equation for equilibrium systems

In this Appendix we give a quick derivation of the Green-Kubo expression to calculate the stress relaxation after a strain step. The distribution of configurations r^{3N} right after the step is given by

$$P_\gamma(r^{3N}) = \frac{\exp\{-\beta\Phi(\vec{r}_1 - \gamma y_1 \hat{e}_z, \dots, \vec{r}_N - \gamma y_N \hat{e}_z)\}}{Z_\gamma} \quad (3.31)$$

where Z_γ is the normalizing constant or partition function, and $\beta = (k_B T)^{-1}$. Expanding Φ to first order in γ , and next the exponential, we obtain

$$P_\gamma(r^{3N}) = \frac{\exp\{-\beta\Phi(r^{3N})\}}{Z_\gamma} (1 + \beta\gamma V \sigma_{yz}(r^{3N})) \quad (3.32)$$

Next we calculate the partition function

$$\begin{aligned} Z_\gamma &= \int d^{3N}r \exp\{-\beta\Phi(r^{3N})\} (1 + \beta\gamma V \sigma_{yz}(r^{3N})) \\ &= Z (1 + \beta\gamma V \langle \sigma_{yz} \rangle), \end{aligned} \quad (3.33)$$

where the angular brackets indicate an equilibrium average. Using that the average stress is zero at equilibrium we find

$$P_\gamma(r^{3N}) = P_{eq}(r^{3N}) (1 + \beta\gamma V \sigma_{yz}(r^{3N})), \quad (3.34)$$

where $P_{eq}(r^{3N}) = \exp\{-\beta\Phi(r^{3N})\}/Z$. Denoting the stress at time t of a system that at time zero had the configuration r^{3N} by $\sigma_{yz}(t; r^{3N})$, we obtain for the modulus:

$$\begin{aligned} G^s(t) &= \frac{1}{\gamma} \int d^{3N} r \sigma_{yz}(t; r^{3N}) P_\gamma(r^{3N}) \\ &= \beta V \int d^{3N} r P_{eq}(r^{3N}) \sigma_{yz}(t; r^{3N}) \sigma_{yz}(r^{3N}), \end{aligned} \quad (3.35)$$

where we have used that $\langle \sigma_{yz}(t) \rangle = 0$. This result may be written in its usual notation as

$$G^s(t) = \frac{V}{k_B T} \langle \sigma_{yz}(t) \sigma_{yz}(0) \rangle \quad (3.36)$$

In equilibrium, when the modulus after a strain step is the same as the one from oscillatory experiments, we may remove the superscript ' s '.

Chapter 4

Brownian Dynamics Simulations of High-functionality Star Polymers Probed by OSR

In this chapter we present the results of OSR simulations with Brownian Dynamics for a system of star-like micelles with functionality 120 at a very high volume fraction compared to that in Chapter 3. These simulations are counterparts to an experimental OSR investigation of a concentrated star-like micellar solution, which found non-standard relaxations in the orthogonal moduli after a critical shear rate. Simulations were carried out for two model representations, one with only the Likos potentials between the micelles and another with an additional transient potential by the Rapid method. We found that after a certain shear rate, the orthogonal moduli develop multiple crossovers in both models. This can be attributed to shear induced lane formation which is clearly seen in the movies and in the mean squared displacements in the gradient and vorticity directions, with lane formation leading to reduced transport in these directions with shear. In model 1, laning occurs due to purely repulsive interactions between the micelles and there is clear shear-induced ordering at high shear rates at which the storage and loss moduli become parallel, yielding a solid like response. No such separation of moduli is seen in model 2 whose response is hence liquid-like at all rates since the transient interactions tend to maintain a given distance distribution between the particles. Although each particle travels in its own lane at high shear rates, there is no crystalline order.

4.1 Introduction

Complex fluids are a state of matter with physical properties intermediate between those of solids and liquids [1]. Colloidal suspensions, being complex fluids, form an interesting class of soft matter [153] that have been used to study various physical phenomena like gelation [154], shear-induced structural changes [155, 156, 157, 158, 159, 160] and the nature of crystalline and glass phases formed by hard spheres and their associated phase transitions [161, 162, 163]. The phase behavior of these systems and hence their response to shear, is controlled by the nature of the inter-particle interactions, their concentration and temperature. With pure repulsions alone, as with hard spheres, only volume fraction determines their structure and rheology. At high volume fractions the particles are trapped in cages and form a glass. Inclusion of attractive interactions is known to melt the glass [164, 165] and shift the glass transition to high volume fractions. More generally the inter-particle interactions can be tuned by a choice of well-designed molecular structure of the particles. Because of the corresponding variety of rheological properties these systems hold great promises for industrial applications. One such category of particles is star-like micelles in solution, which have intrinsic softness [166, 167, 168, 169]. By increasing the number of arms, soft to hard sphere-like rheological responses can be obtained. The response of such systems to a variety of shear flows is an interesting area of modern rheological research and has yielded valuable information about their dynamical properties [35].

Recently, Petekidis and co-workers [35] have studied a concentrated system of star-like micelles with an aggregation number of 120 by the technique of Orthogonal Superposition Rheology (OSR) [26, 33, 37, 119, 120, 121, 122, 123, 124, 125]. This technique has already been applied to various kinds of soft matter systems under shear [148, 135, 137, 136, 133, 34], and has been found to provide rich information about non-linear rheology. Some intriguing observations were made, among which was the appearance of multiple crossovers of the storage and loss moduli above a critical shear rate. Being a concentrated system, it also displayed a yield stress and the flow curve was fitted with a Hershel Buckley model. It has been suggested [170] that these star micelles behave similar to star polymers, and interact through the potential of mean force derived by Likos and co-workers [53]. Following this suggestion, we performed OSR simulations of star-like polymers with a functionality of 120 using Brownian Dynamics (BD). Since it is not clear how well star-like micelles may be represented as star-like polymers under highly dynamical circumstances, we do not expect quantitative agreement between our simulations and experimental results. Nevertheless, we choose system parameters to roughly mimic the experimental system, in order to study similar phenomena with our simulations as are found with experiments. BD simulations of hard spheres with similar goals to ours, have been performed [35], but the OSR moduli were obtained from mean squared displacements of the constituent particles by using the Generalized Stokes-Einstein (GSE) relations developed by Mason and Weitz [142]. This method, however, is known to be not very accurate when applied to particles of the size of the smallest

scale in the system.

In Chapter 3, we studied the OSR response of 13 arm star polymers at a relatively low number density, by performing BD simulations with two simultaneous flow fields encoded in the propagator: a steady deforming shear flow, and an oscillatory small-amplitude probing flow applied orthogonal to the shear. The interactions between stars were purely repulsive and described by the potential given by Likos and co-workers [53]. With a functionality of 13, the inter-star potential was very soft, and no phenomena like multiple crossings of storage and loss moduli were observed. We apply the same method in this work, but this time the concentration is much higher and the interactions are much steeper as a result of the rather high functionality of 120. We thereby probe a different region of the rheological phase diagram and expect to find similar phenomena as in experiments on high functionality dense micellar star systems. Given the high density of the system, we neglect hydrodynamic interactions.

With the model referred to above, *i.e.* a system of point particles interacting through a potential of mean force and at high densities, we reproduce many of the phenomena that have been seen with experiments. As a result of the high densities and the steep repulsions in this model, the system becomes solid-like when the imposed shear rates are high, which is not the case experimentally. We will refer to this model as model 1 and besides this also present results obtained with a second model, denoted model 2. The potential of mean force developed by Likos and co-workers gives rise to forces felt by the centers of mass of the stars, when averaged over all configurations of the arms that are attached to them. In equilibrium simulations, when stars move very slowly, this may be a good approximation to the forces that cause the displacements of the centers of mass, *i.e.* the particles at the coarse level of description applied here. One may well conceive that, when affine flow displaces particles very fast with respect to each other, the arms do not have time to explore all configurations before the centers of mass have displaced again over substantial distances compared to the particles sizes. In these cases the actual forces are different from the average forces and corrections must be included to the potential in order to account for this effect. Here we follow the suggestion by Briels and co-workers to include so-called transient contributions to the pair interactions. These contributions depend on the values of a set of additional dynamic variables, which roughly describe the deviation from equilibrium of the the configuration of the arms of the two interacting stars. If, by whichever demon, the centers of mass are frozen for a while, these dynamical variables, and with them the corrections to the forces, gradually relax to zero. We have chosen the parameters of model 2 such that it gives rise to the same zero shear rheology as model 1.

We divide the chapter into the following sections. The system description and methods of simulation are described in Section 4.2, followed by the results in Section 4.3. We end with a discussion of our results in detail in Section 4.4.

4.2 System and Methods

4.2.1 Models 1 and 2

Our models are devised in order to roughly reproduce the physics of a system composed of star-like micelles, resembling star polymers with 120 arms each. For the BD simulations, each molecule is coarse-grained to a single point, interacting with other points through an effective potential:

$$\Phi(r^{3N}) = \sum_{\langle ij \rangle} \phi(r_{ij}). \quad (4.1)$$

The sum $\langle ij \rangle$ runs through all pairs of particles, and $\phi(r_{ij})$ is the interaction potential between particles i and j at a distance r_{ij} .

Two different models, with different interaction potentials were used in this study. In the first model, the particles interact through the potential of mean force Eq. 4.2, derived by Likos and co-workers:

$$\begin{aligned} \phi_C(r_{ij}) &= \left(\frac{5k_B T}{18} \right) f^{1.5} \left[-\ln \left(\frac{r_{ij}}{\sigma_L} \right) + \left(1 + \frac{\sqrt{f}}{2} \right)^{-1} \right] & r_{ij} \leq \sigma_L \\ &= \left(\frac{5k_B T}{18} \right) f^{1.5} \left(1 + \frac{\sqrt{f}}{2} \right)^{-1} \left(\frac{\sigma_L}{r_{ij}} \right) \exp \left(-\sqrt{f} \left(\frac{r_{ij} - \sigma_L}{2\sigma_L} \right) \right) & r_{ij} > \sigma_L, \end{aligned} \quad (4.2)$$

As is clear from its name, this potential gives rise to the average force between particles i and j , with the average taken over all configurations of the arms of the two particles. The potential is strictly repulsive, mainly due to loss of entropy when two particles come close to each other. The entropic origin is reflected in the fact that the potential is proportional to the absolute temperature $k_B T$, with k_B being the Boltzmann constant. f is the functionality of the stars, *i.e.* their number of arms. In the present application $f = 120$. σ_L sets the length scale of the model.

In the second model, apart from repulsive interactions, we used the RaPiD model developed by Briels *et al.* [171, 172, 173] to include memory effects into the dynamics of the polymers. The total pair-potential is just the sum $\phi = \phi_C + \phi_T$, where ϕ_T is a quadratic, so-called transient potential, modeling the deviation of the arms of neighboring particles from equilibrium at the given distance r_{ij} :

$$\phi_T(r_{ij}) = \frac{1}{2} \alpha (n_{ij} - n_0(r_{ij}))^2. \quad (4.3)$$

The parameter α has units of energy and controls the strength of the transient contribution to the forces. The so-called contact numbers n_{ij} are dynamical variables that represent the

instantaneous number of contacts between segments of molecules i and j , while $n_0(r_{ij})$ is the mean number of contacts at equilibrium with the molecules at a distance r_{ij} . In cases when $n_{ij} = n_0(r_{ij})$, the transient potential and its first derivatives are zero, and the forces are given by the conservative potential of Eq. 4.2. In cases when $n_{ij} \neq n_0(r_{ij})$ transient forces are active, which always drive the particles to new distances r'_{ij} where the new equilibrium values $n_0(r'_{ij})$ are closer to the actual value of n_{ij} than the old $n_0(r_{ij})$, provided $n_0(r_{ij})$ is a decaying function of distance. In particular this means that if two particles are at a distance r_{ij} , and n_{ij} happens to be equal to $n_0(r_{ij})$, on a displacement in whichever direction, the transient forces after the displacement will always be toward the previous configuration. We use the expression for n_0 used previously [174]:

$$n_0(r_{ij}) = \left(\frac{r_{ij}}{R_C} - 1 \right)^2 \quad (4.4)$$

where R_C is the cutoff distance.

4.2.2 Propagators

Since our systems are typical highly overdamped soft matter systems, we use Brownian dynamics to propagate our systems in time.

The Brownian equation of motion for the i 'th particle is given by:

$$d\vec{r}_i = \vec{u}(\vec{r}_i)dt - \frac{1}{\xi} \frac{\partial \Phi}{\partial \vec{r}_i} dt + \sqrt{\frac{2k_B T}{\xi}} dt \vec{\Theta}_i. \quad (4.5)$$

The first term in the right hand side of Eq. 4.5 represents the displacement of the particle resulting from the overall velocity of the fluid at the position of the particle. The second term in the right hand side is just the displacement of the particle caused by all forces acting on that particle, while the last term is a random Brownian displacement that satisfies the fluctuation dissipation theorem. ξ is a friction coefficient and $\vec{\Theta}_i$ is a zero-mean, unit variance standard Gaussian random vector, not correlated with the random vectors of other particles.

As mentioned before, the contact numbers n_{ij} between particles i and j are dynamical variables. They are propagated in time according to:

$$dn_{ij} = -\frac{n_{ij} - n_0}{\tau} dt + \sqrt{\frac{2k_B T}{\alpha \tau}} dt \theta_{ij} \quad (4.6)$$

where τ is a time constant that controls the rate of relaxation of the n_{ij} 's to equilibrium and θ_{ij} is a standard normal random variable. At a fixed configuration the n_{ij} 's will relax towards their equilibrium distribution $\propto \exp[-\alpha(n_{ij} - n_0(r_{ij}))^2]/(2k_B T)$.

4.2.3 Flow fields

In this chapter we present results of simulations of systems subjected to two orthogonal flow fields, phenomenologically described by

$$\begin{aligned} u_x(t) &= \dot{\gamma}y \\ u_y(t) &= 0 \\ u_z(t) &= \gamma_{\perp}\omega\cos(\omega t)y, \end{aligned} \quad (4.7)$$

where $\dot{\gamma}$ is the imposed, perturbing steady shear rate and $\gamma_{\perp}$ the amplitude of the orthogonal oscillatory probing flow. These equations say that a steady shear is applied in the x-direction with gradient in the y-direction and a small-amplitude oscillatory probing flow is imposed in the z-direction, again with the gradient along the y-direction. In this manner we reproduce the experimental conditions in our simulations.

The above flow field must be substituted for the first term in the right hand side of Eq. 4.5. In order to do this, we divide the system into 10 slabs along the y-direction and calculate the average flow velocities $u_{\alpha,x}$ and $u_{\alpha,z}$ in each of these slabs. The propagator for the particles then reads

$$dx_i = -\frac{1}{\xi} \frac{\partial \Phi}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial x_i} dt + \sqrt{\frac{2k_B T}{\xi}} dt \Theta_{x,i} + u_{\alpha_i,x} dt \quad (4.8)$$

$$dy_i = -\frac{1}{\xi} \frac{\partial \Phi}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial y_i} dt + \sqrt{\frac{2k_B T}{\xi}} dt \Theta_{y,i} \quad (4.9)$$

$$dz_i = -\frac{1}{\xi} \frac{\partial \Phi}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial z_i} dt + \sqrt{\frac{2k_B T}{\xi}} dt \Theta_{z,i} + u_{\alpha_i,z} dt, \quad (4.10)$$

where α_i is the slab-number at the position of particle i . In order to measure the average flow velocities, we calculate the average particle velocities $\langle \dot{x}_i(t) \rangle_{\alpha} = \langle dx_i/dt \rangle_{\alpha}$ and $\langle \dot{z}_i(t) \rangle_{\alpha} = \langle dz_i/dt \rangle_{\alpha}$ in each slab α at each time-step. The flow velocities are then updated for every slab according to

$$\begin{aligned} u_{\alpha,x}(t+dt) &= \langle \dot{x}_i(t) \rangle_{\alpha} \left(1 - e^{-dt/\tau_f}\right) + u_{\alpha,x}(t)e^{-dt/\tau_f} \\ u_{\alpha,z}(t+dt) &= \langle \dot{z}_i(t) \rangle_{\alpha} \left(1 - e^{-dt/\tau_f}\right) + u_{\alpha,z}(t)e^{-dt/\tau_f}. \end{aligned} \quad (4.11)$$

In order to smooth the otherwise wildly fluctuating flow velocities we include only part of the present average particle velocities to calculate the flow velocities at the next time. The parameter τ_f characterizes how far in the future the present average velocities co-determine the flow velocities.

The actual flow field that develops in the system is imposed through Lees-Edwards bound-

any conditions, which are applied at the two bounding planes of the box perpendicular to the gradient direction. In the present application, the gradient direction is the same for the steady defining flow and for the oscillatory probing flow. In an OSR simulation, *i.e.* when both flows are present, a particle leaving the box through the upper y-plane comes back into the system through the lower y-plane with a displacement in the x-direction of $-\dot{\gamma}Ht$ (modulo one) and in the z-direction of $-\gamma_{\perp}\sin(\omega t)H$; H is the height of the box in the y-direction. Similar operations are applied when a particle leaves the box through the lower y-plane and enters through the upper y-plane, but now with reversed signs. Furthermore, the average velocities in the lowest slab are not measured locally, but are put equal to those in the uppermost slab reduced by $\dot{\gamma}H$ in the x-direction and by $\gamma_{\perp}\omega\cos(\omega t)H$ in the z-direction.

4.2.4 Methods

Stresses are calculated according to:

$$\sigma_{yz} = -\frac{1}{V} \sum_{i,j} r_{ij,y} F_{ij,z}, \quad (4.12)$$

where the sum runs through all pairs, $r_{ij,y}$ is the y-component of $\vec{r}_i - \vec{r}_j$ and $F_{ij,z}$ is the z-component of the force exerted by particle j on particle i . In model 1, the force arises only due to repulsive interactions, whereas in model 2 there is an additional contribution to the stress arising from the transient interactions. Hence in the second model, the sum of both conservative and transient stresses are added and this resulting total stress is fitted with Equation 4.13.

Phenomenologically, the yz-stress component $\sigma_{yz}(t; \dot{\gamma})$ is given by

$$\sigma_{yz}(t; \dot{\gamma}) = \gamma_{\perp} [G'_{\perp}(\omega; \dot{\gamma}) \sin(\omega t) + G''_{\perp}(\omega; \dot{\gamma}) \cos(\omega t)], \quad (4.13)$$

where it is assumed that for a given steady shear rate $\dot{\gamma}$, there exist orthogonal storage and loss moduli $G'_{\perp}(\omega; \dot{\gamma})$ and $G''_{\perp}(\omega; \dot{\gamma})$ respectively. Here $G'_{\perp}(\omega; \dot{\gamma})$ is the stress per unit strain amplitude that is in phase with the strain and $G''_{\perp}(\omega; \dot{\gamma})$ is the stress per unit strain amplitude that is out of phase with the strain. The equations of motion 4.10 give rise to a sinusoidal yz-stress component $\sigma_{yz}(t; \dot{\gamma})$ for a given shear rate $\dot{\gamma}$ and a given frequency ω . By sampling this signal at a good number of points within an oscillation cycle and by obtaining enough cycles per simulation run, the storage and loss moduli can be obtained by fitting the results with Eq. 4.13.

For a given frequency ω , the time-step dt must be chosen small enough to decently sample the oscillating signal, *i.e.* to have enough points within one cycle. In all runs we made sure that there were at least 20 points per cycle. On the other hand we need enough cycles to be able to fit the results to Eq. 4.13. In all simulations we have aimed for at least 100 cycles per run. In order to obtain a full spectrum, this had to be repeated for different frequencies.

Since the signal obtained per run is rather noisy, some averaging is required to smooth out the noise. Hence, for a given shear rate, we prepared 20 boxes. Each box was run for all the frequency points required in the spectrum, which ran from 0.01 rad/s to 50 rad/s to match the experimental frequency window. We could not obtain the spectrum for frequencies below 0.01 rad/s as the signal to noise ratio was extremely low. Then, for each frequency, one simulation run was divided into three non-overlapping pieces with about 30 cycles per piece and by fitting the sinusoidal $\sigma_{yz}(t; \dot{\gamma})$ to Eq. 4.13, the storage and loss moduli were obtained. These were averaged together to obtain one single value of G' and G'' per frequency, per box. After this, the 20 values per frequency across all the boxes were averaged together to obtain the mean $G'_\perp(\omega; \dot{\gamma})$ and $G''_\perp(\omega; \dot{\gamma})$. The mean and the standard error in the means are the final results of the OSR simulation for a given shear rate $\dot{\gamma}$, which are presented in the section on results.

The concentration of the experimental system was 0.058 g/ml (58 kg/m^3) from which the number density was estimated as follows. The star-like micelles studied in Ref. Poulos et al., [175] were PEP-PEO block co-polymers with a number averaged molar mass (M_n) of 1300 g/mol for the PEP block and 20300 g/mol for the PEO block, giving a total molar mass of 21600 g/mol for a single arm and hence $120 \times 21600 \text{ g/mol}$ for a single particle. From this information, after appropriate unit conversion to SI, the number density can be estimated as:

$$\rho = 58 * N_a / (21.6 \times f)$$

where N_a is Avogadro's number and functionality $f = 120$, giving a value of 1.3477×10^{22} particles per cubic meter. All these parameters are listed in Table 4.1. Remaining model parameters are obtained in section 4.3.1

4.3 Results

In this section we describe our results of performing OSR simulations using models 1 and 2, devised to roughly represent the worm-like micellar system described in the work of Petekidis *et. al.* [175]. First we discuss the results of performing zero-shear simulations using both models in order to determine the friction coefficient ξ and distance parameter σ_L for both models 1 and 2, and the parameters α and τ for model 2. After this, we describe the results of performing orthogonal superposition measurements using both models, followed by an analysis of the mean squared displacements and the observed laning behavior.

4.3.1 Model parameters from zero shear simulations

In order to complete the description of both models 1 and 2, we have calculated zero shear relaxation curves and adjusted the parameters until satisfactory agreement with the experi-

Parameter	Value
Functionality f	120
Temperature T	300 K
Number Density ρ	$1.3477 \times 10^{22} \text{ m}^{-3}$
Number of particles N_t	1004
Box length L_{box}	420.8 nm
Cutoff Radius R_C	72 nm
Friction Coefficient Model 1 ξ	$3 \times 10^{-3} \text{ kg s}^{-1}$
Distance parameter Model 1 σ_L	27 nm
Friction Coefficient Model 2 ξ	$2.5 \times 10^{-2} \text{ kg s}^{-1}$
Distance parameter Model 2 σ_L	22 nm
Strength of polymer interactions α	$145 k_B T$
Relaxation time of contact numbers τ	7 s

Table 4.1: System Parameters

mental data of Petekidis *et. al.* was obtained.

We first notice that the molecular diameter was obtained from dynamic light scattering experiments, and was found to be 72 nm. Since these measurements were done in good solvent, we expect that 72 nm is the largest distance up to which two particles will still feel each others presence. We therefore take 72 nm as our cut off distance for the interactions between two particles, *i.e.* we set $R_C = 72$ nm. This means that once we have obtained σ_L , and therewith the pair interaction ϕ_C , the latter must have decayed to very small values at distances beyond 72 nm. All remaining measurements were done at an overlap concentration of 2.65. Since this is a rather large concentration we assume that hydrodynamic interactions are negligible.

We next set forth to determine the length scale σ_L and the friction parameter ξ for model 1, by reproducing the experimental zero-shear rheological data. Since with BD simulations it is easier to measure data in the time domain, we we have transformed the experimental loss and storage moduli, $G''(\omega)$ and $G'(\omega)$ respectively, to the shear relaxation modulus $G(t)$ by means of the method of Schwarzl [110]. Adjusting σ_L and ξ in order to reproduce the experimental data is simplified a lot by the fact that the time-zero plateau is mainly determined by the length scale σ_L , while the decay rate is determined by the friction ξ . By varying these two parameters we found for model 1 $\sigma_L = 27$ nm and $\xi = 3 \times 10^{-3} \text{ kg s}^{-1}$. The results obtained with these parameters are presented in Figure 4.1a, together with the experimental data.

We now turn to method 2, wherein we introduce transient interactions in addition to the entropic repulsions described by the Likos potential. As stated before, transient interactions describe the deviation of the instantaneous interactions from the average interactions described by the Likos potential. The relaxation of the transient interactions to zero introduce

Figure 4.1: Panel (a) shows the shear relaxation modulus $G(t)$ at zero shear for model 1 with only repulsive interactions given by Equation 4.2, together with the experimental data obtained by converting frequency moduli to time domain by the method of Schwarzl. The length scale parameter σ_L is 27 nm and the friction coefficient ξ is $3 \times 10^{-3} \text{ kg s}^{-1}$. Panel (b) shows the shear relaxation modulus $G(t)$ at zero shear for model 2 with both repulsive interactions given by Equation 4.2 and transient interactions given by Equation 4.3. The red curve shows the conservative contribution, which is now lower than with model 1 due to a smaller value of σ_L , and the green curve shows the transient contribution which is higher in magnitude than the conservative one but decays earlier. The distance parameter σ_L is 22 nm, the friction coefficient ξ is $2.5 \times 10^{-2} \text{ kg s}^{-1}$; furthermore α is $145 k_B T$ and τ is 7 seconds.

a new time scale τ . As a consequence, the zero-shear $G(t)$ obtained with model 2 follows a two-step relaxation. To a good approximation, the shear relaxation modulus is just the sum of two contributions. One contribution, resulting from the Likos forces, has a plateau value determined by σ_L and decay time determined by ξ , as before, while the other contribution results from the transient forces, and has a plateau value roughly determined by α and a decay time determined by τ .

Now that we have four parameters to be fixed, it is not possible to find them by just reproducing the shear relaxation modulus. With any chosen value for σ_L , less than the one used in model 1, we can find an α such that we reproduce the experimental plateau value. Both ξ and τ can be adjusted to roughly reproduce the correct decay. When doing so, we can still choose to let ξ determine the long time decay and τ determine the short time decay, or the other way round. In order to fix all parameters, we must let our model reproduce additional experimental information, for which one may choose the flow curve. Since the experimental system only roughly resembles a star polymer, this procedure is deemed to be very complicated and not to be very accurate at the end. We therefore use the experimental system only as a guide to do simulations in a regime where interesting results may be expected and take the liberty to choose parameters which comply with this more modest goal. We settled on a value of 22 nm after experimenting with a few values below 27 nm which was used in model 1, since even lower values of σ_L do not provide a good fit to the experimental $G(t)$. The choice of 22 nm for σ_L fixes the plateau modulus of the conservative contribution to the shear relaxation modulus. By setting α to $145 k_B T$, the sum of transient and conservative contributions approach the time-zero plateau of the $G(t)$. In order to obtain a good fit to the experimental curve, we had to choose the remaining parameters such that the transient contribution decays at an earlier time than the conservative one. This meant that the friction ξ had to be greater than that of method 1, resulting in a value of 0.025 kg/s and τ was set to 7 seconds. The results are shown in Figure 4.1b.

4.3.2 OSR storage and loss moduli

A brief overview of the experimental results is apt before we describe our simulation results. Experimentally, it was found that the storage and loss moduli from OSR changed shape at a critical shear rate of 0.025 s^{-1} . At lower rates, the crossover frequency was observed to increase and the loss modulus increased in magnitude, showing that the sample is fluidized by increasing shear. The shape of the curves stayed more or less the same. At 0.025 s^{-1} , the curves qualitatively changed shape, showing multiple crossovers of the storage and loss moduli with increasing frequencies.

Figure 4.2: Storage and loss moduli for steadily sheared systems $G'_{\perp}(\omega; \dot{\gamma})$ (black) and $G''_{\perp}(\omega; \dot{\gamma})$ (red) averaged over 20 independent boxes for shear rates of 0.005 (circles), 0.01 (squares), 0.025 (diamonds), 0.05 (triangle up) and 0.1 (triangle down) s^{-1} for a) Model 1 b) Model 2

4.3.2.1 Low shear rates with models 1 and 2

We first present the storage and loss moduli obtained from orthogonal superposition simulations for low shear rates ranging from 0.025 to 0.1 s^{-1} in Fig 4.2. We have not indicated the errors in the mean in these plots as they are very small. At these rates, all moduli are qualitatively similar, differing only in their crossover frequencies which increase with shear rate. In addition, the peak of the loss modulus is only slightly increasing with increasing shear rates, indicating that the curves could possibly be superposed onto one master curve at these values of the steady shear rate. Overall, the moduli are not very interesting compared to the non-standard behavior occurring at larger rates discussed next.

4.3.2.2 High shear rates with model 1

We will discuss results obtained with 4 principal shear rates of 0.25, 0.4, 0.5 and 1.0 s^{-1} respectively. The results are shown in Figures 4.3 and 4.4. Since the curves show a lot of characteristic features, we have repeated all simulations with 20 newly generated boxes for every imposed shear rate and averaged the results. As a consequence all error bars are very small and hence the multiple crossovers, if any, are trustworthy within the limitations of our simulation method.

The first shear rate that we discuss in this section, $\dot{\gamma} = 0.25 s^{-1}$. At this shear rate, the storage modulus has developed a noticeable bump at a frequency of 0.1 rad/s , see Fig. 4.3a, signifying that from this rate onwards some non-linear behavior might set in. Going to the next higher rate of 0.4 s^{-1} , see Fig. 4.3b, we find three crossovers of the storage

Figure 4.3: Storage and loss moduli for steadily sheared systems $G'_{\perp}(\omega; \dot{\gamma})$ and $G''_{\perp}(\omega; \dot{\gamma})$ averaged over 20 independent boxes for model 1. Errors are indicated by plotting both the mean and the mean $\pm$ the error in the mean. Errors are very small, indicating that all features in the plots are properties of the models. a) Steady shear rate of 0.25 s^{-1} , showing regular liquid-like behavior with a single crossover of storage and loss moduli. b) Steady shear rate of 0.4 s^{-1} , showing three crossovers. The unusual crossovers occur at shear rates where the formation of lanes of particles travelling along the flow direction is observed.

and loss moduli. The bump found with the previous shear rate has now developed into a first crossover occurring at a frequency of 0.03 rad/s . After this one, there are two more crossovers at frequencies of about 0.2 and 0.5 s^{-1} . Next in Fig. 4.4a), at a rate of 0.5 s^{-1} , we find that there is only one crossover left at the lowest frequency of 0.03 rad/s , while the higher frequency crossovers seen at 0.4 s^{-1} have disappeared. G' is always larger than G'' at all frequencies larger than 0.03 rad/s , which shows that the shear is making the rheological response increasingly solid-like. At the highest rate of 1 s^{-1} , we see that there are no crossovers and the G' is higher than the G'' at all frequencies, finally rendering the sample a solid at this rate. Although for all shear rates G'' continues to increase at low frequencies, we notice that it consistently decreases across all rates.

It is interesting to notice that the behavior found with this model is very similar to experimental findings [175], although all features occur at substantially larger shear rates than with the experiments.

A look at the simulation movies shows that at all shear rates discussed in this section the particles have started to travel in lanes along the shear direction, a phenomenon that might be considered to be the ultimate form of shear-banding. We will discuss this further in section 4.3.3

Figure 4.4: Storage and loss moduli for steadily sheared systems, $G'_{\perp}(\omega; \dot{\gamma})$ and $G''_{\perp}(\omega; \dot{\gamma})$ averaged over 20 boxes along with the errors in the mean for model 1. a) Steady shear rate of 0.5 s^{-1} . There is a single crossover of storage and loss moduli; the second of the two additional crossovers which occurred at 0.4 s^{-1} has disappeared together with original high frequency crossover. Lane formation becomes more regular and y-transport is suppressed even more. b) Steady shear rate of 1.0 s^{-1} . At this rate, there is no crossover and the system displays solid-like behavior due to extreme laning. The particles now travel along precise well-defined lanes along the shearing direction.

Figure 4.5: Storage and loss moduli for steadily sheared systems. $G'_\perp(\omega; \dot{\gamma})$ and $G''_\perp(\omega; \dot{\gamma})$ averaged over 20 boxes along with the errors in the mean for model 2. a) Steady shear rate of 0.25 s^{-1} . There is only a single crossover, showing regular liquid-like behavior at low frequencies, like with model 1. b) Steady shear rate of 0.4 s^{-1} . Irregular lane formation is seen at this rate, with the particles traveling in clusters.

4.3.2.3 High shear rates with model 2

The inclusion of transient forces leads to quite some changes of the physical content of the model compared to that of model 1. Transient forces have the tendency to distribute the particles such that the prevailing contact numbers agree with the equilibrium numbers going with the prevailing configuration. This means that once clusters are formed they will be more difficult to break than in model 1. Besides this, the repulsive forces are smaller in model 2 than in model 1. Note also, as can be seen from Fig. 4.1b, that the transient forces are the ones that give rise to the slowest shear relaxations.

The same four shear rates will be discussed here as in the previous subsection and the results are shown in Figures 4.5 and 4.6. Again the error bars with this model are very small, meaning that all features visible in the various plots display properties of the model and methods being used.

At the first shear rate of 0.25 s^{-1} , the same features as in model 1 can be seen. There is a single crossover, which is slightly shifted to lower values of frequency as compared to model 1. The upward bump near 0.1 rad/s is also present here. At a rate of 0.4 s^{-1} , the moduli approach each other at lower frequencies and are imminent to cross but do not do so. There is a single crossover like in model 1. At a rate of 0.5 s^{-1} , three distinct crossovers emerge, with the lowest frequency crossover at 0.03 rad/s as with model 1. The behavior is rather similar to that seen at a rate of 0.4 s^{-1} with model 1. Increasing the shear rate further, we see that at the highest rate of 1 s^{-1} , the lowest crossover remains whereas those at higher frequencies

Figure 4.6: Storage and loss moduli for steadily sheared systems. $G'_\perp(\omega; \dot{\gamma})$ and $G''_\perp(\omega; \dot{\gamma})$ averaged over 20 boxes along with the errors in the mean for model 2. a) Steady shear rate of 0.5 s^{-1} . There are three crossovers, with a new low frequency crossover at 0.03 rad/s . The figure resembles the result of method 1 for 0.4 s^{-1} , see Figure 4.3b. b) Steady shear rate of 1 s^{-1} . In contrast with the result of model 1, liquid-like behavior remains at this rate and the moduli do not separate.

disappear. Hence, complete liquid to solid transition is not observed in model 2, which points to the fact that an attractive interaction manages to retain liquid-like behavior even at higher rates. We allude to attraction because transient forces can be either repulsive or attractive depending on the extent to which the contact numbers differ from their equilibrium values.

As with model 1, lane formation is also present with model 2 at the higher shear rates. We will present more information on this in section 4.3.3.

4.3.3 Lane formation

We have noted that in both models shear-induced lane formation occurred at the higher shear rates studied in this chapter. A clear indication of this with model 1 can easily be seen from the snapshots along the flow direction shown in Fig. 4.7. The vertical direction in this plot is the gradient direction, while the horizontal direction is the vorticity direction of the imposed steady shear. It is clearly seen that with a rate of 0.1 s^{-1} in Fig. 4.7a there is no lane formation, while clear laning is seen in Fig. 4.7b with a shear rate of 1 s^{-1} . Similar snapshots are shown in Fig. 4.8 for model 2. Also now, shear induced laning is present at the rate of 1 s^{-1} but cannot be easily seen due to lack of shear induced ordering. Movies of the time evolution, however, show that the particles run along the flow direction in clusters which stay intact for a very long time.

Figure 4.7: Snapshots of the simulation box for model 1 in the flow direction for a rate of 0.1 and 1 s^{-1} in panels (a) and (b) respectively. There is no lane formation in panel (a) with the particles moving in all directions, whereas a clear shear-induced hexagonal order of lanes can be seen in panel (b).

Figure 4.8: Snapshots of simulation boxes for model 2 along the flow direction for a rate of 0.025 and 1 s^{-1} in panels (a) and (b) respectively. There is no lane formation in panel (a) with the particles moving in all directions. Although there is lane formation in panel (b) as can be verified from the movies, it cannot be clearly seen in the snapshot as there is no shear-induced ordering.

In order to investigate laning in more detail, we calculated the mean squared displacements (MSD) in all three directions separately, for all shear rates and with both models. We present MSD's along the y-direction (gradient) and z-direction (vorticity) in Figs 4.9, 4.10 for models 1 and 2 respectively, and along the x-direction (shear) in Fig. 4.11 for both models. The MSDs in the y and z directions contain direct signatures of laning as the lanes organize themselves in the gradient-vorticity plane while flowing along the shear direction. The zero-shear MSD is shown as a dotted line in all these figures. For purposes of clarity we have divided the curves into two groups. The MSD's of the first group, represented by dashed lines, are multiplied by a factor of 10 in order to move them up in the plot, so as to separate them from the MSD's of the second group, represented by solid lines, which indicate the actual MSD values. Both groups behave differently.

We first consider the MSDs of model 1 shown in Fig. 4.9. In the left panel, Fig. 4.9a, the long time MSD's along the gradient direction are seen to increase with shear rate up to a shear rate of 0.1 s^{-1} ; these constitute the first group shown as dashed lines. From a rate of 0.25 s^{-1} onwards, the long time MSD's start to decrease again; these constitute the second group. The shear rate at which the long time MSD's start to decrease roughly coincides with the shear rate at which lane formation starts, indicating that long time diffusion along the gradient direction is severely suppressed when laning starts. A very similar behavior is seen in the long time MSD's along the vorticity direction in Fig. 4.9b, although in this case the decrease starts at a somewhat higher shear rate of 0.4 s^{-1} .

Once laning sets in, the particles only seldom change lane and prefer to stay in their lanes as a result of repulsions from the surrounding lanes. As may be seen in Fig 4.7b the lanes are ordered in a hexagonal structure in the gradient-vorticity plane with one of the diagonals along the gradient direction. At large shear rates, neighboring lanes have rather large velocity differences. Intuitively speaking, therefore, one may say that the particles in a lane 'see' the surrounding lanes as smoothed repulsive lines.

The situation is a bit different for the MSD's of model 2 as shown in Fig. 4.10. The long time MSD's in the gradient direction show similar behavior to the ones of model 1 in the sense that they first increase with shear rate and next decrease with increasing shear rate, as indicated by the two groups of dashed and solid lines in Fig. 4.10a. No such behavior is seen, however, in Fig. 4.10b for the long time MSD's in the vorticity direction.

The MSD's in the flow direction, after subtracting the affine velocities, are shown in Fig. 4.11 for both the methods. All long time MSD's increase with shear rate.

All MSD's discussed so far have a clear super-diffusive regime at intermediate times. In the rest of this section we will restrict ourselves to a discussion of MSD's obtained with model 1. In order to understand the super-diffusive regimes better, we show in Fig 4.12 sample trajectories of a few particles for a shear rate of 0.001 s^{-1} , where no laning occurs, and in Fig. 4.13 trajectories for a shear rate of 1 s^{-1} , where clear laning occurs. While in the no-laning case the trajectories are more or less smoothly wandering around, the trajectories in the laning case show a similar behavior interspersed by rapid jumps, where displacements are very large.

Figure 4.9: MSD's in the y and z direction with shear rate for model 1. Dashed lines represent results MSD's, multiplied by a factor of 10, of simulations with small shear rates. The solid lines represent those occurring at higher rates, where clear lane formation is seen. a) shows MSD's along the gradient direction and b) those along the vorticity direction. Super-diffusion is visible for shear rates from 0.1 s^{-1} onwards.

Figure 4.10: MSDs in the y and z direction with shear rate for model 2 in a) gradient and b) vorticity directions. Dashed lines represent results, multiplied by 10, of simulations with small rates, which increase with shear rates. The solid lines represent those obtained with higher rates where clear lane formation is seen.

Figure 4.11: MSDs in the flow direction after subtraction of the affine flow for a) model 1 and b) model 2. All MSD's increase with shear rate and super-diffusive is seen at intermediate times for higher rates. The zero-shear MSD is shown as a dotted line.

These sudden displacements correspond with jumps of the particles from one lane to another. The jumps are a bit more erratic along the vorticity direction than along the gradient direction. At very late times, *i.e.* at times much larger than the characteristic time between two jumps, τ_j , the motion is diffusive, with the diffusion coefficient roughly determined by the jump-size squared divided by τ_j . With increasing shear rates jumps become less frequent, so τ_j increases and the diffusion coefficient decreases. At intermediate times, from slightly below to slightly above τ_j , the motion is super-diffusive because the probability to make a ‘non-characteristic’ jump increases. One may summarize these findings by saying that apart from the very early times the motion is governed by shear induced diffusion.

By performing simulations with different frictions we confirmed that laning indeed depends on the Peclet number $Pe \propto \dot{\gamma}\xi/k_BT$, *i.e.* with larger frictions laning occurs at lower shear rates and the other way around.

4.3.4 Plateau values of the storage moduli

In the previous chapter, we have given the following expression for the plateau value of the storage modulus under OSR, $\sigma_{\perp}^{(1)}(\dot{\gamma})$, as a function of the steady shear rate

$$\sigma_{\perp}^{(1)}(\dot{\gamma}) = \frac{1}{V} \sum_{i < j} \left\langle \left(\frac{\phi'' z_{ij}^2 y_{ij}^2}{r_{ij}^2} - \frac{\phi' z_{ij}^2 y_{ij}^2}{r_{ij}^3} + \frac{\phi' y_{ij}^2}{r_{ij}} \right) \right\rangle_{\dot{\gamma}}, \quad (4.14)$$

where V is the box volume, ϕ is the inter-particle potential and the angular brackets denote an ensemble average over systems steadily sheared with rate $\dot{\gamma}$; $z_{ij} = z_i - z_j$ for a pair of

Figure 4.12: Sample trajectories at a shear rate of 0.001 s^{-1} at which there is no laning, in the a) gradient direction and b) vorticity direction.

Figure 4.13: Sample trajectories at a shear rate of 1 s^{-1} where clear laning is observed, in the a) gradient direction and b) vorticity direction.

Figure 4.14: The plateau values obtained from direct calculation of Eq. 4.14 (black) and those obtained from OSR (red). The values are in good agreement within statistical bounds.

particles i and j etc.

For given shear rates, we have calculated this quantity for 10 independently prepared boxes, and averaged the results to get a single value of the plateau modulus for that rate. The results are shown in Fig. 4.14, where it is seen that the agreement is indeed very good. This shows that the plateau value can be rigorously calculated as a function of shear rate and can be used to derive the shift factors for time-shear-rate superposition studies.

4.3.5 OSR moduli from the Generalized Stokes Einstein relations:

In previous studies of OSR simulations using BD [176], the Generalized Stokes Einstein (GSE) relations were used to calculate the storage and loss moduli under OSR. The method is based on calculating the moduli from the mean squared displacement in the vorticity direction and the details can be found in the paper by Mason and Weitz [142]. We briefly state the equations involved:

$$G'(\omega; \dot{\gamma}) = |G^*(\omega; \dot{\gamma})| \cos(0.5\pi\alpha(\omega; \dot{\gamma})) \quad (4.15)$$

$$G''(\omega; \dot{\gamma}) = |G^*(\omega; \dot{\gamma})| \sin(0.5\pi\alpha(\omega; \dot{\gamma})) \quad (4.16)$$

where $G'(\omega; \dot{\gamma})$ and $G''(\omega; \dot{\gamma})$ are the storage and loss moduli under steady shear and the other two quantities are given by:

$$|G^*(\omega; \dot{\gamma})| \approx \frac{k_B T}{\pi R \langle \Delta z^2(t; \dot{\gamma}) \rangle \Gamma[1 + \alpha(\omega; \dot{\gamma})]} \quad (4.17)$$

Figure 4.15: Storage and loss moduli obtained from GSE relations (no symbols) vs those obtained from OSR (dashed symbols) for shear rates of 0 (black), 0.025 (red, no laning) and 0.25 (blue, laning) s^{-1} . The radius used in Eq. 4.17 was tuned until the plateau of OSR and GSE storage moduli matched for zero shear, giving a value of 23.3 nm, which is the effective particle radius under the GSE framework.

and

$$\alpha(\omega; \dot{\gamma}) = \frac{d \ln(\langle \Delta z^2(t; \dot{\gamma}) \rangle)}{d \ln(t)} \Big|_{t=1/\omega} \quad (4.18)$$

Before applying this method, let us notice that it has been justified under the assumption, among others, that the mean square displacement $\Delta z^2(t; \dot{\gamma})$ in this expression refers to that of a particle with radius R large enough to consider its environment to be a continuum. In the application by Petekidis *et. al.*, the authors represented the particles that make up the fluid by hard spheres, and then let $\Delta z^2(t; \dot{\gamma})$ be the mean square displacement of one of these hard spheres. Here we stretch the method even further by applying it to the individual star polymers as such. Since in this case the radius R is not uniquely defined, we tuned it to reproduce the storage modulus at zero shear rate as well as possible. The result is shown as a drawn black line in Fig.4.15, with $R = 23.3$ nm. Even when the zero shear G' is very well reproduced, the corresponding G'' is reproduced very badly.

The remaining curves in Fig 4.15, pertain to shear rates of $0.025 s^{-1}$, in which case no laning occurs, and $0.25 s^{-1}$, in which case laning does occur. First, in both cases the loss modulus is reproduced very badly, as with zero shear rate. The storage moduli are also reproduced badly in both cases. At the lower shear rate looks qualitatively correct, but is quantitatively far off. At the higher shear rate G' is even qualitatively incorrect at higher frequencies.

4.4 Discussion and Conclusions

We have performed simulations of Orthogonal Superposition Rheology (OSR) experiments on a concentrated system of star-like polymers with 120 arms attached to a central core. We have studied two models, one in which the interactions between particles are described by the potential of mean force developed by Likos and coworkers, and one in which the interactions are partly described by a Likos potential and partly by transient potentials as advocated by Briels and coworkers in order to include memory in coarse grained models. Parameters in both cases were chosen to roughly mimic, a star-like micellar system experimentally studied by Petekidis *et al.* Given the substantial difference between micellar stars and polymer stars, we did not expect quantitative agreement of our simulations with experiments. Nevertheless most of our findings are qualitatively in very good agreement with experimental results. This makes us believe that the concepts put forward in this study are real and relevant for understanding the experimental results.

As in the experiments, we found that with increasing shear rates the storage modulus develops a bump at low frequencies, which next increases while only little changes occur at higher frequencies. At the same time the loss modulus slowly decreases and shifts to the right. As a result, at intermediate shear rates the loss modulus becomes larger than the storage modulus at low frequencies, thereby creating two new crossings of both curves besides the one at higher frequencies. With increasing shear rates the storage modulus keeps increasing at low frequencies until the two extra crossings disappear when the storage modulus becomes larger than the loss modulus at low frequencies. With further increase of the shear rate, the first model becomes solid like with its storage modulus larger than the loss modulus at all frequencies, while the second model remains fluid with its storage modulus being smaller than the loss modulus at very low frequencies.

Inspection of movies made from our simulations of model 1 reveals that at the higher shear rates particles start to order and move in lanes along the flow direction. Each lane is surrounded by six other lanes in a hexagonal formation perpendicular to the flow direction. Effectively, each particle experiences neighboring lanes as repulsive structureless lines. This picture breaks down when affine displacements along the flow direction are of the same order as Brownian displacements perpendicular to the lanes. Indeed we found that laning phenomena are governed by the Peclet number which compares the corresponding time scales. This is similar to the formation of lanes in driven colloidal mixtures of opposite charge [177, 178]. In model 2, the transient forces have the tendency to collect particles in clusters which run along the flow direction staying intact for long times. This leads to similar behavior as with model 1, except that the hexagonal structure mentioned above is hardly visible, and that the system remains fluid at all shear rates.

An interesting consequence of lane formation occurs at intermediate shear rates, when particles still have the opportunity to once in a while jump from one lane to another. The resulting large displacements, compared to the random Brownian displacements, lead to super-

diffusive behavior at time scales of the order of average time between two such jumps. Such transient super-diffusion was seen in a previous study by Petekidis et al. [158] both in experiments with confocal microscopy and BD simulations.

Chapter 5

Non-monotonic Stress Relaxation in Supra-molecular Assemblies

Stress relaxation upon cessation of shear flow is known to be described by single- or multi-mode monotonic exponential decays. This is ubiquitous in nature. However, we report here a finding that under some conditions, the relaxation becomes anomalous in the sense that an upturn or increase in the relaxing stress is observed. Such observations have been made for physico-chemically very different systems, that have in common that the materials involve attractive interactions. The effect can phenomenologically be described by a generic model based on an order parameter altered by shear. When bonds re-establish, energy flows from stored to thermal and elastic energy, whereas the later one results in work done on the system. If shear has induced order in the system so that the performed work leads to rearrangements of partly aligned elastic domains, the overall stress increases during the relaxation process.

5.1 Introduction

Many experiments and simulations with soft materials ranging from polymer melts or solutions to colloidal suspensions, show that once an initially imposed shear rate is set to zero, the stress relaxes monotonically via one or more distinct exponential processes, reflecting successively the fast retraction of small scale, shear-induced, non-equilibrium structures and the much slower relaxation of structures induced at the larger scales [179, 180, 181, 182, 183]. Often out-of-equilibrium systems such as colloidal glasses, pastes, and gels do not fully relax their stresses, but settle at some residual stress because the induced large scale structures cannot find relaxation pathways and remain permanent in the system [184, 185, 186]. Nonetheless, a common generic feature of all these systems is the *monotonic* decrease of the stress to its final value. At first glance this appears to be the expected behavior, since no work that

Figure 5.1: Large shear magnitudes lead to bond breakage and energy storage due to stretching of polymer chains **1**, which is released upon bond reformation after cessation of flow. Bond reformation leads to work performed on the polymer chains and causes local elastic inhomogeneities, *i.e.* partly aligned and deformed domains around bonds, indicated by yellow lines, resulting in increasing bulk stress **2**, which eventually relaxes by thermal relaxation **3**.

would be able to raise the stress is performed on the system. However, this scenario may not always hold. Indeed, for a particular supra-molecular polymer system, in which bonds were broken during a steady shearing phase, we have found [187, 188] a non-monotonic relaxation of stress following cessation of shear flow, as schematically shown in Fig. 5.1. In order to prove the generic character of our findings, we have investigated two more, physically and chemically very different systems, with different associating mechanisms. All cases have in common that bonds are disrupted by subjecting the systems to steady shear flow, and reform after cessation of that flow. We will argue that a redistribution of the released bond-energy during stress relaxation gives rise to temporary stress increases.

5.2 Experimental Details

The first system consists of 2, 4-bis (2-ethyl-hexyl-ureido) toluene (EHUT) [189, 190] dissolved in dodecane. The EHUT bis-urea based monomers self-assemble in apolar solvents, and above a certain concentration, through the formation of hydrogen bonds between the urea groups. Depending on temperature, thin filaments or thick tubes are formed, with the cross-sectional diameter determined by the solvent and the temperature [191]. Data presented in this work was obtained in the tube region of the phase diagram at a concentration of 12 g L^{-1} , where the tubes are long enough to entangle and exhibit a rich viscoelastic response.

The second system comprises of an aqueous solutions of a synthetic polymer with a molecular weight of 500 kg mol^{-1} , of which 5 % of the monomers are functionalised with ligands [192]. Polymer solutions with concentrations corresponding to the semi-dilute regime (1.35 wt%) were mixed with a stoichiometric concentration of metal ions to ligands. The cation Fe^{3+} , added in form of iron chloride, results in relatively strong metal-ligand bonded supra-molecular hydrogels, with up to three ligands bonded to a single metal ion.

The third system is based on low concentrations (0.35 wt% each) of two polymers dissolved in 0.1 M aqueous NaOH at $\text{pH} \sim 12.5$, bonded by a boronic acid-diol recognition [193]. The first polymer is a partially hydrolysed polyacrylamide grafted with phenylboronic acid moieties (HPAM-g-PBA) with a molecular weight of 780 kg mol^{-1} , and the second polymer is a fully saponified poly(vinylalcohol) (PVA) with a molecular weight of 25 kg mol^{-1} . The phylboronic acid moieties and the 1,3 diols form phenylboronic esters. The bonds are weak enough to form reversible covalent bonds. Despite their low equilibrium constants ($K < 10 \text{ L mol}^{-1}$), strong gels in the semi-dilute non-entangled regime are formed at polymer concentrations below 2 wt%, due to synergistic effects of clusters formed by multiple associations.

The response to shear in the first system was measured immediately after preparation with an ARES rheometer (TA Instruments, USA) equipped with a stainless steel cone and plate geometry of 25 mm radius and 0.04 rad cone angle, at a temperature of 20°C . In order to measure under dry conditions, a homemade drying chamber was used as described by

Louhichi et al. [194]. Measurements on the second system were performed at room temperature in a double-wall Couette geometry on an ARES-G2 rheometer (TA Instruments, USA). Data for the third system were obtained at room temperature with a MCR 502 rheometer (Anton-Paar, Austria) using a cone and plate geometry of 25 mm radius and a mineral oil immersion to reduce evaporation. A steady state of partially broken bond structures was assured for the hydrogels by subjecting them to constant shear rates for a fixed time, between 2000 s and 4000 s, while the EHUT solution was submitted to a fixed deformation of 25 strain units.

Experimental stress relaxation curves are shown in Fig. 5.2 for all three systems and for a selection of initially applied shear rates. Time zero is when the steady shear flow has been stopped, and stresses have been normalized by their values at time zero. In all cases the relaxation is clearly non-monotonic. Stresses in the first system have already decayed substantially at the earliest times shown in the plot. This is because at time zero this system is almost crunched to the molecular scale and relaxation times are therefore initially extremely fast.

Repeat runs of all experiments with newly prepared batches of the various systems confirmed our findings. We conclude that the effect, although unexpected, is real. The main reason for not expecting an upswing of an initially decaying stress is a vague feeling that it might be in disagreement with either of the two laws of thermodynamics. We will now argue that this is not the case. Our considerations will also suggest a very simple, highly approximate phenomenological model to describe our data.

5.3 Model Description

In general terms, the microscopic state of the system is described by local strains, local order tensors, and local bond densities. The steady shear, of strain rate $\dot{\gamma}$ and total strain γ , fixes initial values for these variables. A set of evolution equations then allows the calculation of these variables at later times. The evolution equations should naturally contain random contributions obeying appropriate fluctuation-dissipation theorems. Here, we will restrict ourselves to the more modest task of describing only the stress relaxation after the shear has stopped, thereby eliminating the need to include random contributions to the evolution equations. We will assume that local strains and local order basically describe the same aspect of our systems, and restrict ourselves to strains. Moreover, assuming that stress is a non-decreasing function of strain - ignoring the possibility of shear banding - we replace stresses by strains in the list of state variables. Finally, although we will make use of local arguments, our final model will use only global properties of the system as a whole.

Figure 5.2: During stress relaxation experiments of the supramolecular system 1 (top), system 2 (middle), and system 3 (bottom), bond reformation causes stresses to increase. The shear stress is normalized to the steady state shear stress, and shear rates applied prior to cessation of flow are listed in the legends.

Our considerations will suggest the following set of evolution equations

$$df = -r f dt, \quad (5.1)$$

$$d\sigma_{xy} = -\sigma_{xy} \frac{dt}{\tau} - \sigma_{xy} B df. \quad (5.2)$$

Here f is the fraction of broken bonds and σ_{xy} is the measured shear stress. Both depend explicitly on time with increments df and $d\sigma_{xy}$ during a time interval dt . The parameters r , τ and B depend implicitly on time through their dependence on f . The first equation tells us that the fraction of broken bonds decays with rate r . The second equation says that the stress decays at a time scale τ due to erratic motions in the system, while in addition it increases when bonds are re-established; with df being negative, the effective bond contribution to the stress B must be positive.

For convenience, we consider the system to be isolated immediately after shearing has been stopped and describe how energy redistributes while entropy is increasing. The contribution to the energy density coming from the presence of breakable bonds will be denoted by $U_B = (1 - f)\Phi$. At equilibrium $f = 0$, and the bond energy density equals Φ .

Notice that with this definition Φ is negative, and that by breaking bonds an energy density of $U_S = -f\Phi$ has been stored into the system. The total energy density U_{tot} reads then

$$U_{tot} = U_T + U_E + (1 - f)\Phi, \quad (5.3)$$

where U_T is the thermal energy density, *i.e.* the part of the energy density that depends only on temperature, and U_E the elastic energy density, *i.e.* the part of the energy density that depends both on temperature and on (local) strain. Since we are considering an isolated system, the total energy density will remain constant during the relaxation process, while the individual contributions depend on time.

During the approach to equilibrium, the fraction of intact bonds $1 - f$ will gradually increase from its initial value $1 - f_0$ to unity at equilibrium, while concomitantly the stored energy decreases to zero. We assume that the released binding energy will be partly delivered as thermal energy, and partly as elastic energy. During a small time interval, therefore, we may write

$$\begin{aligned} dU_B &= -\Phi df \\ dU_T &= dU_{err} + (1 - \alpha)\Phi df \\ dU_E &= -dU_{err} + \alpha\Phi df, \end{aligned} \quad (5.4)$$

where α is some number between zero and one. dU_{err} is the amount by which the elastic energy decays due to erratic motions of the associative elements at the scale of the prevailing non equilibrium structures. This is the process that gives rise to the first term on the right hand side of Eq. 5.2. The released energy due to bond formation, $dU_S = -dU_B = \Phi df$,

has been split into a part $(1 - \alpha)\Phi df$ delivered as heat and a part $\alpha\Phi df$ delivered as work done on the elastic component of the energy. Notice that when bonds are formed, df is negative and Φdf is positive. Clearly, we do not know how much of the released energy Φdf is delivered as work, and how much as heat. The second law of thermodynamics demands $(1 - \alpha)\Phi df$ to be large enough so that the corresponding increase of entropy outweighs the decrease of entropy resulting from the change of elastic energy (through a change of local strains). Within these limits, the elastic energy will increase with an amount $\alpha\Phi df$. Near equilibrium, the second law of thermodynamics states that stress increases monotonic with increasing elastic energy. Since force measurements with a rheometer are instantaneous on the time scale of the relaxation process that we are studying, we conclude that the stress increases proportionally to $-df$. In order to comply with the tensor character of the stress, the constant of proportionality has to transform as a tensor. The only tensor we can use is stress itself, leading to the contribution $-\sigma_{xy}Bdf$ in Eq. 5.2.

Notice that B accounts for the combined effect of two different aspects of the relaxation process. First, we have assumed that bond formation can lead to work being done on the surroundings of two associating structural elements. This is easily understood for systems 2 and 3, being polymers that are functionalized with associating groups, provided the association starts at sufficiently large separations and is faster than the local relaxation time of the elastic network. In that case the associating groups will pull the respective polymers and their surroundings towards each other, and thereby create elastic energy. Second, we have attributed a measurable shear stress increase to the locally increased elastic energy. It is easy to understand that in many situations this is actually not the case. Suppose that the bonding process leads to a system containing many randomly oriented domains of elastic deformation. All off-diagonal stress components will then on average be zero, much like the overall magnetization of a collection of magnetized Weiss domains is zero when they are randomly oriented. Only when the overall order and the distribution of functionalized groups allows the re-associating groups to create partially aligned anisotropically deformed elastic domains, will the shear stress be non-zero.

Somewhat related to this is the apparent violation of the Curie principle of irreversible thermodynamics in our equations, which states that thermodynamic forces cannot give rise to fluxes of different tensor character [195]. Application of this principle, however, should be limited to homogeneous systems [196]. As we have emphasized, the origin of the second contribution to the stress increment in Eq. 5.2 lays in the inhomogeneities and anisotropy at the scale of the distribution of reactive groups introduced by the initial shearing deformation.

In order to complete the model, we need constitutive equations for r , τ and B in terms of f . For simplicity, and in order to limit the number of unknown constants, we make the

Figure 5.3: The figure shows the increase of $1-f$ with time along with the stress development for systems 1, 2 and 3, respectively, in red, blue, and green at shear rates of 7 s^{-1} , 10 s^{-1} and 4 s^{-1} . The solid lines are experimental data, dotted lines are the model fits and dashed lines are the associated f values. For system 1 in red, the time axis has been multiplied by 10 so that all data fit in the same plot. Inset: Variation of the inverse effective stress decay time $(\tau_{eff})^{-1}$ with time. Black lines indicate the inverse decay times $1/\tau_l$ to be reached at very long times.

following choice:

$$\begin{aligned}
 r(f) &= r \\
 \tau(f) &= \tau_l - (\tau_l - \tau_s) \frac{f}{f_0} \\
 B(f) &= b(1-f)^{-\kappa}.
 \end{aligned} \tag{5.5}$$

The first says that the relative rate with which new bonds are created is constant. Depending on the type of reaction, one might consider other forms here. The second is a simple linear interpolation in f of the instantaneous relaxation time τ between a short time relaxation time τ_s and a long time relaxation time τ_l . The rationale behind the third is that the process which really matters is the relative increase of the fraction of bonds materialized; in order to be more flexible we have changed the dependence on $(1-f)^{-1}$ into $(1-f)^{-\kappa}$.

5.4 Results and Discussion

With this model we have fitted the experimental findings and plotted the results as drawn lines in Fig. 5.2. First of all, it is clear that the model, given its simplicity, does a good to sometimes very good job in reproducing the experimental data, with the disagreement being

mainly near the minima. It is reassuring to notice that in all cases the position of the maxima are well described, even when they do not depend monotonically on the shear rate.

The main reason why the model is able to describe the data is the fact that the stress evolving with time is the sum of two competing terms, where the first leads to a stress decrease while the second leads to a stress increase. The absolute values of both terms are decreasing with time, which does not imply, however, that they may never become equal. In order to clarify this we combine Eqs 5.1 and 5.2 to find $d\sigma_{xy} = -\sigma_{xy}dt/\tau_{eff}$, where τ_{eff} is an effective decay time given by

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau}(1 - Brf\tau). \quad (5.6)$$

In the inset of Fig. 5.3 we have plotted $1/\tau_{eff}$ as a function of time for system 1 and 3. Initially and at late times τ_{eff} is positive, giving rise to decaying stresses. At intermediate times τ_{eff} is negative, causing the stress to increase. At these times $Brf\tau$ is larger than one, implying that the natural stress decay cannot compete with the stress increase due to the formation of new bonds. Thus, stresses are increasing. When t goes to infinity, f goes to zero and therefore both τ and τ_{eff} go to τ_l . The values of $1/\tau_l$ are indicated as short drawn lines to the right of the inset in Fig. 5.3. It is interesting to notice that the first system has reached this long time limit soon after the stress maximum, *i.e.* soon after the second zero of $1/\tau_{eff}$. As a result, the long time stress decay in this case is basically exponential. The same does not apply in the other two cases, where the increase of the fraction of bonds is much slower. In these cases the stress decay after the maximum could well be described by a stretched exponential with exponents 0.54 for the second system, and 0.85 for the third system. This behavior is clearly seen in Fig. 5.3, where we have plotted the time dependence of both the stress and the fraction of bonds materialized in the system, $1 - f(t)$. Notice that the horizontal axis indicates seconds for the cases of system number two and three, while it indicates tens of seconds for the first system.

In all cases κ was only slightly above one. We have tried to fit the data keeping κ fixed to one, but could not produce stress upswings in that case. Moreover, in all cases the initial value f_0 was only slightly below one. For the EHUT system this is not surprising. For the polymer systems this is an indication that the model in its present form is slightly oversimplified. In these cases, steady shearing has two effects. First it will disrupt bonds leading to a decay of the bond density, as included in our model. Second, depending on the total strain, it shifts the distribution of remaining bonds over internal and external bonds. Apparently there is a maximum to the number of bonds that can be broken, and f quantifies which fraction of these is broken. Therefore, the initial value of f will almost always be very close to one. During the later part of the stress relaxation, the disturbed distribution of bonds over internal and external bonds must be re-established. This needs existing bonds to be broken and re-establish elsewhere. The time-scale for this process must be set by an activation barrier of the order of the binding energy. This is only implicitly described in the present model.

Besides being different for different systems, all model parameters turned out to depend slightly on $\dot{\gamma}$ and γ . This is another indication that the present model uses too few state variables, or that the constitutive equations are too simple.

Let us summarize the ingredients that a system must have to show non-monotonic stress relaxation after having been sheared for a while. First, the system should contain functionalized groups that are able to form bonds. The strength of these bonds must be such that they may be considered permanent, *i.e.* hardly fluctuating, in equilibrium, yet weak enough to be broken during shear. Bond energies in the range of $20 - 60k_B T$ seem to be reasonable. Second, bond formation should be able to locally deform the material and induce corresponding stress. For the associative polymers this sets an upper limit to the bond densities. On the other hand, possible binding partners must have found each other before the order imposed by the shear has relaxed completely. In order to generate macroscopically measurable stresses, the order induced by the shear must be such that stresses induced by the formation of bonds are aligned at different positions in the system. For the EHUT, concentrations must be large enough.

Chapter 6

Analytical Solution of the Rouse Model for Symmetric Star Polymers

The problem of solving the Rouse modes of symmetric star polymers has been solved analytically. This is accomplished by finding the eigenvalues of the Laplacian (Rouse) matrix corresponding to a symmetric star polymer as a function of the number of beads (N) on each arm and functionality (f). Out of a total number of $Nf + 1$ eigenvalues, aside from the diffusive mode corresponding to eigenvalue zero, the spectrum consists of two parts: one set of degenerate spectra repeated $f - 1$ times, numbering $N(f - 1)$ and another unique spectrum of N eigenvalues. While the degenerate spectra are the Rouse modes of an N bead chain with one end connected to the origin, and hence is the same as that found in previous attempts to solve this problem, the unique spectrum is found to differ from that predicted by these same studies. Like in the previous studies, the unique spectrum is found to be very closely approximated by that of an N bead linear chain, but only at high functionality, or for small functionalities and large values of N . While previously it was assumed that the core is the same as the center of mass of the star, this is not the case for stars with low functionality. We show that the difference between the spectrum assumed so far and our derivation of the unique spectrum arises from this physical fact.

6.1 Introduction

The Rouse model of polymer dynamics is one of the earliest attempts to understand the physical properties of polymers, which are a function of their size and shape ([3, 4]). This

model applies mainly to melts and concentrated solutions where hydrodynamic interactions can be neglected and is the simplest bead-spring based model available to describe polymer dynamics. It successfully predicts the relationship of viscosity with molecular weight in melts of unentangled polymers. Even for entangled systems, the Rouse model is the main backbone on which the motion of polymers is described. Reptation theory, which is used to describe entangled systems, is basically rouse motion of the chain constrained by a tube. The Rouse model assumes that the polymer is a freely jointed chain of beads connected together by springs. Depending upon the shape of the polymer, the eigenvalues of the connectivity matrix decide the timescales of relaxation of these modes. For differently shaped polymers, these values can differ substantially, which leads to different properties at the macroscopic level. Branched polymers, like star shaped polymers, are known to have lower viscosities than their corresponding linear counterparts at the same molecular weight. Properties like these can be tailored by adjusting the parameters of the physical shapes of the polymers. Thus, the shape of the polymer plays an important role in deciding the timescales of relaxation and hence its flow properties.

In a previous study by Zimm and Kilb ([106]), it was first theorized that a symmetric star polymer has a set of N degenerate sine modes repeated $f - 1$ times and a set of N non-degenerate cosine modes. The sine modes, which are the modes of a linear chain of N beads held fixed at one end, have a node at the center and the cosine modes, which are the even modes of a free chain with $2N + 1$ beads, do not. The procedure was carried out not by diagonalizing the star Rouse matrix, but by a continuous approximation which enforced the boundary condition that the force on the central core was zero (core is the same as the center of mass). The same philosophy has been used in other studies where the analytical eigenvalues are used ([197, 198, 199]). Our assertion is that the core is not the same as the center of mass. While we do not doubt the validity of the results of Zimm and Kilb and of all the studies that follow it, due to a lack of exact diagonalization, the expression for the symmetric modes are not accurate for all values of f and N especially in the case of small stars, as we show in this work. However, it has to be noted that it is known that the symmetric modes given by Zimm are not accurate in all cases and are only an approximation, as mentioned in Ref. [200]. In addition, the highest magnitude eigenvalue in the spectrum shows strong f -dependence and is approximately given by $f^2/f - 1$, as mentioned in Refs. [201] and [200]. In this chapter we shed light on these issues in the context of the exact diagonalization carried out by us.

We have described the Rouse model in the first chapter and have also successfully generalized it to account for different frictions and spring constants. Further on, we also applied it to the study of the telechelic star polymer system described in that chapter. In this chapter, we will present an exact solution to the problem of finding the eigenvalues of the Rouse connectivity matrix of a symmetric star polymer with functionality f and N beads per arm. We show that the eigenvalue spectrum consists of two sets, one being a set of N degenerate eigenvalues which repeat $f - 1$ times and the other being a unique part consisting of N

eigenvalues. There is also a zero eigenvalue corresponding to the diffusion of the center of mass of the star. In total, these account for $N(f - 1) + N + 1$ values, which are equal to the degrees of freedom of a star with functionality f and N beads per arm.

6.2 Methods

Let us introduce the basic matrices involved in the proof. Consider the connectivity matrix A_{star} of a symmetric star polymer with functionality f and N beads on each arm, shown in Fig. 6.1. The core comprises an additional bead and hence the matrix is of size $Nf + 1$. The first column, which is identical to the first row as the matrix is symmetric, consists of the entry f as the first element, which corresponds to the core being connected to the first bead of each of the f arms. The second element is -1, which corresponds to the spring between the first bead of the first arm and the core. These -1's are repeated every N rows. Thus, the first element of the $N + 2$ 'th row is a -1 and so on. The other entries in this column are zero. Other than the first row and first column, the entire star matrix is composed of blocks of square matrices of size N , which are nothing but the Rouse matrices of an N bead linear chain with one bead connected to the origin, whose eigenvalues are known analytically. This matrix, denoted by A_N , is given by:

$$A_N = \begin{bmatrix} 2 & -1 & 0 & \cdots & 0 \\ -1 & 2 & -1 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & \cdots & -1 & 2 & -1 \\ 0 & \cdots & 0 & -1 & 1 \end{bmatrix}$$

Excluding the first row and column, the remaining square matrix is block diagonal, with A_N forming the matrices along the diagonal. The determinant of a block diagonal matrix is simply the product of the determinants of the individual matrices along the diagonal, which fact will be made use of heavily in the derivation that follows.

$$\begin{bmatrix}
f & \overbrace{-1 \ 0 \ \dots \ 0}^{N, j=1} & \dots & \overbrace{-1 \ 0 \ \dots \ 0}^{N, j=k} & \dots & \overbrace{-1 \ 0 \ \dots \ 0}^{N, j=f} \\
-1 & 2 & -1 & \dots & 0 & \dots & 0 & 0 & \dots & 0 & \dots & 0 & 0 & \dots & 0 \\
0 & -1 & 2 & -1 & \dots & 0 & \dots & 0 & 0 & \dots & 0 & \dots & 0 & 0 & \dots & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \dots & \vdots & \vdots & \vdots & \vdots & \dots & \vdots & \vdots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & \dots & -1 & 1 & \dots & 0 & 0 & \dots & 0 & \dots & 0 & 0 & \dots & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \dots & \vdots & \vdots & \vdots & \vdots & \dots & \vdots & \vdots & \vdots & \vdots \\
-1 & 0 & 0 & \dots & \dots & 0 & \dots & 2 & -1 & \dots & 0 & \dots & 0 & 0 & \dots & 0 \\
0 & 0 & 0 & 0 & \dots & 0 & \dots & -1 & 2 & -1 & \dots & 0 & \dots & 0 & 0 & \dots & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \dots & \vdots & \vdots & \vdots & \vdots & \dots & \vdots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & \dots & 0 & 0 & \dots & 0 & 0 & \dots & -1 & 1 & \dots & 0 & 0 & \dots & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \dots & \vdots & \vdots & \vdots & \vdots & \vdots & \dots & \vdots & \vdots & \vdots \\
-1 & 0 & 0 & \dots & \dots & 0 & \dots & 0 & 0 & \dots & \dots & 0 & \dots & 2 & -1 & \dots & 0 \\
0 & 0 & 0 & 0 & \dots & 0 & \dots & 0 & 0 & 0 & \dots & 0 & \dots & -1 & 2 & -1 & \dots & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \dots & \vdots & \vdots & \vdots & \vdots & \vdots & \dots & \vdots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & \dots & 0 & 0 & \dots & 0 & 0 & \dots & 0 & 0 & \dots & 0 & 0 & \dots & -1 & 1
\end{bmatrix}
\left. \vphantom{\begin{bmatrix} f \\ -1 \\ 0 \\ \vdots \\ 0 \\ \vdots \\ -1 \\ 0 \\ \vdots \\ 0 \\ \vdots \\ -1 \\ 0 \\ \vdots \\ 0 \end{bmatrix}} \right\} N, j = k$$

Figure 6.1: The Rouse matrix of a symmetric star polymer, A_{star}

In order to find the eigenvalues of A_{star} , consider its characteristic polynomial $|A_{star} - \lambda I_{Nf+1}|$. This is simply the determinant of the matrix formed by subtracting the variable λ from the diagonal elements of A_{star} .

An important component of the determinant of A_{star} is the determinant of A_N , which appears along the diagonal as an $N \times N$ block. Let this determinant be denoted by A_N itself for simplicity. Hence, from now on, A_N stands for the determinant of an N bead rouse chain with the first bead connected to the origin by a spring. In addition, let us introduce the notation, $2 - \lambda = x$; and $1 - \lambda = y$, which will simplify the writing of the determinant of A_{star} . With this notation, the following result can be quickly established by expanding A_N along the first column:

$$A_N = xA_{N-1} - A_{N-2} \quad (6.1)$$

where A_{N-1} and A_{N-2} are simply determinants of $N - 1$ and $N - 2$ chains with one end fixed at the origin. This relation will be made use of later on.

The determinant of A_{star} , upon expanding along the j 'th column is given by:

$$|A_{star}| = \sum_{i=1}^{Nf+1} (-1)^{i+j} a_{i,j} M_{i,j}. \quad (6.2)$$

where $a_{i,j}$ is the (i,j) 'th element of the matrix and $M_{i,j}$ is the minor corresponding to this element, which is simply the determinant of the matrix formed by eliminating the i 'th row and j 'th column. Since the matrix A_{star} is quite complicated, there is currently no direct solution of its characteristic polynomial available in the literature. We will attempt to do exactly this in our derivation.

Let us expand $|A_{star} - \lambda I_{Nf+1}|$ along the first column. This expansion has two distinct parts: the first term which corresponds to the first element f ; the second corresponding to the sum of the terms arising from the -1's spread at a distance of N along the column, since the other elements of the column are zero. This first term is formed by eliminating the first row and first column, which leaves us with a block diagonal matrix with the diagonal blocks being just A_N . This term is quite readily seen to be $(f - \lambda)(A_N)^f$ and hence the star determinant is:

$$|A_{star}| = (f - \lambda)(A_N)^f + \sum_{i=2}^{Nf+1} (-1)^{i+1} a_{i,1} M_{i,1} \quad (6.3)$$

We will discuss the signs of the minors shortly, which depend on whether N is odd or even. In the second term of the right hand side of 6.3, the only non-zero elements will be due to the -1's corresponding to the connection between the first bead of each arm and the core. Let us consider the result of eliminating the row corresponding to the -1 entry of the k 'th arm, where $k > 1$ and denote this determinant by A shown in Fig. 6.2.

Now, we have to expand A to obtain the rest of the star determinant. This can be done by expanding along the first row, as this is mostly zeros, except for the -1's which are the same as the -1's in the first column of A_{star} . We will show that the only non-zero contribution to the determinant is the one coming from the -1 in the top row corresponding to the k 'th column. To make this point clear, we divide the expansion along the first row into three parts:

- Arms with index $j < k$
- Arms with index $j > k$
- The k 'th arm itself.

6.2.1 Arms with index $j < k$:

Consider expanding A along the first column. This is a representative case for all $j < k$. The resulting determinant, let us call this A' is (Fig. 6.3):

$$\begin{array}{c}
\overbrace{\begin{array}{ccccc} -1 & 0 & \cdots & \cdots & 0 \end{array}}^{N,j=1} \quad \cdots \quad \overbrace{\begin{array}{ccccc} -1 & 0 & \cdots & \cdots & 0 \end{array}}^{N,j=k} \quad \cdots \quad \overbrace{\begin{array}{ccccc} -1 & 0 & \cdots & \cdots & 0 \end{array}}^{N,j=f} \\
\left[\begin{array}{cccccccccccccccccccc}
x & -1 & \cdots & \cdots & 0 & \cdots & 0 & 0 & \cdots & \cdots & 0 & \cdots & 0 & 0 & \cdots & \cdots & 0 \\
-1 & x & -1 & \cdots & 0 & \cdots & 0 & 0 & \cdots & \cdots & 0 & \cdots & 0 & 0 & \cdots & \cdots & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \cdots & \vdots & \vdots & \vdots & \vdots & \vdots & \cdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
0 & 0 & \cdots & -1 & y & \cdots & 0 & 0 & \cdots & \cdots & 0 & \cdots & 0 & 0 & \cdots & \cdots & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \cdots & \vdots & \vdots & \vdots & \vdots & \vdots & \cdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
0 & 0 & \cdots & \cdots & 0 & \cdots & -1 & x & -1 & \cdots & 0 & \cdots & 0 & 0 & \cdots & \cdots & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \cdots & \vdots & \vdots & \vdots & \vdots & \vdots & \cdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
0 & 0 & \cdots & 0 & 0 & \cdots & 0 & 0 & \cdots & -1 & y & \cdots & 0 & 0 & \cdots & \cdots & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \cdots & \vdots & \vdots & \vdots & \vdots & \vdots & \cdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
0 & 0 & \cdots & \cdots & 0 & \cdots & 0 & 0 & \cdots & \cdots & 0 & \cdots & x & -1 & \cdots & \cdots & 0 \\
0 & 0 & \cdots & \cdots & 0 & \cdots & 0 & 0 & \cdots & \cdots & 0 & \cdots & -1 & x & -1 & \cdots & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \cdots & \vdots & \vdots & \vdots & \vdots & \vdots & \cdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
0 & 0 & \cdots & 0 & 0 & \cdots & 0 & 0 & \cdots & 0 & 0 & \cdots & 0 & 0 & \cdots & -1 & y
\end{array} \right] \left. \vphantom{\begin{array}{c} \overbrace{\begin{array}{ccccc} -1 & 0 & \cdots & \cdots & 0 \end{array}}^{N,j=1} \quad \cdots \quad \overbrace{\begin{array}{ccccc} -1 & 0 & \cdots & \cdots & 0 \end{array}}^{N,j=k} \quad \cdots \quad \overbrace{\begin{array}{ccccc} -1 & 0 & \cdots & \cdots & 0 \end{array}}^{N,j=f}} \right\} N-1, j=k
\end{array}$$

Figure 6.2: The determinant A formed by eliminating the -1 entry in the first column of A_{star} corresponding to the first bead of the k 'th arm connected to the core.

$$N, j = 1 \left\{ \begin{array}{c} \overbrace{\begin{matrix} -1 & \cdots & \cdots & 0 \\ x & -1 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots \\ 0 & \cdots & x & -1 \\ 0 & \cdots & -1 & y \\ 0 & 0 & \cdots & 0 \\ 0 & 0 & \cdots & 0 \end{matrix}}^{N-1, j=1} \quad \overbrace{\begin{matrix} 0 & 0 & \cdots & \cdots & 0 & \cdots \\ 0 & 0 & \cdots & \cdots & 0 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \cdots \\ 0 & 0 & \cdots & \cdots & 0 & \cdots \\ \mathbf{0} & \mathbf{0} & \cdots & \cdots & \mathbf{0} & \cdots \\ x & -1 & 0 & \cdots & 0 & \cdots \\ -1 & x & -1 & \cdots & 0 & \cdots \end{matrix}}^{N, j=2} \quad \overbrace{\begin{matrix} 0 & 0 & \cdots & \cdots & 0 \\ 0 & 0 & \cdots & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & \cdots & \cdots & 0 \\ \mathbf{0} & \mathbf{0} & \cdots & \cdots & \mathbf{0} \\ 0 & 0 & \cdots & \cdots & 0 \\ 0 & 0 & \cdots & \cdots & 0 \end{matrix}}^{N, j=f} \\ \vdots \\ 0 & \cdots & 0 & 0 & 0 & 0 & \cdots & -1 & y & \cdots & 0 & 0 & \cdots & \cdots & 0 \\ \vdots \\ 0 & \cdots & \cdots & 0 & 0 & 0 & \cdots & \cdots & 0 & \cdots & x & -1 & \cdots & \cdots & 0 \\ 0 & 0 & \cdots & 0 & 0 & 0 & 0 & \cdots & 0 & \cdots & -1 & x & -1 & \cdots & 0 \\ \vdots \\ 0 & \cdots & 0 & 0 & 0 & 0 & \cdots & 0 & 0 & \cdots & 0 & 0 & \cdots & -1 & y \end{array} \right]$$

Figure 6.3: The determinant A' obtained by expanding A along the first column.

Consider the structure of A' . All the blocks corresponding to arm $k + 1$ to f , which are to the right of the block representing arm k , form a square block to the lower right, of size $(f - k) \times N$, since no rows or columns have been eliminated from them. The part comprising of columns 1 to $(kN) - 1$ and rows 1 to $(kN) - 1$, forms the remaining square block. The determinant of the latter (lower right) block is simply $(A_N)^{f-k}$, while we show now that the determinant of the former block is zero.

To see why this is so, consider expanding the upper left block of A' . We can see that the -1's are along the diagonal now, and form a lower diagonal structure. Expanding along these -1's, which simply, due to the lower diagonal nature, is the product of these $N - 1$ -1's, we arrive at the block from row N onwards. This block has a row of zeros, marked by bold, which is basically the row of zeros immediately above the block corresponding to arm 2. Hence, the contribution of the upper left block is zero, which renders the entire determinant A' zero.

The case is the same when expanded along any $k_1 < k$. This is because, for k_1 strictly greater than 1, all arms $j < k_1$ form a square block of size $(k_1 - 1)N$ at the upper left, in addition to the block of size $(f - k)N$ at the lower right, and the remainder comprising of arms from k_1 to k . The latter contribution will always be zero, exactly like in the case of $k_1 = 1$ shown above. As we keep expanding along the -1's of this block, we will arrive at a row of zeros, immediately above the block corresponding to arm $k_1 + 1$.

6.2.2 Arms with index $j > k$:

We now show that expanding along a -1 corresponding to an arm $j > k$ in the top row of A also produces a zero. To see why this is so, notice that in this case, the determinant consists of two blocks: an upper left square block of size $(k - 1) \times N$, comprising all the arms with index less than k , whose determinant is simply A_N^{k-1} , and a remainder square block of size $(f - k + 1)N - 1$. The final determinant is the product of the determinants of these two blocks. Just consider the lower right block, A'' , shown below, whose determinant we show to be zero for all expansions $j > k$.

$$N-1, j=k \left\{ \begin{array}{c|c|c} \overbrace{N, j=k} & \overbrace{N, j=k+1} & \overbrace{N, j=f} \\ \hline \begin{array}{ccccc} -1 & x & -1 & \cdots & 0 \\ 0 & -1 & x & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & \cdots & \cdots & -1 & y \\ 0 & 0 & \cdots & 0 & \mathbf{0} \\ 0 & 0 & \cdots & 0 & \mathbf{0} \end{array} & \begin{array}{ccccc} 0 & 0 & \cdots & \cdots & 0 \\ 0 & 0 & \cdots & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & \cdots & \cdots & 0 \\ -1 & x & -1 & \cdots & 0 \end{array} & \begin{array}{ccccc} 0 & 0 & \cdots & \cdots & 0 \\ 0 & 0 & \cdots & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & \cdots & \cdots & 0 \\ 0 & 0 & \cdots & \cdots & 0 \end{array} \end{array} \right.$$

For this case, it does not matter which $k_1 > k$ 'th column we expand along. The key point to note is that since one row is taken away from A_{star} corresponding to arm k , and another column from an arm $k_1 > k$ from the subsequent determinant A to yield A'' , the lower right block is square of size $(f - k + 1)N - 1$. Now, inspecting the structure of A'' , we see that the -1's from the first element of the first row onwards are now along the diagonal of this block, and form an upper diagonal structure. Expanding this determinant along the -1's, we see that the first $N - 1$ terms are simply the product of the -1's along the diagonal. After this stage, we arrive at a square submatrix with a column of zeros, highlighted in bold in A'' . This is nothing but the column of zeros immediately to the left of the block corresponding to arm $k + 1$. Hence, regardless of which $j > k$ we expand along, we always encounter this column of zeros, rendering the entire determinant zero.

6.2.3 The k 'th arm, $j = k$:

We show that the only nonzero contribution to the determinant A arises from the term corresponding to the -1 in the top row of the k 'th arm itself. To see why this is so, consider

expanding along column $j = k$. The resulting determinant A''' is shown below:

$$\begin{array}{c}
 \overbrace{\quad\quad\quad}^{N, j=1} \quad \quad \quad \overbrace{\quad\quad\quad}^{N-1, j=k} \quad \quad \quad \overbrace{\quad\quad\quad}^{N, j=f} \\
 \left[\begin{array}{cccccc|cccc|cccc}
 x & -1 & \cdots & \cdots & 0 & \cdots & 0 & \cdots & \cdots & 0 & \cdots & 0 & 0 & \cdots & \cdots & 0 \\
 -1 & x & -1 & \cdots & 0 & \cdots & 0 & \cdots & \cdots & 0 & \cdots & 0 & 0 & \cdots & \cdots & 0 \\
 \vdots & \vdots & \vdots & \vdots & \vdots & \cdots & \vdots & \vdots & \vdots & \vdots & \cdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
 0 & 0 & \cdots & -1 & y & \cdots & 0 & \cdots & \cdots & 0 & \cdots & 0 & 0 & \cdots & \cdots & 0 \\
 \vdots & \vdots & \vdots & \vdots & \vdots & \cdots & \vdots & \vdots & \vdots & \vdots & \cdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
 0 & 0 & \cdots & \cdots & 0 & \cdots & x & -1 & \cdots & 0 & \cdots & 0 & 0 & \cdots & \cdots & 0 \\
 0 & 0 & \cdots & \cdots & 0 & \cdots & -1 & x & \cdots & 0 & \cdots & 0 & 0 & \cdots & \cdots & 0 \\
 \vdots & \vdots & \vdots & \vdots & \vdots & \cdots & \vdots & \vdots & \vdots & \vdots & \cdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
 0 & 0 & \cdots & 0 & 0 & \cdots & 0 & \cdots & -1 & y & \cdots & 0 & 0 & \cdots & \cdots & 0 \\
 \vdots & \vdots & \vdots & \vdots & \vdots & \cdots & \vdots & \vdots & \vdots & \vdots & \cdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
 0 & 0 & \cdots & \cdots & 0 & \cdots & 0 & 0 & \cdots & 0 & \cdots & x & -1 & \cdots & \cdots & 0 \\
 0 & 0 & \cdots & \cdots & 0 & \cdots & 0 & 0 & \cdots & 0 & \cdots & -1 & x & -1 & \cdots & 0 \\
 \vdots & \vdots & \vdots & \vdots & \vdots & \cdots & \vdots & \vdots & \vdots & \vdots & \cdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
 0 & 0 & \cdots & 0 & 0 & \cdots & 0 & 0 & \cdots & 0 & \cdots & 0 & 0 & \cdots & -1 & y
 \end{array} \right] \left. \vphantom{\begin{array}{c} \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \end{array}} \right\} N-1, j=k
 \end{array}$$

A''' is simply composed of f block diagonal elements, $f-1$ of which are A_N , introduced earlier, which arise from all arms $j \neq k$. The elimination of the column with -1 in the top row corresponding to the k 'th arm, along with the removal of the row corresponding to the same arm from A_{star} in the previous step, leaves behind a square block of size $N-1$, which is nothing but A_{N-1} , also introduced earlier. Since the determinant is simply the product of the individual blocks, the magnitude of the contribution of the k 'th arm to A_{star} is simply $(A_N)^{f-1} A_{N-1}$.

6.2.4 Sign of the minors:

Let us now discuss the sign of this term. At this point, we have managed to show that, starting from A_{star} , the first element is readily obtained in 6.3. After this, the second term in 6.3 only has contributions from the expansions along the -1's spread along the first column at a distance of N from each other. From the analysis in the previous subsections, we have shown that the result of expanding A_{star} along the $N(k-1) + 2$ 'th row, which is nothing but the -1 due to the first bead of the k 'th arm, is a term of magnitude $(A_N)^{f-1} A_{N-1}$. We now have to determine the sign of this general k 'th term.

In order to reach the factor $(A_N)^{f-1} A_{N-1}$, we expanded two determinants, A_{star} and A . In both of these, we expanded along the same element -1, in the first column of A_{star}

at row number $N(k-1) + 2$ and the first row of A at column number $N(k-1) + 1$. The raw product of these two -1's, excluding the signs premultiplying them in 6.2, is of course +1. The raw element products, then, is always +1 and the final sign of $(A_N)^{f-1}A_{N-1}$ will be determined by the sign factors (+1 or -1) multiplying the minors of these two -1s.

The sign factor preceding the -1 element of the k 'th row in the expansion of A_{star} will be $-1^{1+N(k-1)+2}$, and will subsequently be multiplied by the sign factor $-1^{1+N(k-1)+1}$ from A . From these expressions of the two sign factors, we can see that if one of them is -1, the other one is always +1 and vice versa. Thus, the two sign factors always multiply to yield a -1 and then, the elements -1 themselves multiply to yield a +1. The sign of the factor $(A_N)^{f-1}A_{N-1}$, thus is always -1.

Thus, we have seen that for both even and odd values of N , the contribution to the second term of 6.3 is $-(A_N)^{f-1}A_{N-1}$, and hence, the determinant is:

$$|A_{star}| = (f - \lambda)(A_N)^f - f(A_N)^{f-1}A_{N-1}, \quad (6.4)$$

which can be simplified to:

$$|A_{star}| = (A_N)^{f-1}((f - \lambda)A_N - fA_{N-1}). \quad (6.5)$$

which when equated to zero gives the eigenvalues λ . These numbers describe the timescales of decay of the stress response of star-shaped polymers.

There are two factors in 6.5, which can be written as:

$$|A_{star}| = RU. \quad (6.6)$$

where the roots of $R = (A_N)^{f-1}$ form the repeated part of the spectrum and the roots of $U = ((f - \lambda)A_N - fA_{N-1})$ form the unique part of the spectrum.

We have verified our procedure by numerically obtaining the eigenvalues of A_{star} for a few combinations of f and N and then splitting it into degenerate and non-degenerate sets. Then we separately obtained the roots of R and U and compared it with the degenerate and non-degenerate eigenvalues of A_{star} , which were found to match exactly. Hence we have rigorously verified that the characteristic polynomial of A_{star} is given by Eq. 6.5.

R is an $f - 1$ fold polynomial, which is A_N repeated $f - 1$ times, whose roots are the eigenvalues forming the degenerate part of the star spectrum. These are known analytically and form the degenerate sine modes, which are just the rouse modes of an N bead linear chain, one of whose ends is held fixed at the origin. The second part, U , is a polynomial, whose solution, in the general case, is not analytically tractable. We will first show that U , being a polynomial of degree, $N + 1$, has the same number of roots, of which one is zero. Of the remaining N roots, all except the largest one are of magnitude less than 4 and are very closely approximated by the non-zero roots of an N bead linear chain with free ends for large functionalities. On the other hand, the largest root, let us refer to this as λ_{max} is shown to be

very well approximated by $f^2/f - 1$ from numerical considerations and cannot be derived from the linear chain determinant.

Let us work back from the polynomial U to obtain its corresponding matrix of size $N + 1$, denoted by B , given by:

$$B = \begin{bmatrix} f & -1 & 0 & \cdots & 0 \\ -f & 2 & -1 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & \cdots & -1 & 2 & -1 \\ 0 & \cdots & 0 & -1 & 1 \end{bmatrix}$$

It is clear from inspection that the $N + 1$ matrix B has rank N . This can be verified by adding the rows of B from the last to the first. It can also be said that B has N independent rows. Hence, the characteristic polynomial U of B has exactly one zero.

In the limit of large functionality f , the polynomial U , approaches the characteristic polynomial of an N bead linear chain. To see this consider the $N \times N$ rouse matrix of a linear chain, L_N :

$$L_N = \begin{bmatrix} 1 & -1 & 0 & \cdots & 0 \\ -1 & 2 & -1 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & \cdots & -1 & 2 & -1 \\ 0 & \cdots & 0 & -1 & 1 \end{bmatrix}$$

Like before, let us use the notation L_N itself for the characteristic polynomial of the matrix L_N for simplicity. Just like equation 6.1, we can write a recursive relation for L_N given by:

$$L_N = (x - 1)A_{N-1} - A_{N-2} \quad (6.7)$$

where $x - 1 = 1 - \lambda$.

Now consider taking out the factor f from U , yielding:

$$U = f \left(\left(1 - \frac{\lambda}{f} \right) A_N - A_{N-1} \right) \quad (6.8)$$

In the limit of large functionality f , we can neglect the factor λ/f in Eq. 6.8 (The reader should note that this does not work for the largest root $f^2/f - 1$, which can only be determined numerically so far). To find the roots of U we of course equate it to zero, hence the polynomial finally reduces to:

$$A_N - A_{N-1} = 0 \quad (6.9)$$

Using the relation 6.1 and the above, we have:

$$(x - 1)A_{N-1} - A_{N-2} = 0 \quad (6.10)$$

This, however, is the same as 6.7 which is nothing but the characteristic polynomial of a linear N bead chain. Thus, the roots of U approach the roots of L_N at large functionalities f .

To summarize, we have shown that the eigenvalue spectrum of an f functionality star with N beads along each arm can be divided into two parts by factoring the characteristic polynomial of its rouse matrix A_{star} . One part is the degenerate sine modes repeated $f - 1$ times and the other part comprises of the unique modes, which start resembling the symmetric cosine modes of an N bead linear chain only in limit of high-functionality f . In addition, there is the zero eigenvalue corresponding to diffusion of the center of mass and the also a large eigenvalue well approximated by $f^2/f - 1$. We present some results in the next section.

6.3 Results

In this section we present some numerical results. We will first compare the differences between unique spectrum found from our method and the spectrum of an N bead linear chain which has been so far assumed to be the unique spectrum. The section concludes with a few comments on λ_{max} .

6.3.1 Difference between unique spectra

The polynomial U is given by:

$$U = ((f - \lambda)A_N - fA_{N-1}) \quad (6.11)$$

Since we have already said that of the $N + 1$ roots of U , one is zero and the other is λ_{max} , we will only compare those eigenvalues of U which are comparable in magnitude to the $N - 1$ non-zero eigenvalues of the N bead linear chain L_N . The eigenvalues of L_N , let us call them λ_{lin} , are given by:

$$\lambda_{lin} = 4\sin^2\left(\frac{k\pi}{2N}\right) \quad (6.12)$$

Denoting the roots of U by λ_U (of which we exclude 0 and λ_{max}), we compute the percentage error in eigenvalues for a given N, f pair:

$$perror(N, f) = \frac{|\lambda_U - \lambda_{lin}|}{\lambda_U} \times 100 \quad (6.13)$$

The figures 6.4, 6.5 and 6.6 show $perror(N, f)$ for a few representative (N, f) pairs. For

Figure 6.4: Percentage errors in the unique spectra for stars with a) 3 beads per arm and b) 4 beads per arm. It can be seen that the error is very large for the small bead case.

Figure 6.5: Percentage errors in the unique spectra for stars with a) 10 beads per arm and b) 20 beads per arm. The difference has reduced significantly compared to Figs. 6.4a and 6.4b.

each of the graphs, the x-axis is the index of the eigenvalue when they are sorted in ascending order. An index of 1 means the smallest magnitude eigenvalue for any (N, f) pair. For a star with $N = 10$, an index of 9 on the x-axis represents the eigenvalue with largest magnitude, since such a star has 10 eigenvalues in the unique spectrum, of which λ_{max} , being the 10th and largest one, is excluded from our comparison as stated earlier. In all cases, we see that the difference in the spectra reduces with functionality for a given number of beads.

Since the difference between spectra are largest for the smallest arm lengths and functionalities, the figure 6.7 shows the effect of the different spectra on the shear relaxation modulus $(G(t))$ normalized by its plateau value, for two stars with functionality 3 and 3 and 10 beads along each arm. The friction coefficient and Kuhn length from chapter 2 is used to obtain these curves. Since we have shown that the degenerate spectrum is the same in our derivation

Figure 6.6: Percentage errors in the unique spectra for stars with a) 50 beads per arm and b) 100 beads per arm. At these large arm lengths the difference between spectra is negligible.

and previous studies, we will not show its contribution to the total $G(t)$ and instead only show the part contributed by the unique spectrum as determined by us and contrast it with the $G(t)$ resulting from the linear chain spectrum. The solid lines show the normalized $G(t)$ from the spectrum derived in this chapter (roots of U) and the dashed lines are those contributed by the unique modes from the linear chain. There is a difference in the two spectra for both arm lengths of 3 and 10. The difference is larger for the smaller star with 3 beads per arm.

6.3.2 The largest eigenvalue λ_{max}

Our decomposition of the star characteristic polynomial into repeated and unique parts still leaves out the maximum eigenvalue λ_{max} . In this subsection we present some figures of a couple of numerical tests showing the evolution of λ_{max} for different values of N and f .

First of all, for the case of $f = 1$, we simply have a linear chain of $N + 1$ beads and hence the eigenvalues are clear. For a case of $f = 2$, we again have a linear chain of $2N + 1$ beads, with one bead being the central core and with N beads on each of the two arms. We can now compare our star-oriented method with the well-known eigenvalues for a linear chain. The repeated spectrum in our case consists of the eigenvalues of an N bead chain with one end held fixed at the origin. These are nothing but the odd sine modes of a $2N + 1$ bead chain. The unique part of the spectrum, excluding the zero, should correspond to the remaining even cosine modes of the same linear chain of $2N + 1$ beads. Fig. 6.8a shows the unique spectrum calculated by numerically solving 6.11 for a representative case of $N = 10$ beads and the even cosine modes of a 21 bead long chain, which match exactly. This is also to be expected intuitively.

The key thing to note from this analysis is that λ_{max} now has a value of 4 for any value of N and $f = 2$. To shed further light on the behaviour of λ_{max} with functionality, we have solved 6.11 for fractional values of f as well between 1 and 3, which are plotted in Fig 6.8b.

Figure 6.7: Difference in the normalized shear relaxation modulus $G(t)$ for 3 arm stars with 3 beads and 10 beads along each arm.

(a)

(b)

Figure 6.8: a) The unique spectrum (solid blue) for $f = 2$ with $N = 10$ beads on each arm. The red symbols are the even cosine modes of a $2N + 1 = 21$ bead chain. b) Eigenvalues of the unique spectrum for $N = 10$ and continuous f between 1 and 3. The topmost line represents the largest eigenvalue λ_{max} , which can be seen to be continuous with f and starts increasing from a value of 4 at $f = 2$.

On the x-axis is the functionality and on the y-axis is the eigenvalue itself. The topmost line in red represents λ_{max} and we can see that it is continuous in f .

6.4 Discussion and Conclusions

In this chapter we have diagonalized the Rouse matrix of a symmetric star polymer of functionality f and N beads per arm. This was accomplished by factorizing the grand characteristic polynomial of the star into two parts. One part gives the degenerate sine modes repeated $f - 1$ times and the other part gives the zero eigenvalue corresponding to center of mass diffusion, the unique part of the eigenspectrum and the maximum eigenvalue which is numerically shown to be well approximated by $f^2/f - 1$ and is continuous in f . Previous studies have obtained the correct eigenvalues for the degenerate case ([202, 198]) but the cosine eigenmodes for the symmetric case were obtained based on the consideration that the core is the center of mass. These cosine modes were theorized to be the same as the even modes of a free linear chain of length $2N + 1$, whose analytical form is well known. From our method, the polynomial corresponding to the unique part of the spectrum only yields this assumed spectrum in limit of large functionality f . This can be intuitively understood, since in the limit of large functionality, the mass distribution becomes increasingly homogeneous around the core and the core becomes the center of mass. This difference between the correct unique spectrum as derived in the present chapter and that assumed previously is not much numerically and depends on the number of beads per arm. However, for small stars, with functionality 3 to 5 and about 3 to 10 beads per arm, the difference between the correct unique spectrum and the analytical form assumed so far in literature are quite substantial which could lead to differences in macroscopic calculation of shear relaxation moduli, etc.

The largest eigenvalue λ_{max} is shown to be continuous with f and increases from a value of 4 at $f = 2$, with the whole unique spectrum being the even modes of a linear chain with $2N + 1$ beads. After $f = 2$, the other eigenvalues of the unique spectrum stay bounded less than 4 while the largest increases approximately as $f^2/f - 1$. This behaviour of the largest eigenvalue could give theorists more insight into future studies of the Rouse spectra of stars.

Chapter 7

Summary

In this thesis we have mainly studied the rheology of different kinds of soft matter systems by Brownian Dynamics (BD) simulations. A range of systems like telechelic star polymers, non-telechelic stars at different volume fractions and supramolecular systems were studied. In this process we have generalized the Rouse model of polymer dynamics and studied the technique of Superposition Rheology in great detail and thus have contributed to fundamental theoretical development in rheology. The following paragraphs details these contributions per chapter.

In Chapter 2 we have studied the rheology of a telechelic star polymer gel with functionality 13. The experimental stress relaxation moduli for the non-network forming precursor and the gel network were known. From the radius of the star, the number of Kuhn segments per arm was determined to be 7 taking as input a Kuhn length of 4 nm. First the rheology of the precursor was fitted with a model where the friction grows quadratically outward from the core to the arm tip, using the Generalized Rouse model (GRM) developed by us. According to the GRM, the normal modes of a polymer obeying the Rouse model are still uncorrelated as long as the Rouse matrix is symmetric. This opens up a way to obtain the relaxation moduli of polymers with arbitrary frictions, spring constants and also for semi-flexible polymers as all these have a symmetric Rouse matrix. Using this insight, we used a hybrid simulation method where the cores of the stars were displaced according to the inter-star potential developed by Likos and co-workers and the arms were moved by updating their Rouse modes in time and converting them back to real-coordinates to determine the forces on the core. The precursor was modified by adding an eighth sticker bead of one-sixth the mass of a regular bead at the arm tip, according to experimental values and then allowed to form networks with different cross-link percentages. Gelation set in at about 11 % and the relaxation modulus developed a power law tail for crosslink percentages leading up to this value. We analyzed the exponents of the power laws and fitted an expression for them. By matching the relaxation moduli of the simulated boxes with different crosslink percentages, we determined that the

experimental system has crosslink percentage of 25% of all arms.

In Chapter 3 we performed BD simulations of Orthogonal Superposition Rheology (OSR) of a system of star polymers again with functionality 13. The orthogonal superposition moduli were obtained for different steady shear rates by applying a small amplitude sinusoidal oscillatory strain perpendicular to the direction of shear with the gradient in the same direction, and then fitting the resulting stress by an in-phase and another out-of-phase sinusoid whose coefficients give the storage and loss moduli respectively for that particular steady shear rate. We show that the relaxation modulus obtained after inverse Fourier transforming the moduli to time-domain is different from the stress response after a unit impulse in the orthogonal direction, unlike in linear viscoelasticity, with the former developing a power law tail while the latter always decaying exponentially. The plateau value of both moduli are the same, only the tail becomes increasingly algebraic with shear rate. In addition, a plot of the power law exponents with shear rate reveals that the Maxwellian slope of 2 for the storage modulus at zero-shear seems to be a singular point. We also give an expression for the plateau value of the storage time which can be directly calculated from a simulation and we also link it to the perturbation in the pair distribution function.

OSR simulations with BD are carried out in Chapter 4 for a system of star-like micelles with functionality 120 at a very high volume fraction compared to that in Chapter 3. These simulations are counterparts to an experimental OSR investigation of a concentrated star-like micellar solution, which found non-standard relaxations in the orthogonal moduli after a critical shear rate. Simulations were carried out for two model representations, one with only the Likos potentials between the micelles and another with an additional transient potential by the Rapid method. We found that after a certain shear rate, the orthogonal moduli develop multiple crossovers for both models. This can be attributed to shear induced lane formation which is clearly seen in the movies and the mean square displacements in the gradient and vorticity directions, with lane formation leading to reduced transport in these directions with shear. In model 1, laning occurs due to purely repulsive interactions between the micelles and there is clear shear-induced ordering at high shear rates at which the storage and loss moduli become parallel, yielding a solid like response. No such separation of moduli is seen in model 2 whose response is hence liquid-like at all rates since the transient interactions tend to maintain a given distance distribution between the particles. Although each particle travels in its own lane at high shear rates, there is no crystalline order.

In Chapter 5, non-monotonic stress relaxation after stoppage of steady shear was modeled for three different experimental systems with associative interactions. Generally the stress decays exponentially after steady shear is stopped since there is no work performed on the system. However, in the experiments, the stress decays non-monotonically with an initial decay followed by an increase and eventually decays to zero. We describe the effect phenomenologically by a generic model based on an order parameter altered by shear. When bonds re-establish, energy flows from stored to thermal and elastic energy, whereas the latter one results in work done on the system. If shear has induced order in the system so that the

performed work leads to rearrangements of partly aligned elastic domains, the overall stress increases during the relaxation process. A differential equation for the stress is provided with two competing terms. One of them accounts for the steady decay of the stress with a rate that depends on the present state of the system and another that causes the increase.

Chapter 6 has a decomposition of the Rouse matrix of a symmetric star polymer with functionality f and N beads on each arm into a product of two polynomials whose roots give the unique and degenerate spectra. We show that the degenerate part of the spectrum is that of a Rouse chain held fixed at one end repeated $f - 1$ times, in agreement with existing theory and the unique part consists of the roots of the other polynomial. At moderate to high functionalities, the unique spectrum approaches that of a free N -bead linear chain. This contrasts our findings with that generally used in literature where the unique spectrum is always taken to be that of a linear chain, which is due to the assumption that the core is always the center of mass, which is not the case for small functionalities but becomes increasingly true for larger values of f due to a more symmetric mass distribution about the center. In addition, we also report the existence of the largest eigenvalue in the unique spectrum, which is well-approximated by the value $f^2/f - 1$ and has been described earlier in literature as well. We show that this root is continuous in f , which might be a clue for additional study.

Chapter 8

Samenvatting

In dit proefschrift hebben we de reologie van verschillende soorten zachte materie bestudeerd met behulp van Brownse Dynamica (BD) simulaties. Een reeks systemen van telechelische en niet-telechelische sterpolymeren werd bestudeerd bij verschillende volumefracties en supramoleculaire structuren. In de loop van dit onderzoek hebben we het Rouse-model voor polymeerdynamica gegeneraliseerd en de techniek van Superpositie Reology uitvoerig bestudeerd en zodoende bijgedragen tot fundamentele theoretische ontwikkelingen in de reologie. In de volgende paragrafen worden deze bijdragen per hoofdstuk beschreven.

In Hoofdstuk 2 hebben we de reologie van een telechelisch sterpolymeer-gel met een functionaliteit van 13 bestudeerd. De experimentele stress-relaxatie moduli voor de niet-netwerkvormende precursor en het gel-netwerk waren bekend. Aan de hand van de eveneens experimenteel bekende straal van de ster werd het aantal Kuhn-segmenten per arm op 7 gesteld met een Kuhn-lengte van 4 nm als invoer. Eerst werd de reologie van de precursor beschreven met een Rouse-model waarin de wrijving per Kuhn-segment kwadratisch naar buiten toe groeit van de kern naar de punt van de arm. In dit door ons ontwikkelde Generalized Rouse-model (GRM) zijn de fundamentele collectieve bewegingen van een polymeer, kortweg Rouse-modes, niet gecorreleerd, vooropgesteld dat de Rouse-matrix symmetrisch is. Dit opent een manier om de relaxatiemodulus van polymeren met willekeurige fricties, veerconstanten en ook voor semi-flexibele polymeren te verkrijgen, omdat deze allemaal een symmetrische Rouse-matrix hebben. Met behulp van dit inzicht hebben we een hybride simulatiemethode ontwikkeld waarin de kernen van de sterren verplaatst worden op basis van het interactiemodel voor de gemiddelde kracht tussen twee sterren ontwikkeld door Likos en collega's en de armen werden verplaatst door hun Rouse-modes op tijd bij te werken en ze terug te converteren naar echte coördinaten om de krachten op de kern te bepalen. De precursor werd vervolgens gemodificeerd door een achtste zogenaamde sticker-kraal toe te voegen aan het einde van iedere arm, met een frictie gelijk aan $\frac{1}{n}$ zesde van die van een regelmatige kraal. Vervolgens werd deze stickers toegestaan in paren te binden, en zodoende netwerken

te vormen met verschillende verknopingspercentages. Bij voldoende lage verknopingspercentages vertoonde de relaxatiemodulus een algebraïsch verval bij lange tijden. Analyse van de exponenten van deze machts-wetten als functie van het verknopingspercentage leerde dat gelering inzet bij 11% van de maximale toegestane verknoping. Door de relaxatie-modulus van gesimuleerde boxen met verschillende verknopingspercentages te vergelijken met de experimentele waarden, hebben we vastgesteld dat het experimentele systeem een verknopingspercentage had van 25% van de maximale waarde.

In Hoofdstuk 3 hebben we BD-simulaties van Orthogonale Superpositie Reologie (OSR) uitgevoerd van een systeem van sterpolymeren, opnieuw met functionaliteit 13. De orthogonale superpositiemoduli bij verschillende constante afschuifsnellheden werden verkregen door een sinusoidaal oscillerende vervorming met kleine amplitude op te leggen, loodrecht op de richting van de stationaire afschuiving en met gradiënt in dezelfde richting als deze laatste. De resulterende spanning werd vervolgens beschreven met een sinusoidale oscillatie in fase met de opgelegde vervorming en een andere uit fase hiermee. De bijbehorende coëfficiënten leveren respectievelijk de opslag- en verliesmodulus. We hebben laten zien dat de relaxatiemodulus, verkregen na Fourier transformatie van de opslag- en verliesmoduli naar het tijdsdomein, verschilt van de stressrespons na een instantane eenheidsvervorming in de orthogonale richting, waarbij de eerstgenoemde een algebraïsche staart ontwikkelt terwijl de laatste altijd exponentieel relaxeert. Dit is tegenstelling tot lineaire visco-elasticiteit bij evenwicht, waar beide moduli gelijk zijn. Bovendien blijkt uit een grafiek van de machtswet exponenten als functie van de afschuifsnellheid dat de Maxwelliaanse helling van 2 voor de opslagmodulus bij evenwicht een enkelvoudig punt lijkt te zijn. De plateauwaarde van beide moduli daarentegen is voor beide moduli gelijk, onafhankelijk van de opgelegde constante afschuifsnellheid. We geven ook een uitdrukking voor deze plateauwaarde die direct kan worden berekend uit een simulatie met constante afschuifsnellheid, zonder oscillerende component, en we laten zien hoe deze samenhangt met de verstoring van de paarverdelingsfunctie als gevolg van de stationaire afschuiving.

OSR-simulaties met BD worden beschreven in Hoofdstuk 4 voor een systeem van sterachtige polymeren met functionaliteit 120 bij een zeer hoge volumefractie vergeleken met die in Hoofdstuk 3. Deze simulaties zijn representanten van een experimenteel OSR-onderzoek van een geconcentreerde sterachtige micellaire oplossing, waarin niet-standaard relaxaties in de orthogonale moduli werden gevonden boven een kritische stationaire afschuifsnellheid. Simulaties werden uitgevoerd voor twee modelrepresentaties, $\tilde{\Gamma} \tilde{\Gamma}'$ met alleen Likos-interacties tussen de micellen en een andere met Likos-interacties plus zogenaamde transiënte interacties, die als doel hebben geheugen in de simulaties te introduceren. We hebben ontdekt dat, voor beide modellen, de orthogonale moduli boven een bepaalde stationaire afschuifsnellheid meerdere crossovers ontwikkelen. Dit gedrag is gerelateerd aan shear-geïnduceerde rijvorming die duidelijk te zien is in films en in de gemiddelde kwadratische verplaatsingen in de gradiënt- en vorticiteitsrichtingen. Deze baanvorming leidt tot verminderd transport in beide richtingen loodrecht op de stroomrichting. In model 1 treedt rijvorm-

ing op als gevolg van zuiver afstotende interacties tussen de polymeren en is er een duidelijke shear-geïnduceerde ordening bij zeer hoge afschuifsnelheden. Onder deze omstandigheden is de opslagmodulus groter dan de verliesmodulus over het hele frequentie bereik en lopen zij min of meer parallel. Een dergelijk vaste stof gedrag wordt niet gezien in model 2, waarvan de respons onder alle omstandigheden vloeistofachtig is. De transiënte interacties hebben de neiging om een de deeltjes te verzamelen in dynamische clusters die niet kristallijn ordenen zoals in het eerste model.

In Hoofdstuk 5 werd de stressrelaxatie na het stoppen van een constante afschuifstroming gemodelleerd voor drie verschillende experimentele systemen met associatieve interacties. vrijwel altijd neemt de spanning monotoon af nadat de constante afschuiving is gestopt om uiteindelijk geheel te verdwijnen. Bij de experimenten aan associatieve systemen beschreven in dit hoofdstuk vervalt de spanning echter niet-monotoon: de spanning vervalt aanvankelijk zeer snel, maar neemt na enige tijd weer toe om vervolgens na een maximum volledig naar nul te relaxeren. We beschrijven het effect fenomenologisch door een generiek model op basis van het aantal bindingen per volume en een orderparameter, beide gewijzigd door de krachten die optreden tijdens de vooraf opgelegde afschuifstroming. Tijdens deze fase van het experiment worden bindingen tussen de polymeren sneller verbroken dan zij kunnen herstellen, waardoor *de facto* minder bindingen bestaan onder stationaire afschuifstroming dan in evenwicht. Wanneer de afschuifstroming wordt gestopt neemt de bindingsdichtheid geleidelijk weer toe, waarbij bindingsenergie vrij komt. Deze laatste kan als warmte vrijkomen, maar ook gedeeltelijk worden gebruikt om lokaal de elastische energie te verhogen. Als afschuiving de juiste orde in het systeem heeft geïnduceerd, kunnen onder omstandigheden de elastische domeinen gedeeltelijk uitlijnen, waardoor de algehele spanning kan toenemen. Uiteindelijk is het bindingsdichtheid weer gelijk aan die in evenwicht en zal de overgebleven stress relaxeren naar nul. Wij hebben een differentiaalvergelijking voor de stress afgeleid, die de verandering van de stress per tijdseenheid beschrijft met twee concurrerende termen. Eén term beschrijft het gestage verval van de stress bij onveranderde bindingsdichtheid, terwijl de tweede term de toename van de stress beschrijft wanneer nieuwe bindingen gevormd worden. Dit eenvoudige model is zeer wel in staat de experimentele data te beschrijven.

Hoofdstuk 6 beschrijft een ontbinding van de Rouse-matrix van een symmetrisch sterpolymeer, met functionaliteit f en N korrels op elke arm, in een product van twee polynomen waarvan de wortels respectievelijk een uniek en een gedegenereerd spectrum geven. We laten zien dat het gedegenereerde deel van het spectrum $f - 1$ maal dat van een Rouse-keten is, die aan één kant gefixeerd is en N kralen bevat, in overeenstemming met de bestaande theorie. Het unieke deel van het spectrum bestaat uit de $N + 1$ wortels van het andere polynoom. Bij matige tot hoge functionaliteiten benadert het unieke spectrum dat van een unieke wortel plus het spectrum van een vrije lineaire N -keten uitgezonderd de diffusieve mode. Aan dit geheel wordt tenslotte nog de diffusieve mode toegevoegd. Dit contrasteert onze bevindingen met de in de literatuur gebruikelijke aanname dat het unieke spectrum altijd hetzelfde is als dat van een lineaire keten. Deze aanname is identiek aan de aanname dat de centrale bead

altijd de positie van het zwaartepunt inneemt, hetgeen niet het geval is voor kleine functionaliteiten. Deze aanname wordt beter naarmate de functionaliteit f toeneemt, omdat dan de massadistributie welhaast symmetrische rond de centrale bead is. Tedslotte vermelden we dat de grootste wortel bij hoge functionaliteit goed wordt benaderd door de waarde van $f^2/f - 1$. We laten zien dat deze wortel continu in f is, wat nuttig kan zijn voor aanvullend onderzoek.

Chapter 9

List of Publications

- V. Metri, A. Louhichi, J. Yan, G.P. Baeza, K. Matyjaszewski, D. Vlassopoulos and W.J. Briels,
Physical Networks from Multifunctional Telechelic Star Polymers: A Rheological Study by Experiments and Simulations,
Macromolecules, 51, 2872-2886, (2018).
- V. Metri and W.J. Briels,
Brownian Dynamics Investigation of the Boltzmann Superposition Principle for Orthogonal Superposition Rheology,
J. Chem. Phys., 150, 014903 (2019).
- J. Hendricks, A. Louhichi, V. Metri, et al.,
Non-monotonic stress relaxation after cessation of steady shear flow in supramolecular assemblies
Submitted to Physical Review Letters.
- V. Metri, E. Moghimi, A. Poulos, G. Petekidis and W.J. Briels,
Brownian Dynamics Simulations of High-functionality Star Polymers Probed by Orthogonal Superposition Rheology,
In Preparation.

Chapter 10

Acknowledgments

As I reach the end of my PhD journey, I must say there are many names that come to mind that have directly or indirectly helped me in my endeavors so far. I feel really humbled to be writing this, as there were moments when I imagined that I might never reach this stage. However, because of the guidance, support and love of so many people around me, I could finish my thesis on time and am very grateful to all. The following paragraphs contain my recollections of the journey so far.

First of all, in typical Indian fashion, I would like to thank my Guru, Prof. Wim J. Briels. Right from the first day, he has played the role of advisor to perfection, and has been an excellent guide and motivator. I distinctly remember, I was with my friends in Goa when I received an email saying Wim wanted to interview me. At that point I was 26, and did not really know what I wanted to do next. Looking at the waves, I realized that if I land this interview, my life will never be the same. And my, was I right! Coming from Bangalore to Enschede was quite a change, but Wim made me feel right at home, especially with his prodigious knowledge of music. It is rare, indeed very rare, to find a unique combination of talents as Wim, with his jovial persona, charisma and breadth of knowledge, and what's more, for him to be one's advisor! And yes, I must elaborate on his talents as a physicist, since in my humble opinion, his thought process represents a continuation of the the great traditional physicists of yore. Not only did he teach himself several concepts of Physics, but watching him solve arm-length equations with a twinkle in his eye taught me that being a scientist is more than a profession, its a *personal* calling! I can write a book on this great physicist, but let me stop here and summarize by saying that I will do my best to continue this line of thinking wherever I go next. It is said in India that at the right time in one's life, a guru appears to guide one. Though it might sound mystical, I must say that it has remarkably come true in my case, and it has been a stupendous honour to be moulded at the hands of one who has studied physics out of pure passion. I hope Prof. Briels keeps continuing on this remarkable journey and I would be honoured to contribute in any future research.

Next I would like to thank Wouter den Otter, who continually amazes me with his astounding knowledge of physics and history. Again, he is one of the most brilliant physicists I have met, and I greatly enjoyed conversing with him on a wide array of subjects. Being a student of Wim, I must say he embodies the same spirit of enquiry, and tackles research questions from very fundamental standpoints, something that I admire in today's world of 'fashionable' research driven by this nonsensical concept of 'impact factors' and what not. I wish you all the best Wouter in all future research and will keep my eyes open for more papers from you! Also I must mention Claudia, the head of CCP, who has been a very good person all along and would drag us all to lunch on time. And of course, the highly efficient Els has been a wonderful secretary, she is more accurate than an atomic clock. I think we need to take her to India to train some of our lazy bureaucrats! Thanks for all the help!

Next I must move on to my friends in the group. Our ritual (and long) coffee breaks were hotbeds of discussion for all kinds of topics, from the sacred to the profane, from the profound to the frivolous. Matteo has been a very good friend all along, his passion for computing (and Star Wars) is something to be admired. He helped a lot in setting up new nodes of our cluster and I greatly enjoyed our conversations, especially on politics (described by Wim as 'leftish'). Csaba is a brilliant mind and we had some shared interests in philosophy which led to interesting discussions. Ioana has also been a very good friend and group member and being the senior member has guided me every now and then. And thanks to Riccardo and Habib, who were good companions in our lunch breaks. I would also like to thank Barry for lively conversations during his 'guest appearances'! Special thanks to my paronymph Monika, and our new arrival Alice, for the help and support! They have taken care of my computer when I moved out, and were very good companions in the second incarnation of our group. Your dedication to seeking out great food will be missed. All the best to you two, Monalice! And yes, I dropped the idea of getting dogs to keep you two away, as there are many stray cats in Weesp that keep me company, so you are welcome anytime. And also thanks to Jonas for the support!

I must say special thanks to a dear friend, my namesake Vishal Ahuja. Now this guy again deserves a book. On my first day of arrival in Enschede, it was raining (big surprise) and to make matters worse, my baggage did not arrive. But Vishal helped me out and made me feel at home! We have very similar backgrounds in India, and we could connect on so many issues of shared interest, right from politics to inter-cultural dilemmas. I have learned a lot from his sharp mind and keen logical sense and he was the first one to explain the basics of Rheology to me. I still remember him explaining the fact that liquids respond to 'rates of shear', with the example of dipping a finger into a glass of water: dip it slowly and there is no resistance, dip it fast and it splashes. This simple explanation is something I will remember for life. I wish you all the best in your professional and personal life!

All this would not have been possible without the Marie Curie grant which brought me to the Netherlands. On this I wish to thank the entire SUPOLLEN team, who have become very good friends. We are almost a family and I learnt so much of rheology directly from the

meetings organized periodically in exotic European capitals. Especial thanks to Lawrence, Gunwoo, Ameer, Guilhem, Jan, Ashwin for the collaborations and support. I would also like to thank Evelyne for the support and encouragement and Daniel for the amazing lectures on polymer dynamics. I sincerely thank Dimitris, who has been a wonderful father figure in the world of rheology. It is an incredible honour to have collaborated with you! I remember your encouragement and friendly words of advice, especially after my talks, and your simplicity and dedication to work amazes me. Also, being a distinguished scientist in the field, you listened to the ideas of a total newcomer like me. This gave me the confidence that even though I had no rheological background, I could understand the theories and contribute my own ideas to the field. Kudos to the SUPOLEN team!

My time in Enschede was made lively by my friends Kriti and Sahana, who have been very good companions indeed. Thanks to you two, I found a good support base and our group with Vishal has seen some great times indeed! I wish you all the best for the future and of course we will continue poking fun at each other for a long time to come. By the way, nobody calls me Metri other than this group, haha! Of course, special mention has to be made of my brother Abhishta, with whom I have shared some amazing times. You are quite an extraordinary talent, and have been a solid support throughout these years. Not only did your presence give me a sense of security, with your calm manner and general intelligence, but you are also a fantastic human being, who is already on the way to great things ahead. Keep rocking bro!

I must definitely thank my good friends Durai, Thejas, Deepak and Sudeshna, the group members from the ‘other side’ for being good company. It was very good to talk to Durai about our work since we were working in similar conditions and the chats now and then helped me get a grip on things. I would also like to thank Poorvi, Devashish, Himanshu, Manas and the great Dada, Anirban. Dada is an amazing brain and I know he will accomplish some more path-breaking research in the future. All the best to you guys! Also thanks to Pramod who has been a good friend here and it is refreshing to be able to speak to someone in Kannada every now and then! Also thanks to my new friend Anoop, who also hails from my state of Karnataka. I must also thank my friends at Electric Ant Labs, my new workplace, for being so kind and accommodating during my initial days at the job, as I was busy with thesis completion then. Special thanks to the genius Eric who has put Computational Rheology to action. This thesis logically leads to EAL and I know we will accomplish nice things together!

I would also like to thank the whole Bangalore gang for their constant encouragement and motivation in helping me reach this far. Arvind, Shambhavi, Prithvi, Mayoor, Ananth, Sumukh (Smokey), Swaroop and of course Srinivas for all their love and support. The seeds were sown very early, and together we will march ahead. There is much work to be done. All the best to Muse Inc for the future! And also thanks Ravi from Goobe’s! Also thanks to Suman for the yogic initiation, we will carry on the work. Of course, special thanks to my other brother, Hemant, who helped guide me to where I am today. Keep up the classical

music studies bro, I will join you soon.

A special place has to be given to Srinivas (Satan), Roshan and Pradeep, my brothers in arms. It is incredible, that from our times together a decade ago in Mathikere, we managed to get together magically in Europe. I can scarcely imagine that providence weaves such exquisite threads that extend so far into the future, and it has been quite a journey my brothers. I will forever be grateful to Roshan for his extensive knowledge of the arts, and I will always remember our Wacken 2017 experience! It is incredible to have seen all those bands live, whose music has nurtured and guided us. The experience was nothing short of spiritual, and thanks to you buddy! All the best to your time in France! And Srinivasa, you are the microcontroller genius that will tame the stethoscope, be on track and storm the castle! I cannot quantify your support in words, it has been an indescribable journey macha.

Also thanks to all my friends and relatives in India for the support! Thanks to mama and mami for the constant guidance! Also thanks to Neetal and family for being there for me! I will conclude by saying that the greatest thanks has been reserved for my parents, who have been the driving force behind my life. This whole work is laid at your feet. You know that doing Physics has always been my life's dream, from my visits to the library in Karwar to reading biographies of scientists to burning stuff in our courtyard. Now it has come true, only due to your love. I cannot thank Aai and Baba enough for instilling the culture in me and nurturing my thought process to always aim for the stars, and beyond.

Lastly, I must say that the Netherlands is a spectacular country with an amazing culture. The west and the east are two different things indeed, and the methodical, pragmatic nature of Holland is something to learn from. Having said this, I must say that although India and its culture might seem too obsessed with the divine and mystical to the average westerner, it is only by growing up in India and experiencing its culture that emphasizes simplicity over pomp, learning over pointless wealth-gathering, and numerous other spiritual values, that one truly appreciates its value in the modern world. Today the world is wracked by greed and excessive consumption, the planet stands at the brink of destruction due to climate change, political systems are undergoing tectonic shifts, still, the ancient land of Bharat, having experienced all these in its long history, shows us the way out. Indian teachings maintain that engaging in worldly pursuits is although necessary for survival and a fine thing in and of itself, true victory is only to be gained over the Self, and to understand it, for it is the instrument with which we interface with reality. Hence, if such a thing is indeed possible, I humbly offer my thanks to this ancient land and its teachings that have always maintained (constantly taught in our schools), that *Vasudhaiva Kutumbakam* - The whole world is one family.

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Soft matter is ubiquitous in our daily lives in the form of polymers, gels, cosmetics to even biological tissue. The unique viscoelastic properties of such materials are a consequence of their molecular structure and are studied in this thesis using Computational Rheology. By probing the stress relaxations of various soft materials like network forming telechelic star polymers, worm-like micelles and other supramolecular systems, the rheological properties of this interesting class of matter which will form the bedrock of emerging nano-material science have been explored using Brownian Dynamics Simulations and polymer theory. The thesis also has basic theoretical breakthroughs like the generalization of the Rouse model of polymer dynamics to arbitrary frictions and springs and a deep exploration of the Boltzmann Superposition Principle, the cornerstone of linear response theory.

“The task is, not so much to see what no one has yet seen; but to think what nobody has yet thought, about that which everybody sees.”

- Erwin Schrödinger