Computer Simulations of Polymer Gels

Structure, Dynamics, and Deformation

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Abstract

This thesis presents the results of computer simulation studies of the structure, dynamics, and deformation of cross-linked polymer gels. Obtaining a fundamental understanding of the interrelation between the detailed structure and the properties of polymer gels is a challenge and a key issue towards designing materials for specific purposes. A new off-lattice method for constructing a closed network is presented that is free from defects, such as looping chains and dangling ends. Using these model networks in Brownian dynamics simulations, I show results for the structure and dynamics of bulk gels and describe a novel approach using spherical boundary conditions as an alternative to the periodic boundary conditions commonly used in simulations. This algorithm was also applied for simulating the diffusion of tracer particles within a static and dynamic network, to illustrate the quantitative difference and importance of including network mobility for large particles, as dynamic chains facilitate the escape of particles that become entrapped.

I further investigate two technologically relevant properties of polymer gels: their stimuli-responsive behaviour and their mechanical properties. The collapse of core-shell nanogels was studied for a range of parameters, including the cross-linking degree and shell thickness. Two distinct regimes of gel collapse could be observed, with a rapid formation of small clusters followed by a coarsening stage. It is shown that in some cases, a collapsing shell may lead to an inversion of the core-shell particle which exposes the core polymer chains to the environment. This thesis also explores the deformation of bimodal gels consisting of both short and long chains, subject to uniaxial elongation, with the aim to understand the role of both network composition as well as structural heterogeneity on the mechanical response and the reinforcement mechanism of these materials. It is shown that a bimodal molecular weight distribution alone is sufficient to strongly alter the mechanical properties of networks compared to the corresponding unimodal networks with the same number-average chain length. Furthermore, it is shown that heterogeneities in the form of high-density short-chain clusters affect the mechanical properties relative to a homogeneous network, primarily by providing extensibility.

Keywords: computer simulations, Brownian dynamics, polymer gel, microgel, spherical boundary conditions, hypersphere, core-shell, deswelling, mechanical properties, uniaxial elongation

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urn:nbn:se:uu:diva-332575 (http://urn.kb.se/resolve?urn=nbn:se:uu:diva-332575)
A scientist in his laboratory is not a mere technician: he is also a child confronting natural phenomena that impress him as though they were fairy tales.

— Marie Curie

To Schubby.
List of papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


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Nomenclature

**Latin alphabet**

- $a$: Polymer unit radius
- $b$: Bond length
- $b$: Bond vector
- $C_s$: Normalised cluster size
- $d'$: Scaled tracer particle diameter
- $D$: Diffusion coefficient
- $D_0$: Diffusion coefficient for free diffusion
- $f_s$: Fraction of short chains
- $k_B$: Boltzmann constant
- $L$: Inter-wall distance
- $L_0$: Initial inter-wall distance
- $n$: Number of bonds in a chain
- $N$: Number of units in a chain
- $n_c(c)$: Number of clusters of size $c$
- $P_2$: Second order Legendre polynomial
- $r$: Position vector
- $R$: 3-sphere radius
- $R'_{ee}$: Scaled end-to-end distance
- $R'_g$: Scaled radius of gyration
- $T$: Temperature
- $V$: Volume
**Greek alphabet**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>Strain</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>Core/shell mass ratio</td>
</tr>
<tr>
<td>( \varepsilon' )</td>
<td>Scaled Lennard-Jones energy parameter</td>
</tr>
<tr>
<td>( \zeta )</td>
<td>Angular displacement</td>
</tr>
<tr>
<td>( \eta )</td>
<td>Viscosity</td>
</tr>
<tr>
<td>( \theta )</td>
<td>Angle between two bond vectors</td>
</tr>
<tr>
<td>( \rho_n )</td>
<td>Cross-linking density</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>Stress</td>
</tr>
<tr>
<td>( \sigma' )</td>
<td>Scaled stress</td>
</tr>
<tr>
<td>( \phi )</td>
<td>Volume fraction</td>
</tr>
</tbody>
</table>
1. Introduction

What is life?
It is the flash of a firefly in the night.
It is the breath of a buffalo in the wintertime.
It is the little shadow which runs across the grass and loses itself in the sunset.
— Isapo-Muxika

The question of how life emerged from the absence of life has inspired a lot of speculation. It is estimated that the first steps of life appeared on this planet over 3.8 billion years ago in the form of simple unicellular organisms from which complex multicellular organisms eventually evolved. [1] Life relies on some form of self-replicating molecule which has the capacity to store the information required to synthesise biological compounds and to transfer that information from generation to generation. In more modern cells, these two roles are fulfilled by the polymers DNA and RNA. Thus, in perhaps the most sophisticated example of their importance, polymers define life itself.

Polymers are macromolecules that are ubiquitous in nature and permeate every facet of our lives through both natural and man-made materials. The range of applications of polymers far exceeds those of other classes of materials, extending from adhesives, foams, coatings, plastic containers to textiles, electronic devices, optical devices, and many more (see Figure 1.1). Plants and animals use natural polymers as building blocks, storage substances, and in biochemical reactions. Polymers account for a great part of the human body, for example in the form of proteins and carbohydrates. Cellulose is the main structural component of plants and the most abundant organic compound on this planet. It is also the major constituent of this thesis. Another polymer produced by plants is rubber, which can be harvested in the form of latex from, e.g., *Hevea brasiliensis* (more commonly referred to as the rubber tree). These are all examples of different types of polymers that serve radically different functions. Variations in the sequence and spatial arrangement of the units in polymers give rise to materials with a tremendous physical and mechanical diversity.

While the reader will encounter many different types of materials every day, ancient cultures were limited to the native plants, soil, and stones that were available to them. Throughout human history, technological advances were made possible by mixing and modifying natural materials to obtain improved ones. For example, processed rubber was in use already 1600 BCE
by Mesoamericans, where latex was mixed with the juice of a local vine to create bouncing rubber balls for ritual ballgames and for offerings in temples. [2] Some millennia later, in 1839, Charles Goodyear accidentally discovered vulcanisation, a cross-linking process which combines natural rubber with sulphur under heat to produce a significantly more durable material than latex. Vulcanised rubber is most commonly used today in automobile tires. Leo Baekeland invented one of the first synthetic plastics (called Bakelite) in 1907. Intrigued by the differences between natural and synthetic polymers, Hermann Staudinger studied a variety of polymers and in 1920 published his classic paper entitled "Über Polymerisation", which proposed that polymers are macromolecules formed by many repeating units that are covalently bonded to form long chains. [3] At a time when the reigning theory was that all chemical compounds were low molecular weight entities that could potentially "aggregate", the theory of polymers as macromolecules was met with skepticism. Nonetheless, Staudinger’s publication heralded intense research, and polymers gradually started to become recognized as separate from colloidal systems. Since the 1930s, with significant steps taken by Wallace Carothers in the manufacturing of synthetic polymers through the creation of nylon and neoprene, and the subsequent inventions of polyethylene, Teflon, Kevlar, etc.,

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1In fact, in response to a lecture given by Staudinger in favour of the existence of macromolecules, he was reportedly told by a fellow scientist to "leave the concept of large molecules well alone; organic compounds with a molecular weight above 5000 do not exist... There can be no such thing as a macromolecule." Met with this hostile reception, Staudinger concluded his lecture with the words "Here I stand, I cannot do otherwise." [4]
the polymer industry boomed and has now become larger than the aluminium, copper, and steel industries put together. [5]

The type of polymeric structure that is of particular interest for this thesis is one in which the polymer chains are linked together by cross-links, forming a 3-dimensional network that is swollen in a solvent. Such a system is called a polymer gel. Cross-linking means that the chains lose some of their ability to move as individual entities and, unlike polymer solutions, a gel can maintain its shape under its own weight. Gels can be fabricated into a diverse range of architectures and there is a trend towards gels with increasingly complex and sophisticated morphologies, such as multilayered films, [6] topological gels where the chains are linked by slide-rings, [7] and interpenetrating networks. [8] Among some of the properties of polymer gels that are of importance for their use in applications are their swelling/deswelling ability and mechanical properties. Stimuli-responsive polymers, i.e., polymers that can undergo a dramatic change in volume in response to a small change in their environment (such as the temperature, pH, or salt concentration), are of great interest, notably in medical applications as controlled drug delivery vehicles, actuators and artificial muscles, and tissue engineering scaffolds. [9–21] Some applications also rely on a load-bearing function, for example in tissue engineering as bio-scaffolds to guide the growth of new tissue. [22, 23] Conventional hydrogels, however, are known to be mechanically weak and unable to withstand large deformations. These poor mechanical properties may be a major limitation. The swelling and mechanical properties of gels are influenced by the topology of the network, such as the degree of cross-linking as well as the presence of defects (such as free chain ends and loops) and entanglements. Considering the abundance of polymers in modern society, it is of great importance from a fundamental and technological viewpoint to understand the basic structure-property relation of polymer gels, for example to guide experimental procedures to prepare gels with tailored properties.

Polymer science is a multidisciplinary scientific field that brings together researchers from a very wide range of academic areas. In the quest for exploring the nature of matter, scientific methods and theories have been applied since early times to extract information from the world around us. With the advent of computers in the 1940s, a new approach to studying chemical phenomena became accessible. No longer confined to laboratories, amid beakers, burettes, and Bunsen burners, scientists could now perform studies virtually by implementing the mathematical models in computer programs that mimic laboratory settings. Tremendous advances in high performance computers since then have made computer simulations, in combination with theory and experiments, a powerful tool in driving innovation and for reaching a deeper understanding of the properties of, e.g., polymers.

In modelling the complex behaviour of polymer systems, the researcher simplifies the problem by focusing on aspects of the system that are supposedly relevant to the observed behaviour. Simulations have, for example,
been useful in improving our understanding of the dynamics of polymer melts [24, 25] and rubber elasticity. [26–28] Simulations of cross-linked polymer networks started in the 1980s,\(^2\) notably by Eichinger et al. [30–32] Today, there are a variety of simulation methods to choose from to study the equilibrium and dynamic properties of macromolecular systems. Unlike experiments, where the network topology may contain a number of unknown structural features in the form of network imperfections and inhomogeneities, [33–35] the molecular architecture in a simulation can be carefully chosen. This makes it possible to decouple different effects in a systematic manner and study a succession of network models in atomistic detail under fully controlled conditions, in order to better understand the relationship between the structure and properties of polymer gels. Simulations of polymer gels can, however, become very time-consuming due to the large system sizes and long relaxation times involved, meaning that there is a need to find more efficient ways to model these systems.

In this thesis, we employ Brownian dynamics simulations, which is a coarse-grained approach that facilitates the simulation of much larger systems compared to atomistic simulations, to study the structure, dynamics, and deformation behaviour of cross-linked polymer gels. Chapter 1 will introduce some simple theoretical models and shape descriptors of polymer chains, which can also be applied for the chains in a polymer network, as well as the topology and properties of polymer gels. Chapter 2 will give an overview of how to perform a computer simulation, including the Brownian dynamics algorithm. Here, we also present a method to form a closed, defect-free polymer network as well as a novel approach for avoiding surface effects in simulations of polymer gels, by using spherical boundary conditions (SBC). The latter is achieved by working in a higher dimensional space, namely the surface of a ball in four dimensions. The results of simulations of tracer particles of various sizes diffusing through a static and dynamic network with SBC are presented in chapter 3. Using this method of constructing model networks, we next examine the deswelling and mechanical properties of polymer gels. Specifically, in chapter 4 we investigate the response of nanogel particles with a core-shell structure when the solvent quality is switched to induce a collapse. The physical coupling of the two compartments means that both the core and the shell dynamically influence each other. This is illustrated by the effect of shell thickness and cross-linking density on the detailed dynamics of the core-shell particles. In chapter 5, we examine the mechanical properties of bimodal gels subject to a steady uniaxial elongation. Bimodal networks have previously been found to be mechanically strong and tough. Different types of bimodal structures are considered, with the aim of understanding the underlying reinforcement mechanism.

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\(^2\)A review of these early simulation works has been published by Escobedo and de Pablo. [29]
1.1 Description and modelling of polymers

A polymer is generically defined as a macromolecule composed of a sequence of many copies of one or more repeating units, called monomers, that are joined through covalent bonds. The average number of monomers per molecule, referred to as the degree of polymerisation, may be in the range of several tens of thousands. These monomers can be arranged in many different ways, forming, e.g., linear or branched polymer chains, such as the ones shown in Figure 1.2, as well as more sophisticated architectures such as star polymers, comb polymers, and brush polymers. Of particular interest in this thesis is the case where polymer chains are cross-linked into a large 3-dimensional network structure.

![Figure 1.2. Examples of some different architectures of polymers, ranging from linear chains to branched chains and cross-linked networks.](image)

Before delving into the properties of polymer networks, we begin by discussing some of the models that are used to describe the structure of single polymer chains.

1.1.1 Polymer chain models and conformations

Due to rotations about the bonds in the polymer backbone and the large degree of polymerisation that is typically involved, a polymer chain with a given sequence of monomers can assume an enormous number of possible conformations or ways of arranging itself in space. It is therefore suitable to discuss the conformations by applying statistical methods, where the shape and size of a polymer are characterised by averaging over many different polymer chains.

As an example, let us consider a linear polymer chain consisting of \( N \) units connected by \( n = (N - 1) \) bonds, shown in Figure 1.3. The units in the chain may be represented by their position vectors \((r_1, ..., r_N)\) or by the bond vectors \((b_1, ..., b_n)\) connecting consecutive units (where \( b_i = r_{i+1} - r_i \)). The angle between \( b_i \) and \( b_j \) is denoted by \( \theta_{ij} \).

There are various ways of characterising the size of the polymer chain (see Figure 1.4). We could, for example, use the contour length, \( \mathcal{L} \), which can

---

3For example, ultra-high molecular weight polyethylene used in orthopaedic applications typically has a degree of polymerisation of as much as 200,000 repeating units, with a molecular weight between \( 3.5 - 7.5 \cdot 10^6 \) g/mol. [36]
Figure 1.3. A schematic of a polymer chain modelled as $N$ spherical beads.

be pictured as the length the chain would have if it were in a fully extended rod-like state. The contour length is given by $L = \sum_{i=1}^{n} |b_i|$. Another measure of the chain size is given by the end-to-end distance. The end-to-end vector, $\mathbf{R}_{ee}$, is the vector connecting the first and last unit in the chain,

$$\mathbf{R}_{ee} = \mathbf{r}_N - \mathbf{r}_1 = \sum_{i=1}^{n} \mathbf{b}_i. \quad (1.1)$$

The maximum end-to-end distance corresponds to the contour length. A drawback of using the end-to-end distance is that it is only well-defined for linear chains. A more general and intuitively meaningful size descriptor that is also valid for, e.g., branched and cyclic chains, is the radius of gyration, $R_g$, which corresponds to the root mean-square distance of all polymer units from the centre of mass ($\mathbf{r}_{cm}$) of the polymer,

$$R_g^2 = \frac{1}{N} \sum_{i=1}^{N} (\mathbf{r}_i - \mathbf{r}_{cm})^2. \quad (1.2)$$

Alternatively, the radius of gyration can be computed from the gyration tensor defined by [37]

$$G_{mn} = \frac{1}{N} \sum_{i=1}^{N} (r_i^{(m)} - r_{cm}^{(m)})(r_i^{(n)} - r_{cm}^{(n)}), \quad (1.3)$$

Figure 1.4. The contour length ($L$), end-to-end distance ($\mathbf{R}_{ee}$), and radius of gyration ($R_g$) for a linear polymer chain.
where \( r^{(m)} \) is the \( m \)-th Cartesian component of the position vector. The sum of the corresponding eigenvalues, \( \lambda_k \), squared gives \( R^2_g = \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \). These eigenvalues can also be combined to describe the chain asphericity, [38]

\[
S = \frac{27 \langle \prod_{i=1}^{3} (\lambda_i - \bar{\lambda}) \rangle}{\langle (\sum_{i=1}^{3} \lambda_i^3) \rangle}, \tag{1.4}
\]

where \( \bar{\lambda} \) is the average eigenvalue and \( \langle ... \rangle \) denotes an ensemble average over chain configurations. Being bounded by the interval \(-0.25 \leq S \leq 2\), positive values correspond to prolate ellipsoid-like shapes and negative values to oblate shapes.

There exists a variety of models that are used to describe a polymer chain. Depending on the type of constraints that are imposed, the resulting properties may vary between different models. The simplest model used to describe a polymer chain is the ideal freely-jointed chain model. In this model, the potential energy only consists of the pairwise energy term that describes the connectivity of successive units. All bonds have a fixed length of \( b \) and the directions of the sequential bond vectors are completely uncorrelated, meaning that the bond angles may assume all values with equal probability, \( i.e., \langle \cos \theta_{ij} \rangle = 0 \) for \( i \neq j \). The lack of correlation in the direction of consecutive units along the chain means that the conformation may be represented by a 3-dimensional random walk. Since the directions of the bond vectors are statistically independent in this model, the average end-to-end vector becomes \( \langle R_{ee} \rangle = 0 \). Using the mean-square end-to-end distance instead gives

\[
\langle R_{ee}^2 \rangle = b^2 \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \cos \theta_{ij} \rangle = nb^2. \tag{1.5}
\]

Taking the freely-jointed chain model and restricting the bond angles to a fixed value (while maintaining that all torsion angles are equally probable and independent) gives the freely-rotating chain model. This additional constraint of a fixed bond angle is reflected in the mean-square end-to-end distance, which now becomes [39]

\[
\langle R_{ee}^2 \rangle = nb^2 \left( \frac{1 + \cos \theta}{1 - \cos \theta} - \frac{2 \cos \theta (1 - \cos^n \theta)}{n (1 - \cos \theta)^2} \right). \tag{1.6}
\]

It may be noted that the scaling law \( \langle R_{ee}^2 \rangle \propto n \) is a common feature of ideal chains (for large \( n \)).

Imposing bond angle restrictions introduces correlations that are transferred along the bond vectors in the backbone. The bond orientational correlation between two chain segments decays exponentially, [40]

\[
\langle \cos \theta(s) \rangle = e^{-s/P}, \tag{1.7}
\]
where $\theta(s)$ is the angle between the tangent vectors at two different points separated by length $s$ along the chain and the characteristic length scale of decay, $P$, is called the persistence length. On length scales that are much smaller than the persistence length ($s << P$), there are strong bond angle correlations and the chain segment essentially behaves as a stiff rod. Over larger length scales ($s >> P$), the bond angle correlations become negligible and the chain appears flexible. The persistence length may thus be used to characterise the stiffness of the chain.

1.1.2 Effect of solvent quality

So far, the discussion of polymer chain conformations has assumed ideal conditions, where secondary interactions, such as those between different chain segments and between the polymer chain and solvent molecules, were not considered. Treating the polymer chain as a random walk allows chain segments to overlap and pass through each other. In reality, chain segments have a physical size, prohibiting multiple occupancy of the same region in space. This excluded volume interaction is treated in the self-avoiding random walk. The introduction of an excluded volume between non-bonded units reduces the number of available conformations and causes the chain to expand relative to a random walk chain. The effective size of the chain is also influenced by the solvent quality. A good solvent is one in which the attraction between polymer segments and the solvent molecules is energetically more favourable than that between the polymer segments themselves. This means that the polymer swells upon mixing with solvent, adopting an expanded coil conformation. In a poor solvent, the polymer self-interactions dominate over the polymer-solvent interactions, and there will be a net attraction between the chain segments instead. The chain collapses into a compact globular state in order to minimise the free energy.

The effective interactions may be expressed in terms of the dimensionless parameter $\chi$, introduced in the lattice-based Flory-Huggins theory and defined as [41]

$$\chi = \frac{z}{k_BT} \left( \epsilon_{ps} - \left( \epsilon_{pp} + \epsilon_{ss} \right)/2 \right),$$

(1.8)

where $z$ is the coordination number of the lattice (i.e., the number of nearest neighbours to each lattice point) and $\epsilon_{AB}$ is the interaction energy between species $A$ and $B$ (where subscript $p$ stands for polymer and $s$ for solvent). The $\chi$-parameter characterises the relative strength of attraction between different species, such that $\chi > 1/2$ corresponds to a poor solvent and $\chi < 1/2$ to a good solvent. [40] Since the conformation adopted by the chain depends on the solvent quality, changing the solvent composition or temperature can induce a collapse transition, referred to as the coil-to-globule transition (Figure 1.5). In terms of the scaling law $<R_{ee}^2> \propto n^{2v}$, the exponent $v$ changes from $v \approx 3/5$ in a good solvent to $v = 1/3$ in a poor solvent. At the theta temperature, the
polymers. Self-interaction balances the polymer-solvent interaction and \( v = \frac{1}{2} \), which can be recognized as the ideal chain relation, described by Eq. (1.5).

### 1.2 Polymer gels

A polymer gel is on a basic level an assembly of polymer chains that are linked together into a 3-dimensional network that is swollen in a solvent. Depending on the cross-linking mechanism, gels are commonly classified as "physical" or "chemical".\(^4\) In physical gels, the chains are held together by relatively weak and temporary associations between chains, which may include hydrophobic interactions or hydrogen bonds. Due to the reversible nature of these cross-links, chain segments are able to easily break and reform. Chemical gels, on the other hand, are formed by covalent bonds that are difficult to break once formed. We will focus solely on chemical gels in this thesis.

In this section, we will explore the topology and properties of polymer gels.

#### 1.2.1 Gel topology and inhomogeneities

The structure of a polymer gel may be envisioned as a sponge penetrated by nano- to millimeter-sized pores, as illustrated in Figure 1.6. By a perfect network structure, we mean one in which all chains are connected at both ends to two different junction sites and there are no entanglements between the chains. In reality, most chemically cross-linked polymer gels, in particular those obtained by conventional radical copolymerisation of monomers and cross-linkers, are structurally complex and display deviations from a perfect structure. There may be different types of defects and inhomogeneities that

---

\(^4\)Not all gels easily fit into these two categories. For example, the slide-ring gels developed by Okumura and Ito [7] are formed by using figure-eight shaped cross-links that are free to slide along the chain. Such topological gels which are held together by physical constraints could be considered a different class of gels.
span multiple length scales. [33–35] A schematic of some of these is shown in Figure 1.7.

![Figure 1.6](image1.png)

*Figure 1.6.* Environmental scanning electron microscopy (ESEM) images showing various porous structures of synthetic hydrogels. Reprinted with permission from Institute of Macromolecular Chemistry AS CR.

![Figure 1.7](image2.png)

*Figure 1.7.* Illustration of different types of network imperfections and defects. Dangling chains are connected to the network at only one chain end, while loops are connected at both ends to the same cross-linker. Trapped entanglements can only be released by breaking bonds. Clusters consist of regions of highly cross-linked chains.

Gels typically contain an unknown number of dangling chains that are attached to the network only by one end, loops that have both ends of a chain connected to the same cross-linker, as well as trapped entanglements between chains. Aside from chain length polydispersity, there may also be a heterogeneous spatial distribution of cross-links, with highly cross-linked domains or clusters. Such imperfections at the molecular level may impact the material properties. For example, dangling chains and loops typically do not contribute to the network elasticity and may result in a mechanically softer gel, while
Chain entanglements may act as supplementary cross-links and improve the stiffness of the gel. An analysis of structure-property relations is complicated by the presence of unknown or uncontrollable features in the gel structure.

Experimental approaches have been developed that allow for greater control of the structure, in order to produce more homogeneous gels with fewer defects,\(^5\) including end-linking pre-existing polymer chains, [46] although the synthesis of highly regular and reproducible topologies with a desired distribution of elastically active strands remains an important challenge for synthetic chemistry.

1.2.2 Mechanical properties

The chemical cross-linking of polymer chains means that the gel will behave rubber-like when it is extended, producing a restoring elastic force which brings back the material to its original shape once the external force is removed. For sufficiently large deformations, beyond the elastic limit, covalent bonds are severed and the gel is ultimately fractured. The mechanical properties of materials may be obtained by performing, e.g., uniaxial tensile testing. In an experimental setup, a specimen of length \(L_0\) and cross-sectional area \(A\) is mounted between two grips and a tensile force is applied in one direction which elongates the sample. The stress, \(\sigma\), is defined as the applied force per unit area. The associated deformation per unit length is called the strain, \(\alpha\), and is defined as the ratio of the change in length in the stretching direction relative to the initial length, \(\text{i.e., } \alpha = \Delta L/L_0\). By running the tensile testing until fracture and monitoring the stress-strain behaviour, it is possible to obtain information about several mechanical properties, such as the stiffness or elastic modulus\(^6\) through the initial slope of the stress-strain curve. The tensile strength corresponds to the maximum stress before the material breaks, and the energy required to reach fracture, referred to as the toughness of the material, is given by the area under the curve.

The mechanical properties of polymers are important in many practical applications that rely on their load-bearing function, for example in tissue engineering as bio-scaffolds. \([22, 23]\) Scaffolds used for bone tissue growth, for example, require good mechanical properties to be able to provide temporary mechanical integrity upon implantation. \([47]\) The biocompatibility of hydrogels (\(\text{i.e., } \)water-swollen networks) makes them appealing candidates in biomedical applications. Depending on the application, however, it might be necessary to improve the mechanical characteristics to make the material more suitable. Much research has been devoted to finding ways of improving the mechanical properties. For example, Sakai et al. used end coupling of

\(^5\)See, for example, [42–45].

\(^6\)For a tensile stress, the elastic modulus is called the Young’s modulus. Under shear forces (\(\text{i.e., } \)forces parallel to the surface), one obtains the shear modulus.
tetra-arm polyethylene glycol (PEG) chains to form tetra-PEG gels that have a relatively homogeneous network structure and high mechanical strength. [44] Gong et al. combined two networks with very different cross-linking densities to form a double network that exhibited a greater toughness, which are promising candidates in, e.g., bioengineering. [48–53] Mark et al. also employed a bimodal molecular weight distribution by end-linking a mixture of very short and long chains to form bimodal elastomers (i.e., rubber-like solids) that have in some cases shown substantial improvements in mechanical strength and toughness. [54–60]

1.2.3 Swelling and volume phase transition
When a polymer network is immersed in a good solvent, the chain segments and solvent molecules tend to mix, whereby solvent molecules permeate and swell the network. The strength of this tendency to mix can be represented by the osmotic pressure, Π. Using the Flory-Huggins lattice model of polymer solutions, the osmotic pressure may be written as [41]

$$\Pi(\phi) = \frac{k_BT}{v_c} \left( -\ln(1 - \phi) - \phi - \chi \phi^2 \right)$$

(1.9)

where $v_c$ is the volume of a lattice site. At the same time, network dilation entails deformation of the chains, which produces an elastic reaction that acts against the swelling. The gel reaches its equilibrium swelling level when the mixing contribution and the elastic contribution are balanced, which may be written as [41]

$$\Pi(\phi) = G_0 \left( \frac{\phi}{\phi_0} \right)^{1/3}$$

(1.10)

where $G_0$ is the shear modulus of the network before swelling, and $\phi_0$ and $\phi$ are the polymer volume fractions before and after swelling, respectively. If $\phi << 1$ then Eq. (1.9) may be simplified and Eq. 1.10 can be solved for $\phi$ to give

$$\phi = \phi_0 \left[ \frac{G_0 v_c}{k_BT \phi_0^2 (1/2 - \chi)} \right]^{3/5}.$$  

(1.11)

It can be seen that if $(1/2 - \chi)$ is large then $\phi$ is small and the gel is swollen. A rapid shrinking takes place (i.e., $\phi$ increases) as $\chi$ approaches 1/2.

The effective interactions between the polymer and solvent may be highly sensitive to external conditions (such as the temperature, pH, or salt concentration). Gels that undergo a dramatic change in volume in response to a small change in their environment are called stimuli-responsive or smart gels. This reversible swelling/deswelling ability makes these materials of great interest in medical applications. For example, stimuli-responsive polymers have been used as self-adjusting valves. [16, 17, 61] If the liquid that flows through the
valve changes properties, the gel can respond by either opening or closing the valve. Charged gels that react to changes in an electric field are used in the development of artificial muscles, for example in the construction of robots. [62] Stimuli-responsive gels are also used as drug carriers to deliver drugs to a specific site in the body, by exploiting variations in physiological conditions. [12, 18, 20, 21] The design of gels with a core-shell architecture, which are composed of a different type of stimuli-responsive polymer gel in the core and the shell compartment, have been particularly interesting as multi-responsive materials (i.e., materials that are responsive to two or more different stimuli). [12, 63–68]
2. Computer Simulations

Owing to the rapid development of computers, simulations have become an indispensable tool in a number of disciplines, for elucidating phenomena observed in experiments or for making predictions of systems that have not yet been studied. Various simulation methods exist, such as Monte Carlo, Molecular dynamics, Brownian dynamics, and dissipative particle dynamics, which have been extensively utilised for studying the properties of polymer materials. [69] The choice of method depends on the purpose of the study. Since the concept of time is lacking in traditional Monte Carlo simulations, this is typically used to study equilibrium properties by generating random configurations. ¹ If the aim is to follow time dependent dynamic properties, then Molecular dynamics simulations could be used. A typical Molecular dynamics simulation uses Newton’s equations of motions to compute the trajectories of all particles in the system (usually at an atomistic level). It is also possible to describe the dynamics of only a selected group of particles (e.g., the polymer units), with the remainder of particles (e.g., the solvent molecules) acting as a continuum bath. The implicit-solvent approach is the premise of the Langevin equation, used in Brownian dynamics simulations, and has the advantage of being computationally less expensive, thereby allowing the study of larger systems during longer time scales. As we are interested in the long-time dynamics of large polymeric systems, Brownian dynamics simulations are used in this thesis and will be discussed more extensively in section 2.4.

One of the first tasks in performing a computer simulation is to decide on the level of detail necessary to capture the essential features of interest. In order to keep calculations tractable, it is common to use coarse-graining when modelling polymer chains. Next, the influence of essential intermolecular and intramolecular interactions are introduced by choosing a functional form of the effective interactions, which may include bonded and non-bonded terms. An initial configuration must then be generated for the system that is ideally close to the state of interest. This initial configuration might need to be relaxed,

¹Monte Carlo schemes have been developed which could be used to study time dependent phenomena. [70–72]
during which the structural properties of the system may be monitored until equilibrium is obtained. The equilibrated system is then used as a starting structure to produce trajectories which can be subsequently analysed for the properties of interest.

In this section, we will look at some of the steps and procedures of performing a simulation study of a polymer system.

### 2.1 Coarse-graining and effective interaction potentials

A physical system can often be described on a wide range of time and length scales. When modelling a system in a computer simulation, we would ideally try to describe it as accurately as possible.\(^2\) If the aim is to study the qualitative long-time dynamics of polymer chains as a whole, then the atomic scale is generally less important to capture the relevant physics of interest. The simulation efficiency may be improved by merging several atoms into one unit.

The most common representation of a polymer chain, which is also adopted in this thesis, is the generic bead-spring model, where a chain is described as a string of beads of radius \(a\). The beads are connected through a harmonic stretching potential,

\[
U_s = \frac{k_s}{2} \sum_i (b_i - 2a)^2 , \tag{2.1}
\]

where \(k_s\) is the stretching force constant and \(2a\) is the equilibrium bond length. Although the harmonic potential does not take into account bond dissociation, a simple way of including finite extensibility is to introduce a cut-off for the potential at a desired bond breaking distance.

Chain stiffness is accounted for through an angular potential,

\[
U_b = \frac{k_b}{2} \sum_i (\cos \theta_i - \cos \theta_0)^2 , \tag{2.2}
\]

where \(\theta_0\) is the angle of minimum bending potential energy, \(\theta_i\) is the angle between bond vectors \(b_i\) and \(b_{i+1}\), and the bending force constant, \(k_b\), is determined from the persistence length, \([73]\)

\[
P = \frac{<b>}{1-<\cos \theta>^n} \tag{2.3}
\]

where \(<b>\) and \(<\cos \theta>\) denote the chain-averaged bond length and bond angle cosine, respectively.

---

\(^2\)This would entail working in the quantum mechanical realm. The number of units in a simulation of polymers, however, is often in the order of tens of thousands. A detailed description of the electronic structure of all molecules would not be feasible for simulating the long-time dynamics of such large systems on present-day computers. When atomic detail is not necessary, larger systems may instead be studied using classical mechanics.
In a real polymer chain, two or more segments cannot occupy the same space. This excluded volume effect may be accounted for by introducing a soft repulsive potential between non-bonded particles, such that the force is given by [74]

\[ F_{\text{rep}}^{i} = \frac{\varepsilon_{\text{rep}} k_B T}{4a^2} \sum_j \left( \frac{2a}{r_{ij}} - 1 \right) r_{ij} \hat{n}_{ij}, \]  

(2.4)

where \( \varepsilon_{\text{rep}} \) is a dimensionless force constant and \( \hat{n}_{ij} \) is the unit vector from particle \( j \) to \( i \).

To model the effect of solvent quality, a Lennard-Jones (LJ) potential is commonly used, which is composed of a short-range repulsion term and a long-range attraction term. The potential is usually truncated in order to speed up the computing time. To avoid a discontinuity in the forces at the cut-off distance, we use the following form of the LJ potential, [75]

\[ U_{\text{LJ}} = 4\varepsilon_{\text{LJ}} \left[ \frac{\sigma_{\text{LJ}}^{12}}{r^{12}} - \frac{\sigma_{\text{LJ}}^{6}}{r^{6}} + Cr^6 + D \right], \quad r < r_c \]  

(2.5)

where \( r \) is the distance between the interacting units, \( \varepsilon_{\text{LJ}} \) is a measure of the interaction energy, \( \sigma_{\text{LJ}} \) is effectively the diameter of one particle, and \( r_c \) is the cut-off distance for the potential. The constants \( C \) and \( D \) correspond to

\[ C = -\sigma_{\text{LJ}}^6 r_c^{-12} + 2\sigma_{\text{LJ}}^{12} r_c^{-18}, \quad D = 2\sigma_{\text{LJ}}^6 r_c^{-6} - 3\sigma_{\text{LJ}}^{12} r_c^{-12}. \]  

(2.6)

The quality of the solvent can be modified by varying the attraction via the LJ interaction parameter. As \( \varepsilon_{\text{LJ}} \) increases, the strength of the attraction between the chain units increases, representing a decrease in solvent quality.

Although not considered in this thesis, there may also be electrostatic forces present in the system. The most common way to handle electrostatics in a system with periodic boundaries (see section 2.3) is by using the Ewald summation technique. [76–78] Alternatively, it is possible to use spherical boundary conditions by embedding the 3-dimensional system onto the surface of a ball in four dimensions, as discussed in section 2.3.2.

### 2.2 Modelling of a closed network

Computer simulations can provide valuable information of cross-linked polymer gels by enabling us to work with well-defined network structures, where the topology is known \textit{a priori} or can readily be determined. Different models of polymer networks have been used, ranging from simple idealised lattice structures, [28,79–84] typically a diamond or cubic lattice, with a highly regular topology to more realistic models that include more sophisticated dynamic polymerisation and cross-linking procedures that naturally introduce structural defects during network formation. [85–93] In this thesis, a new algorithm has
been developed for generating an off-lattice, closed network (papers I and II) that may either be used to form discrete gel particles, or, in combination with suitable boundary conditions, to study bulk properties. Structural defects or inhomogeneities may be introduced in a controlled manner, meaning that their effect on the material properties can be examined systematically.

![Figure 2.1. Schematic of the various steps involved in forming a closed network. See the text for a description of each step.](image)

A schematic of the network formation procedure is shown in Figure 2.1. The tetravalent cross-linking nodes are randomly distributed within a specified volume, under the restriction that no two particles are generated within a certain minimum distance from one another (step (i)). Each node is then connected to its four nearest neighbours that are unsaturated, i.e., that have fewer than four connections (step (ii)). As nodes within proximity start to become fully occupied, this procedure will eventually result in some of the connected pair of nodes being far apart. These long connections are reduced by a process of reconnection (step (iii)), described in paper II. Next, the polymer chains are generated by placing the constituting beads along the path connecting each pair of nodes, forming a closed network (step (iv)). The number of beads per chain may either be fixed, or it may be determined iteratively for each node-node connection by using the equations for the persistence length and the end-to-end distance (see paper I), forming a network with a distribution of chain lengths and pore sizes. Finally, the network structures are equilibrated (step (v)).
2.3 Boundary conditions

In a simulation, it is also important to specify the boundary conditions, e.g., free or no boundaries, rigid boundaries, periodic boundaries, or a mixture of boundary conditions. The choice of boundary condition will depend on the type of system being investigated.

A simulation is usually performed on a comparatively small number of particles, due to limitations in memory and/or CPU time. For small system sizes, a large fraction of particles will reside on the surface of the sample. If the interest is in bulk properties, then surface effects are commonly overcome by implementing periodic boundary conditions. An alternative route, using spherical boundary conditions, is presented in this thesis for the simulation of polymer networks, which should also be advantageous for charged systems.

2.3.1 Periodic boundary conditions

Periodic boundary conditions (PBC) are a common choice for mimicking a bulk phase. Here, all units in the simulation cell (typically a cubic box) are replicated throughout space to form an infinite lattice. A displacement of a particle in the main cell leads to a displacement of all its mirror images in the replicas. The original particles can interact with other particles in the cell as well as with the infinite number of mirror images. If the interactions are short ranged, it is common to use the minimum image convention, which means that for each particle, only the interaction with the nearest neighbour of each of the remaining particles is taken into account. For systems with long-range interactions, several neighbouring particles might need to be included. For electrostatic forces in particular, an infinite number of replicas should in principle be included, which results in a slowly converging sum over all charges. There are different methods for dealing with electrostatics, of which the most popular one has been the Ewald summation method, which entails splitting the sum into two rapidly converging sums. [76, 77] This method is, however, still computationally demanding.

2.3.2 Spherical boundary conditions

Although periodic boundary conditions are the most common choice to avoid possible surface effects, we could approach the problem by thinking outside the box. In a simulation with spherical boundary conditions (SBC), the 3-dimensional system is embedded on the surface of a 4-dimensional ball (i.e., a hypersphere), denoted $S^3$, which is a closed space without boundaries. [94] Living on a spherical surface, distances must be computed along geodesics in

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3For example, for 1000 particles in a 10x10x10 cube, about 49% of the particles will appear on the surfaces. For $10^6$ particles, the percentage at the surfaces decreases to 6%.
order for the particle trajectories to be confined to the surface, meaning that the algorithm used to displace the particles will need to be slightly modified compared to the case in $\mathbb{R}^3$. When simulating charged systems, SBC offer the advantage that calculations are considerably simplified. Rather than needing to calculate a sum over periodic images, the electrostatic forces on $S^3$ are given by a closed expression, making the calculations more computationally efficient.\textsuperscript{4} This property was developed in a series of studies by Caillol and Levesque. [95–98]

Despite their potential merit, relatively few simulation studies have used SBC. [94, 99–105] For polymer systems, the diffusion of free chains has been investigated on $S^3$ and in $\mathbb{R}^3$ and found to give identical results with respect to both structure and dynamics. [105] In this thesis, the use of SBC has been extended to simulate polymer networks embedded on $S^3$. Various ways of forming a defect-free, closed network on a hypersphere are presented in papers I and II, as well as the diffusion of tracer particles within such a gel (paper II).

### 2.3.3 Free boundaries

While surface effects are limited using PBC or SBC in the study of bulk properties, in some cases it may be more suitable or even necessary to work with free boundaries, for example to study the structure of finite-sized gels [106] or to simulate the diffusion of molecules from nanoparticles. [107]

In studies of the mechanical properties of polymer networks under uniaxial tension, it is common to impose an affine deformation, [40] which means modifying the periodic simulation cell size and rescaling particle coordinates to the new box size at each time step, followed by relaxation. [108–118] This is contrary to an experimental setup, where the strain is transmitted to the sample through the imposed motion of a boundary in the form of grips. Some studies have cleared periodicity and used a boundary driven deformation instead. [119–121] A boundary driven deformation is achieved by replacing PBC with free boundaries and introducing molecular grips perpendicular to the strain axis, which can move the sample ends apart while allowing for all possible chain movements. Free boundaries are used in papers III–V.

### 2.4 Brownian dynamics simulations

In 1827, during a microscopic study of pollen grains submerged in water, a Scottish botanist named Robert Brown noted that the tiny particles discharged

\textsuperscript{4}For systems consisting of a few hundred molecules, the computation time may be reduced by a factor of 2–3 compared to simulations using the Ewald method with a cubic box and periodic boundary conditions. [95]
by the pollens undergo an erratic random motion.\textsuperscript{5} Although it took nearly a century before this perpetual irregular motion was explained, \cite{122–124} we now know that Brownian motion is due to incessant collisions with the solvent molecules.

2.4.1 The Langevin equation

At the core of a Brownian dynamics simulation is the Langevin equation, which is a stochastic differential equation used to describe the motion of a particle in a viscous continuum. The Langevin equation is given by \cite{124, 125}

$$m \frac{d\mathbf{u}_i}{dt} = -f_i \mathbf{u}_i + \mathbf{B}_i + \mathbf{F}_i, \quad (2.7)$$

where \(m\) is the particle mass, \(\mathbf{u}_i\) is the velocity of particle \(i\), \(f = 6\pi a\eta\) is the friction coefficient, \(\eta\) is the viscosity, \(\mathbf{B}_i\) is a random force, and \(\mathbf{F}_i = -\nabla U(\mathbf{r})\) is the total direct force arising from, e.g., interactions between particle \(i\) and other particles.

The basic premise of the Langevin equation is to replace the explicit solvent molecules and describe their collective effect on the dynamic behaviour of the solute by adding a stochastic force (\(\mathbf{B}_i\)) and by imposing a frictional drag force on the motion of the particle through the solvent which is proportional to the velocity of the particle. By treating the solvent molecules implicitly and only considering their average properties, this simulation method becomes less computationally intensive than, for example, fully atomistic molecular dynamics simulations which require the input of all forces present. The reduction in computation time is not only due to the smaller number of explicit particles present, but also due to that larger time steps may be used, enabling the study of phenomena that occur over relatively long time periods.\textsuperscript{6}

2.4.2 Algorithm for Brownian dynamics in \(\mathbb{R}^3\)

In order to calculate the displacements of particles over successive time intervals, it is necessary to integrate the Langevin equation. For the simulations in this thesis, we use the algorithm developed by Ermak. \cite{127, 128} In this scheme, the time evolution of the position of unit \(i\) is given by

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \frac{D_0 \Delta t}{k_B T} \mathbf{F}_i + \mathbf{A}_i, \quad (2.8)$$

\textsuperscript{5}This phenomenon was initially thought to be unique to living organisms, with the movements being forms of life. However, Brown soon recognized that the random motion persists even with inorganic particles.

\textsuperscript{6}For comparison, Widmalm and Pastor performed Molecular dynamics (MD) and stochastic dynamics simulations of an ethylene glycol molecule together with 259 water molecules. \cite{126} The MD simulation required 1500 hours whereas the stochastic dynamics simulation of solute alone required just 24 minutes.
where \( \Delta t \) is the time step and \( D_0 = k_BT/(6\pi\eta a) \) is the diffusion coefficient. The stochastic displacement, \( \mathbf{A}_i \), is given by a Gaussian vector with the properties

\[
\langle \mathbf{A}_i \rangle = 0, \quad \langle \mathbf{A}_i \cdot \mathbf{A}_j \rangle = 6D_0\Delta t \delta_{ij}.
\] (2.9)

In a typical simulation in this thesis, the input parameters, such as the time step, temperature, and viscosity, are first specified. An initial configuration is generated according to the method of constructing a network (as described in section 2.2). A random number is generated for each unit which describes the Brownian motion, and the total force on each particle is calculated. The polymer units in the system are displaced according to the integrated Langevin equation of motion (Eq. (2.8)). These last two steps are repeated, resulting in a trajectory that specifies how the particle positions vary with time, which may then be analysed.

### 2.4.3 Algorithm for Brownian dynamics on \( S^3 \)

The Brownian dynamics algorithm for generating a trajectory using spherical boundary conditions looks slightly different compared to the one in \( \mathbb{R}^3 \), although the principles are the same. The new position of particle \( i \) originally at position \( \mathbf{p}_i \) is given by

\[
\mathbf{p}_{i,\text{new}} = \cos(|\Delta \mathbf{r}_i|/R)\mathbf{p}_i + R\sin(|\Delta \mathbf{r}_i|/R)\Delta \mathbf{r}_i/|\Delta \mathbf{r}_i|,
\]

where \( R \) is the radius of the 3-sphere and

\[
\Delta \mathbf{r}_i = \frac{D_0\Delta t}{k_BT} \mathbf{F}_i + \mathbf{A}_i.
\]

The functional form of the forces will be different since distances are now calculated along geodesics instead of straight lines. While the random numbers, \( \mathbf{A}_i \), in \( \mathbb{R}^3 \) are sampled from the solution of the corresponding diffusion equation (\( i.e., \) Gaussian random numbers), on \( S^3 \) these are now obtained from the solution of the diffusion equation on the 3-sphere, which is given by

\[
P(\zeta, \Delta t) \propto \frac{1}{\sin \zeta} \sum_{k=-\infty}^{\infty} (\zeta + 2\pi k) \exp(-R^2(\zeta + 2\pi k)^2/4D_0\Delta t),
\]

where \( \zeta \) denotes the angular displacement. For simulations of polymer systems, the solution can be simplified with very good accuracy by keeping only the \( k = 0 \) term in the sum. The details and derivation of this algorithm can be found in [104].
3. Simulations of Polymer Networks on the 3-sphere

It is sometimes important for science to know how to forget the things she is surest of.
— Jean Rostand

Computer simulations of bulk systems commonly use periodic boundary conditions to reduce surface effects. As discussed in section 2.3, spherical boundary conditions are an appealing alternative to periodic boundary conditions. A Brownian dynamics algorithm for simulating diffusion processes of particles on $S^3$ has previously been developed, [104, 105] where it was also shown that using spherical boundary conditions results in the same structural properties and dynamics for polymer chains as in the ordinary Euclidean 3-dimensional space. With this algorithm available, the use of spherical boundary conditions has been extended in this thesis to also include bulk gels, by developing a novel method for constructing a closed polymer network. This model would, for example, be a suitable option in further applications exploring the properties of polyelectrolyte gels.

3.1 Construction of a closed polymer network on $S^3$

Papers I and II outline alternative ways for constructing a closed network that is embedded on the 3-sphere. The task of forming a closed network is one that requires bookkeeping in order to keep track of the connectivity. In a first approach, the network is formed in a multi-step method, starting in $\mathbb{R}^3$, by placing the cross-linking nodes on a cubic lattice structure (as described in paper I). Next, specific nodes on the boundaries of two such identical cubes are connected together and the coordinates of all nodes are mapped to a disk and finally to the northern and southern hemispheres of $S^3$. The structure of the resulting networks is analysed in paper I. A possible disadvantage of this approach, however, is that the underlying regular starting structure introduces a bias in the chain length distribution. Also, the symmetry of the construction and the way in which the two cubes are connected mean that the number of cross-linking nodes cannot be chosen freely. A more direct way to form a closed network is to randomly distribute the cross-linking nodes on $S^3$ and
connect each node to its four nearest neighbouring nodes that have vacancy (as outlined in paper II). This method offers the advantage of avoiding any bias in the initial node distribution. A straightforward implementation, however, leads to the presence of a number of long chains, as nodes within proximity start to become fully occupied. This may be corrected by performing a process of reconnection to reduce long distances of the node-node connections. The basic principles of this approach are the same as described in section 2.2, except that distances here are measured along geodesics.

![Figure 3.1](image)

**Figure 3.1.** Equilibrium probability distribution for (a) the end-to-end distance and (b) the pore sizes, both scaled with the diameter of a network unit. Unfilled symbols represent a smaller system size and $\phi = 0.02$. The error bars correspond to the standard deviation for five independent initial network structures.
For the purpose of studying the diffusion of particles in a bulk gel, polymer networks with three different volume fractions (\(\phi\)) are generated directly on \(S^3\) and subsequently equilibrated. The relaxed structures are analysed with respect to the end-to-end distribution and the pore size distribution, where the latter is determined by using an expanding bubble scheme. [129] In this scheme, a small bubble is inserted at a non-overlapping random position within a fixed network configuration and allowed to diffuse and expand at each time step. Excluded volume interactions between the bubble and the network units mean that the bubble will eventually become trapped and can no longer expand. The final bubble diameter is used to define the size of the pore in which it has become lodged. Repeating this process for a sufficiently large number of bubbles inserted at random positions results in a distribution of pore sizes. The method of inserting the bubbles, however, is biased towards larger pores, which may be corrected for by only accepting unique bubbles that do not overlap with each other.

The pore size distribution is correlated with the chain end-to-end distribution, as shown in Figure 3.1 for different volume fractions. A lower volume fraction corresponds to a wider distribution of end-to-end distances, which translates to a broader distribution of pore sizes.

3.2 Diffusion of particles through a polymer gel

It is rather common in computer simulations of diffusion processes to treat a crowded environment as an assembly of immobile obstacles. [129–133] This may be a reasonable approximation for stiff network structures, but may not capture the correct properties for more flexible networks. It is therefore relevant to also explore the role of both static and dynamic obstacles on the diffusive motion of a tracer particle.

A single tracer particle is introduced at a random, non-overlapping position in the network, where the tracer particle diameter, \(d'\), is chosen from the pore size distribution (shown in Figure 3.1b). A range of particle sizes is selected to probe different length scales of the porous network structure. The displacement of the tracer particle as it diffuses in the gel is monitored as a function of time for 100 different starting positions.

For a particle diffusing freely in \(\mathbb{R}^3\), the mean square displacement is given by the simple relation \(< r^2 > = 6D_0 t\). This proportionality is, however, only valid in the limit of short times for particles diffusing freely on \(S^3\), when they have not yet started to experience the curvature. Since the particles are unable to escape to infinity, the long-time limit of the mean square displacement on \(S^3\) is a constant given by [104]

\[
< r^2 > = R^2 \left( \frac{\pi^2}{3} - \frac{1}{2} \right),
\]  

(3.1)
where $R$ is the radius of the 3-sphere.

The diffusion coefficient may be obtained through the relation [134]

$$< \cos \zeta >= \exp(-3Dt/R^2),$$

where $\zeta$ denotes the angular displacement of the diffusing particle. The displacement of the tracer particles, expressed as $-\ln < \cos \zeta >$ as a function of the reduced time $t/\tau$ (where $\tau = R^2/3D_0$), as they diffuse through both a static and a dynamic network is shown in Figure 3.2. The smallest tracer particles experience the environment as a connected porous medium with little obstruction, diffusing freely with a constant slope close to unity. On this length scale, the dynamics of the network has no effect on the mean square displacement. For tracer sizes more comparable to and greater than the average size of the pores (i.e., for larger tracer sizes or polymer volume fractions), the network obstructions become more significant and the reduced accessible volume for the particles leads to lower diffusion rates and a non-linear time dependence of the mean square displacement. While the qualitative trends are the same for diffusion in the static and dynamic networks, the quantitative difference increases as the environment becomes more crowded. Within the static networks, the largest particles appear to have become permanently trapped. These trapped particles are forced to escape by their own Brownian motion. For the dynamic networks, however, there will be transient openings through which the particle can escape. By looking at the individual particle displacements, it can be seen that although each individual particle may not have necessarily

![Figure 3.2](image-url)
traveled farther in the dynamic networks, the particles that do manage to escape through the fluctuating pores contribute to a larger displacement, leading to overall greater diffusion rates.

Figure 3.3. Reduced diffusion coefficients for static (open symbols) and dynamic (filled symbols) networks of different volume fractions as a function of tracer size, shown on a logarithmic scale. The inset shows the same plot on a linear scale.

The reduced diffusion coefficient, $D/D_0$, is shown in Figure 3.3 on a logarithmic scale as a function of tracer size. The diffusion coefficient decreases for larger tracer sizes, being larger where mobility of the polymer network is included. The plot quantitatively shows the importance of the dynamics of the gel matrix in facilitating the diffusional transport for larger particle sizes that would otherwise have become permanently trapped. One should also note that diffusion is still possible even for particle sizes well above the mode ($i.e.$, the peak) of the pore size distribution.
4. Investigating the Collapse Dynamics of Core-Shell Nanogels

The most exciting phrase to hear in science, the one that heralds new discoveries, is not ‘Eureka!’ (I found it!) but ‘That’s funny ...’
— Isaac Asimov

A central issue in many technological fields is the development of new polymeric materials, where the properties have been tailored for a specific end-use. Multi-stimuli responsive composites, which incorporate a combination of two or more stimuli-responsive polymers, play an important role in the development of novel smart materials. One type of multi-responsive design consists of spatially separating the different kinds of polymers into a core and a shell, forming so-called core-shell particles. These particles are, for example, of interest as controlled drug delivery vehicles. Various factors influence the degree of swelling/deswelling of the two compartments, such as the shell thickness and the cross-linking density. Tailoring core-shell particles for specific applications thus requires knowledge of the detailed structural properties under different swelling conditions. The local swelling and collapse of polymer gels have been investigated in simulations using periodic boundary conditions. Some simulations have considered discrete gel particles and fewer have looked at core-shell nanoparticle gels.

In this chapter, we will explore the dynamics of core-shell particles when the solvent quality is changed (paper III). The gel particles are created with a homogeneous distribution of cross-linkers and equilibrated with a soft repulsive potential between non-bonded units (Eq. (2.4)). To cause a collapse, the inter-bead potential is switched to include an attractive term through a LJ potential (Eq. (2.5)). The quality of the solvent may be changed by varying the LJ interaction parameter, such that a decrease in solvent quality corresponds to increasing $\varepsilon_{LJ}$. The correlated changes in the structure of the core and shell that arise from the mechanical coupling of the two compartments are analysed for different cross-linking densities ($\rho_n$), core/shell mass ratios ($\gamma$), and $\varepsilon_{LJ}$. The results below are expressed using the dimensionless parameter $\varepsilon' = \varepsilon_{LJ}/(k_B T)$ and time $\tau = D_0 t/4a^2$, and all lengths are scaled with the diameter of a polymer unit ($2a$).

$^1$For example, a poorly water-soluble drug could be localised in the core compartment, with the shell acting as a protective barrier from the hydrophilic external environment.
4.1 General features of a collapsing homopolymer gel

We first examine the collapse of homopolymer gel particles with different cross-linking densities. An example of such a collapse is shown in Figure 4.1 at two different stages, illustrating the initial local formation of clusters and the final compact globule.

![Simulation snapshots using VMD [151] of a homogeneous network taken shortly after starting the collapse (left image), illustrating locally formed clusters, and at the end of the simulation (right image), when the network has collapsed into a globule. Here, $\rho_n = 0.59 \cdot 10^{-2}$ and $\epsilon' = 2.0$.](image)

The time dependence of the radius of gyration of the nanoparticle is shown in Figure 4.2. A faster collapse rate is achieved by increasing the cross-linking density or the LJ parameter, where increasing the latter also leads to a more compact final state. While the radius of gyration captures the macroscopic

![Time dependence of the radius of gyration for homopolymer networks collapsing with different $\epsilon'$. The filled symbols correspond to a higher degree of crosslinking, $\rho_n = 2.0 \cdot 10^{-2}$, and the hollow symbols to $\rho_n = 0.59 \cdot 10^{-2}$. The total number of network units is approximately the same.](image)
volume change, this parameter alone is not sufficient to distinguish between the different stages of the network collapse.

The coil-to-globule transition of single polymer chains is often described by a two-stage model proposed by de Gennes, [152] where connected blobs of locally collapsed regions are first formed along the chain backbone, followed by a slower process of chain contraction and thickening to form a compact globule. Computer simulations have demonstrated the formation of

\[ \begin{align*}
\tau & = 0.5 \\
\epsilon' & = 0.75 \\
\epsilon' & = 1.0 \\
\epsilon' & = 2.0 \\
\end{align*} \]

Figure 4.3. (a) Number of clusters as a function of time (where the inset shows an extended time scale), and (b) normalised average cluster size over time for homopolymer networks.

\[ \begin{align*}
\tau & = 0.5 \\
\epsilon' & = 0.75 \\
\epsilon' & = 1.0 \\
\epsilon' & = 2.0 \\
\end{align*} \]

\[\begin{align*}
\langle C_s \rangle & < 0.001 \\
\tau & > 10 \\
\end{align*}\]

2Since de Gennes, other variations have been proposed to describe the collapse. See, for example, refs [153–155].
pearl-necklace conformations during the collapse of polymer chains in poor solvents. [156–162] Such conformations have also been observed in simulations of polymer gels. [141] To be able to identify the different stages of a collapse, we define a cluster as the smallest set of non-bonded units that are within a critical inter-particle distance. The growth and merging of the clusters formed during the collapse is followed by computing the average cluster size, normalised by the total number of polymer units \((M)\) in the network, \(i.e., \langle C_s \rangle = \frac{1}{M} \sum c n_c(c) \), where \(c\) is the cluster size, and \(n_c(c)\) is the number of clusters of size \(c\).

The time evolution of the number of clusters, as well as the average cluster size, are shown in Figure 4.3. The results suggest that the network collapse also takes place in two stages, similar to the kinetics of a single chain under poor-solvent conditions. In the first stage, there is a rapid formation of locally compact small-sized clusters, followed by a cross-over to a coarsening stage, where the clusters merge and the network forms a more compact globule. Both through visualisation and by analysis, it can be seen that the clusters are initially formed near cross-linking nodes, due to the higher density of units in these regions. For larger values of the LJ parameter, \(\langle C_s \rangle\) reaches unity, while for lower values of \(\varepsilon'\), the attractive forces are too weak to cause a complete compaction and instead there are fluctuations, with clusters merging and separating.

### 4.2 Core collapse dynamics

Having looked at the collapse of homopolymer networks, we now turn to the dynamics of nanoparticles with a core-shell morphology. By switching the soft repulsion to a LJ potential between a limited set of chains, namely those within a predefined distance from the centre of mass of the nanogel particle, it is possible to bring about a collapse of only the core, while the shell remains swollen.

Similar to the homopolymer collapse, there is first a rapid stage where small clusters are initially formed near the cross-linking nodes in the core, followed by the merging of clusters and ultimately the collapse of the core. Since the core and shell are coupled through covalent bonds, the collapse of the core will necessarily exert a retracting force on the shell. This can be seen by looking at the radius of gyration of the entire particle as a function of the size of the core, shown in Figure 4.4. (The inset shows the decay of the radius of gyration as a function of time.) The relaxation time for the shell units is, however, significantly longer than the core collapse transition time; the shell continues to relax well after the core has formed a globule. For larger values of \(\gamma\), \(i.e.,\) a thinner shell, the shell units are more strongly affected by the collapsing core.
4.3 Shell collapse dynamics

For the reversed case, the LJ potential is only introduced between units in the shell, thereby inducing a shell collapse around a swollen core. From the radius of gyration, shown in Figure 4.5, it can be seen that the final size of the gel particle with a collapsed shell is smaller than that of the original core. This has also been observed in experiments, suggesting that the shell restricts the core to a more compact structure. [136] In the first stage, the initial formation of clusters in the shell causes the core to slightly expand, shown as a first recoil (in Figure 4.5). During the coarsening stage, as the clusters begin to merge, the core starts to become compressed. An interesting feature, however, is that there is a second recoil for the larger LJ parameters. Visualisation of the trajectories reveals a new type of structure, viz. a core-shell inversion, where the shell has collapsed into the core compartment and squeezed out the core (see Figure 4.6). This inversion becomes more pronounced with decreasing degree of cross-linking and increasing LJ parameter. Increasing the core/shell mass ratio prevents the shell units from permeating the core to the same extent, instead resulting in large clusters nested inside the core compartment but segregated by the bulky core. Such inversions and patchy surface structures have recently also been observed in simulations by Ghavami et al., where it was also shown that the structural changes are reversible. [150] By carefully choosing, e.g., the core/shell mass ratio, this inversion mechanism of exposing the core polymers to the environment could possibly be used to design novel smart materials.

![Figure 4.4](image-url) Figure 4.4. The radius of gyration of the entire particle shown as a function of the size of the core (for \( \rho_n = 2.0 \cdot 10^{-2} \) and \( \gamma = 0.2 \)). The inset shows the decay of the radius of gyration for the entire particle (filled symbols, upper set) and the core (hollow symbols, lower set).
Figure 4.5. The radius of gyration of the entire particle shown as a function of the size of the core for networks for $\rho_n = 2.0 \cdot 10^{-2}$, (a) $\gamma = 0.4$ and (b) $\gamma = 0.1$.

Figure 4.6. Simulation snapshots using VMD [151] taken at the end of the trajectory for a collapsing shell (with $\rho_n = 2.0 \cdot 10^{-2}$ and $\gamma = 0.2$), from left to right: $\epsilon' = 0.5, 0.75, 1.0$, and 2.0. Shell units are shown in pink and core units in blue.
5. Investigating the Mechanical Properties of Bimodal Gels

Research is to see what everybody else has seen, and to think what nobody else has thought.
— Albert Szent-Györgi

Many applications of polymer materials require particular mechanical properties, such as high stretchability and high toughness. In tissue engineering, for example, materials for the replacement of damaged cartilage in human joints or of spinal discs need to be able to deform under compression and tension without breaking. Most conventional hydrogels, however, are fragile, exhibiting a low mechanical strength and elastic modulus. Various methods have been used over the past decades to reinforce polymers and this is still an ongoing research field.¹

One way of strengthening polymer gels is by forming cross-linked networks with a bimodal molecular weight distribution, which may be considered a type of double network. In some cases, these bimodal networks have been found to be unusually tough compared to their unimodal short-chain or long-chain counterparts, depending on, e.g., the fraction of short chains and the relative molecular weights of the short and long chains. [54–60] While the studies on bimodal networks have primarily focused on elastomers, there has not been any systematic study on the deformation behaviour of bimodal gels.

In this chapter, we isolate the effect of bimodality and investigate the deformation behaviour and mechanical properties of bimodal gels by applying a continuous boundary driven uniaxial tension (along the $z$-axis) until failure. The macroscopic deformation may be analysed by following the orientation and rupture of chains, as well as the stress-strain relation. The chain segmental orientation along the strain axis is described by the second order Legendre polynomial, [167]

$$P_2 = \langle 3 \cos^2 \varphi - 1 \rangle / 2,$$

where $\varphi$ is the angle between the direction of extension and the local chain axis of the polymer segment. In simulations, the mechanical stress tensor on the atomistic scale may be evaluated according to [41]

$$\sigma = -\frac{1}{V} \sum_i \sum_{j>i} f_{ij}(r_i - r_j).$$

¹See, for example, [48, 163–166].
Results below are presented using the reduced stress \( \sigma' = (4\pi a^3/(3k_BT))\sigma \). The strain is given by \( \alpha = (L_c - L_0)/L_0 \), where \( L_c \) is the current distance between the grips and \( L_0 \) is the initial distance.

5.1 Uniaxial deformation of homogeneous bimodal gels

The deformation of defect-free bimodal networks with various fractions of short chains \( f_s \) is first investigated and compared with equivalent unimodal networks with a similar cross-linking density (see paper IV). The networks are generated as cylindrical specimens, with a homogeneous distribution of short and long chains of fixed lengths. Bonds that extend beyond a distance of \( 3a \) during an elongation are severed.

Simulation snapshots taken at various stages during a deformation are shown in Figure 5.1.

Figure 5.1. Simulation snapshots using VMD [151] taken during uniaxial elongation of a system with 5000 chains and \( f_s = 0.90 \), showing the short (blue) and long (purple) chains of length \( N_s = 6 \) and \( N_l = 30 \), respectively.

Applying tension in one direction leads to a greater average orientation of chain segments in the direction of the strain axis, as shown in Figure 5.2, and eventually to bond breaking and network failure. The extent to which the networks can be stretched before failing depends on the fraction of short chains, with lower values of \( f_s \) leading to much larger ultimate strains.

Comparing the two different types of chains (in Figure 5.2), the short chains are more strongly oriented than the long chains for all network compositions. The orientation of the short chains during deformation, however, is almost unaffected by changes in \( f_s \). This is a consequence of the homogeneous distribution of chains, which means that the short chains form percolating structures between the mechanical grips (for the fractions of short chains considered
failure, it can be shown that the first chains to rupture are the short chains that are initially aligned along the strain axis.

As the applied strain eventually leads to stretching of the chain backbone, the stress, shown in Figure 5.3, increases dramatically. Networks containing a large fraction of short chains behave similar to a pure short-chain network, with a rapid increase of stress and failure after a relatively small additional strain, at a high ultimate stress. Decreasing $f_s$ decreases the ultimate stress. For all compositions considered, however, the stress is not uniformly shared among the short and long chains (see Figure 5.3b). Analogous to the orientation curves, the stress on the short chains is much larger for all network compositions, whereas the long chains are in comparison only marginally affected at smaller strains.

While bimodal networks have been found to show improved mechanical properties compared to their constituent pure short-chain and long-chain networks, it is also of interest to compare their behaviour with equivalent unimodal networks having the same number-average molecular weight of chains, to see if this reinforcement is indeed a result of the bimodal distribution of chain lengths. At small fractions of short chains, the ultimate properties of the bimodal networks are poorly predicted by the equivalent unimodal networks. In the absence of defects and trapped entanglements, a bimodal molecular weight distribution alone is sufficient to alter the mechanical properties at lower fractions of short chains. The bimodal networks can be stretched much further than the equivalent unimodal networks before reaching failure, giving rise to a greater toughness (i.e., area under the stress-strain curve). This difference in mechanical properties is, however, reduced when $f_s$ is increased.
Figure 5.3. (a) The scaled stress-strain curves for networks with \( f_s = 0.50 - 1.00 \). The dashed lines correspond to unimodal networks with similar cross-linking densities (\( N = 8 \) (yellow), 10 (green), 16 (purple)). (Note that the unimodal network with \( N = 16 \) has a cross-linking density lying between \( f_s = 0.50 \) and \( f_s = 0.65 \)). (b) The corresponding stress-strain curves, showing the stress from the short and long chains. The solid lines represent the short chains and the dashed lines long chains.

5.2 Role of structural heterogeneities

In the previous section, we considered bimodal networks where the short and long chains were homogeneously distributed. Experiments have, however, found that bimodal networks often are spatially heterogeneous, as the short chains tend to segregate into clusters during synthesis. [168–173] While macroscopically phase-separated bimodal networks have generally been found to be weak, [174, 175] some studies have found that bimodal networks with nanoscale clusters are reinforced, suggesting that there may also be a structural component to the reinforcement mechanism. [60,176] Structural effects on the
deformation behaviour and mechanical properties are considered by generating bimodal networks containing dense clusters of cross-linked short chains and comparing these with the homogeneous networks of the corresponding cross-linking densities (see paper V). A schematic of a homogeneous and heterogeneous bimodal network is shown in Figure 5.4.

Looking at the probability distribution of the end-to-end distances, shown in Figure 5.5, it can be seen that the long chains on average assume larger end-to-end distances at equilibrium in the unperturbed heterogeneous network, as clustering removes some of the constraints at the junction points. During elongation, both short and long chains are pulled apart in the homogeneous network, due to the intimate coupling between the chains, and it can be seen that both maxima have shifted at network failure. In contrast, the short chains in
the clusters are substantially shielded from stretching. The end-to-end distribution of the short chains is almost unchanged after elongation, with only a minor shoulder appearing as chains at the periphery of the clusters are deformed.

During deformation, the shielding of short chains within the clusters means that these chains are significantly less oriented than their counterparts in the homogeneous bimodal network, as shown in Figure 5.6. The short-chain orientation of the heterogeneous networks, however, increases with increasing fraction of short chains, due to the presence of larger agglomerates of clusters that eventually percolate between the top and bottom grips. This trend is also observed in simulations of dynamically end-linked bimodal networks, which tend to form clusters during the end-linking. [177] Similar to the homogeneous bimodal networks, the first chains to rupture in the heterogeneous networks are the ones that are already aligned along the strain axis in their unperturbed state.

Looking at the stress-strain curves, shown in Figure 5.7, it can be seen that the ultimate stress is much lower for the heterogeneous networks than the corresponding homogeneous networks, even at large fractions of short chains. Furthermore, the stress on the short chains is also significantly lower in the heterogeneous networks (Figure 5.7b). These results are sensitive to how firmly the clusters are embedded within the gel matrix, which is reflected by the average number of connections between a cluster and nodes that do not belong to this cluster. When the number of connections is decreased, the short chains in the clusters become even more isolated and the number of elastically active short-chains is reduced. Consequently, the ultimate stress is decreased even further. While clustering does not affect the maximum extensibility at small fractions of short chains, it does delay fracture at large $f_s$. 

![Figure 5.6. Segmental chain orientation with increasing strain for the short chains in a homogeneous (dashed lines) and heterogeneous (solid lines) bimodal network with $f_s = 0.65$, 0.80 and 0.90.](image-url)

[177]
Figure 5.7. (a) Stress-strain curves for bimodal networks with $f_s = 0.65 - 1.0$. The solid lines correspond to the heterogeneous networks, the dashed lines to the homogeneous networks, and the dotted lines to the unimodal networks of the corresponding cross-linking densities. (b) The corresponding stress-strain curves, showing the stress from the short and long chains, for homogeneous and heterogeneous networks with $f_s = 0.65$ and $f_s = 0.90$. The solid lines correspond to the short chains and the dashed lines to the long chains.

thereby slightly improving the toughness, also compared to equivalent unimodal networks with the corresponding number-average chain length. This would suggest that clustering might play a role in the reinforcement mechanism at large fractions of short chains.
6. Summary and Outlook

Polymers are widely used materials that can be found almost everywhere in our daily life. Polymer gels, in particular, are involved in many important applications. From both a fundamental and technological viewpoint, a deeper understanding of the structure-property relation for polymer gels could lead to the design of materials with properties tailored to specific applications. For this purpose, computer simulations can shed light on the underlying mechanisms of important phenomena in polymer systems, through the possibility to vary different parameters independently of each other and to correlate the detailed structural features with the physical properties.

In this thesis, Brownian dynamics simulations have been used to investigate the structure, deswelling and deformation of chemically cross-linked polymer gels with controlled structures, with the aim of contributing to the understanding of various structural parameters on the dynamics of polymer gels. In the first part, a new method was developed for constructing a closed, cross-linked polymer network. Simulations of polymers entail a large amount of computational effort, due to the large system size and long simulation times involved. Methods for accelerating the simulation speed are thus invaluable for facilitating more extensive studies. A novel approach for simulation polymer gels has been proposed using spherical boundary conditions (SBC) to avoid possible surface effects, which could also be a suitable option to more efficiently simulate charged systems. This is achieved by embedding the system on the surface of a ball in four dimensions, *i.e.*, a hypersphere. Using SBC, the diffusion of tracer particles of various sizes through both a static and dynamic network of different volume fractions was simulated. A slowdown with increasing tracer particle size was observed, eventually leading to trapped diffusion for particle sizes well above the peak in the gel pore size distribution. The quantitative effect of the network dynamics was illustrated through an increase in the diffusion coefficient of the tracer particles compared to a static gel structure. Mobile polymer chains facilitate the escape of trapped tracer particles, and it was shown that this escape mechanism becomes particularly important for large particles.

With the method of constructing a closed network at hand, two technologically relevant properties of polymer gels were investigated, namely their stimuli-responsive behaviour and mechanical properties. The collapse dynamics of core-shell nanogel particles of various degrees of cross-linking and mass ratios between the core and shell was studied. Core-shell particles are particularly interesting as multi-responsive materials that can respond to variations in their environment, *e.g.*, for use as drug carriers. In the simulations, a
collapse was induced by switching the pair interactions from an effective excluded volume to a Lennard-Jones (LJ) potential, for different strengths of the LJ interaction parameter to show the influence of the solvent quality. Two distinct stages could be observed after changing the quality of the solvent: an initial rapid formation of small-sized clusters near the cross-linking nodes and a subsequent cross-over to a slower coarsening stage. A faster collapse rate was observed by increasing the degree of cross-linking or the LJ interaction parameter, where the latter also resulted in a more compact final state. In contrast, for the smallest value of the LJ parameter, the attractive forces were too weak to cause a complete collapse, resulting instead in the formation of transient clusters. In the case of a shell collapsing around a swollen core, the particles formed structures with a patchy surface through core units protruding from the shell. One particularly interesting feature was observed in some cases, namely an inversion of the core-shell particle. This mechanism of exposing the core polymer chains to the environment could provide a novel route for designing functional nanomaterials.

The final parts of the thesis concerned the deformation of bimodal gels (i.e., networks consisting of both short and long chains) with various fractions of short chains, subject to uniaxial elongation. Understanding the tunability of the mechanical properties of materials is important to fulfil practical requirements and to expand the applicability of the material. Bimodal networks have previously shown substantial improvements in strength and toughness compared to their corresponding short-chain or long-chain unimodal networks. However, while previous studies on bimodal networks have focused on elastomers, a systematic study of bimodal hydrogels has been missing. Two types of network structures were considered here: in the first type, the short and long chains were distributed homogeneously within the network to isolate the effect of bimodality. In the second type, the short chains were arranged in dense clusters to also investigate the structural component, since experiments have shown that bimodal networks are usually spatially heterogeneous, with short chains aggregating into clusters during the synthesis. In both types of gels, the first chains to rupture were short chains initially aligned along the strain axis. For the homogeneous bimodal networks, the bimodal molecular weight distribution alone was sufficient to strongly alter the mechanical properties of the network at lower fractions of short chains, compared to unimodal networks of the corresponding number-average chain length, resulting in both a greater maximum extensibility and toughness. This difference became less pronounced for larger fractions of short chains. In contrast, the heterogeneous bimodal networks containing clusters were generally weaker in comparison, due to the substantial shielding of the short chains within the clusters. Networks with small scale clustering did, however, show an enhancement in the ultimate strain and also a minor improvement in the toughness for large fractions of short chains. These results suggest that clustering can be anticipated to play a role in the reinforcement mechanism at large fractions of short chains.
In real gels, however, there may be collateral effects from a short-chain length polydispersity, network defects, and trapped entanglements, which have so far been excluded from the model. Further studies are needed to investigate these effects on the mechanical properties of polymer gels.
7. Acknowledgements

Many people have contributed to this thesis in one way or another over the years. Although this list might not be comprehensive, those not mentioned are certainly not forgotten. I would like to specifically thank the following people:

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8. My Contribution

The following is a brief summary of my specific contribution to the papers presented in this thesis:

**Paper I:** Implemented the multi-step method for constructing a closed network on a hypersphere. Designed and implemented the method of forming the network directly on the hypersphere. Performed all the simulations and analyses. Took part in writing the manuscript.

**Paper II:** Designed the method for reconnecting the network. Implemented the algorithm. Formulated the scientific questions together with co-author. Performed all the simulations and analyses. Main responsible for writing the manuscript.

**Papers III-V:** Initiated and formulated the scientific questions together with co-author. Developed and implemented the algorithms. Performed all the simulations and analyses. Main responsible for writing the manuscript.
9. Summary in Swedish

Det skulle vara svårt att föreställa sig ett modernt samhälle utan den typ av molekyler vi kallar polymerer. Produkter som innehåller polymerer finns överallt runt omkring oss, från textilier till plast, målarfärg, epoxydim och många många fler. Polymerer finns också i alla levande organismer i form av t.ex. DNA, proteiner och kolhydrater.

Polymerer är stora molekyler (makromolekyler) som är uppbyggda av ett stort antal ihopkopplade mindre molekyler (s.k. monomerer). Variationer i typen av monomerer och i vilken ordning monomererorna är ihopkopplade ger upphov till material med en enorm mångfald av egenskaper. Många polymerer består av en linjär kedja men de kan också bilda t.ex. grenade eller stjärnformerade strukturer. I denna avhandling är vi intresserade av det fall där kedjorna är tvärbundna i något lösningsmedel och bildar ett stort tredimensionellt nätverk. Denna typ av system kallas en gel. Exempel på geler är gelatin och agar. Några av egenskaperna hos polymergeler som är viktiga för deras användning är deras förmåga att absorbera stora mängder lösningsmedel samt deras mekaniska egenskaper. Polymerer som kan genomgå en kraftig strukturförändring vid en liten förändring av någon yttre variabel (såsom temperatur, pH, eller salthalt), är av stort intresse som "intelligenta material" för medicinska tillämpningar, t.ex. för att kontrollera frisättningen av läkemedel, som självjusterande ventiler eller som artificiella muskler. De mekaniska egenskaperna hos geler är också viktiga i många praktiska tillämpningar som bygger på att de kan fungera som stödjande material. För många tillämpningar kan det emellertid vara nödvändigt att förbättra de mekaniska egenskaperna. Hos konventionella hydrogeler (d.v.s. geler där lösningsmedlet är vatten) är dessa ofta dåliga och är en begränsande faktor.

För att förbättra vår förståelse av material där polymerer ingår och även för att tolka resultaten från experiment är datorsimuleringar ett ovärderligt verktyg, genom möjligheten att kunna variera olika parametrar oberoende av varandra samt att kunna relatera materialegenskaperna till den atomära strukturen. Den detaljerade strukturen hos en gel är svår att kontrollera vid framställningen, vare sig det är i ett laboratorium eller industriellt. Det kan finnas lösa kedjor såväl som intrasslingar av polymerkedjorna. Det kan också finnas områden som innehåller en hög koncentration av tvärbundna polymerkedjor och mer utspädda domäner, vilket medför en heterogen struktur. De fysikaliska egenskaperna hos geler påverkas av hur kedjorna i nätverket är sammanlänkade, men dessa strukturella defekter och inhomogeniteter är svåra att mäta i experiment och komplicerar en analys av sambandet mellan den mikroskopiska strukturen och de efterfrågade materialegenskaperna. Strukturen hos en gel
kan dock väljas noggrant i en simulering, vilket gör det möjligt att på ett systematiskt sätt studera olika effekter separat för en serie nätverksmodeller under fullt kontrollerade förhållanden. Från både ett grundläggande och ett tekniskt perspektiv kan en djupare förståelse av gelers struktur och egenskaper leda till utvecklingen av material som är skräddarsydda för specifika tillämpningar.

En utmaning är att simuleringar av polymerer vanligtvis kräver en stor beräkningssats på grund av det stora antalet partiklar och de långa tidsskalorna som är inblandade. Utvecklingen av nya algoritmer och metoder för att öka simuleringshastigheten är således ovärdeliga för att underlätta mer omfattande studier och för att kunna lära oss mer om dynamiska processer hos polymerer.


I denna avhandling undersöktes också deformationen av nätverk med en bimodal molekylviktsfördelning (d.v.s. med korta och långa kedjor sammankopplade i ett nätverk) under mekanisk töjning. En förståelse av de mekaniska egenskaperna är av stor betydelse för att kunna uppfylla praktiska krav och för att utvidga materialets användbarhet. Bimodala nätverk har tidigare visat väsentliga förbättringar i styrka och seghet jämfört med ett motsvarande nätverk bestående av endast korta eller långa kedjor. Tidigare studier har emellertid fokuserat på elastomerer, medan en systematisk studie av bimodala hydrogeler har saknats. Den sista delen av denna avhandling fokuserar på deformationen och förstärkningsmekanismen för bimodala geler. Två typer av nätverkskonstruktioner studerades: i den första typen fördelades de korta och långa kedjorna homogen i nätverket för att isolera effekten av bimodalitet utan att behöva ta hänsyn till möjliga effekter av exempelvis kedjeaggregation. I den andra typen bildade de korta kedjorna kluster, vilket möjliggjorde en undersökning även av strukturkomponenten. Experiment har nämligen funnit att bimodala nätverk är heterogena, med en tendens för de korta kedjorna att aggregera under syntesen. I båda typerna av geler var de första kedjorna som bröts under töjningsprocessen korta kedjor som redan från början var orienterade längs töjningsaxeln. För de homogena nätverken var den bimodala molekylviktsfördelningen tillräcklig för att kraftigt påverka de mekaniska egenskaperna vid lägre andel av korta kedjor, jämfört med unimodala nätverk av motsvarande genomsnittlig kedjelängd. En bimodal molekylviktsfördelning ledde till att materialet kunde dras ut ytterligare samt till en ökad seghet. Denna skillnad blev mindre uttalad för en större andel av korta kedjor. Däremot visade närvaron av kluster i allmänhet inte en förbättring i de mekaniska egenskaperna, på grund av den avsevärda avskärmningen av de korta kedjorna. Resultaten för små kluster vid en hög andel korta kedjor visade en förbättring i den maximala töjningen och även i segheten. Dessa resultat tyder på att det skulle kunna finnas en strukturkomponent i förstärkningsmekanismen. I praktiken kan det dock finnas andra bidrag från t.ex. defekter i strukturen samt intrassling av polymerkedjor som hittills har uteslutits från modellen. Fler studier behövs för att undersöka effekten av dessa på de mekaniska egenskaperna.
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A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology. (Prior to January, 2005, the series was published under the title “Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology”.)