Computational modelling of the rheological behavior of branched polymer melts

van den Akker, E.A.T.

Award date:
2005
Computational modelling of the rheological behavior of branched polymer melts

by

E.A.T. van den Akker

supervisors:

Dr.Ir. A.A.F. van de Ven (TUE)
Prof. Dr. J.J.M. Slot (DSM)

Eindhoven, 18th July 2005
Abstract

An algorithm that predicts the linear viscoelasticity of a melt consisting of different branched polymers is presented. The derivation of this algorithm is based upon the tube model. Polymers, linear or branched, can relax by reptation or retraction. Knowing the molecular structure of the polymer melt, the relaxation function can be calculated. The algorithm is implemented in Fortran. Numerical results are compared with available experimental data.
## Contents

1 Introduction .................................................. 1  
   1.1 DSM .................................................. 1  
   1.2 Background of the problem .............................. 1  
   1.3 Project formulation ..................................... 2  
   1.4 Overview of report ...................................... 3  
   1.5 Important results and conclusions ...................... 3  

2 Viscoelasticity ................................................. 5  
   2.1 Conservation laws ........................................ 5  
   2.2 Constitutive equations .................................... 6  

3 Tube model .................................................... 9  
   3.1 Reptation ............................................... 10  
      3.1.1 Bead-spring model .................................. 10  
      3.1.2 Diffusion model ..................................... 19  
      3.1.3 Relaxation equation for reptation .................. 21  
   3.2 Arm retraction ........................................... 22  
      3.2.1 Derivation of the stochastic differential equation 22  
      3.2.2 Derivation of the differential equation for the density distribution 26  
      3.2.3 Solution of the stochastic differential equation .... 29  
      3.2.4 Chain end probability ................................ 30  
      3.2.5 Approximation of the density distribution .......... 31  
      3.2.6 Dynamic dilution .................................... 34  
   3.3 Waiting time ............................................. 34  
      3.3.1 Simplest situation ................................... 34  
      3.3.2 Backbones relaxing .................................. 36  
      3.3.3 Multiple relaxing arms ............................... 37  
      3.3.4 Initial waiting times ................................ 40  
      3.3.5 Three-arm star ...................................... 41  
   3.4 Supertube ................................................. 42  
   3.5 Relaxation function ...................................... 43  
   3.6 Summary of the tube model ............................... 45  

4 Implementation ................................................. 47  
   4.1 Sieving .................................................. 47  
   4.2 Coarsegraining .......................................... 47  
   4.3 Relax ................................................... 47  
   4.4 Modulus ................................................ 49  

5 Testing .......................................................... 51  
   5.1 Literature data ............................................ 51  
      5.1.1 Retriction data ...................................... 51  
      5.1.2 Reptation data ....................................... 52  
      5.1.3 Waiting times data ................................... 52  
   5.2 Laboratory data ........................................... 53
6 Results, conclusion and recommendations

6.1 Model ................................................. 57
   6.1.1 Reptation .................................. 57
   6.1.2 Arm retraction ................................. 57
   6.1.3 Waiting times ................................. 57

6.2 Conclusions ........................................... 57

References .............................................. 59
### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>Initial entanglement length</td>
</tr>
<tr>
<td>$a(t)$</td>
<td>Entanglement length</td>
</tr>
<tr>
<td>$b$</td>
<td>Bond length between two Rouse segments in the Rouse model</td>
</tr>
<tr>
<td>$C_2$</td>
<td>Covariance of end points</td>
</tr>
<tr>
<td>$C_v^2$</td>
<td>Variance of end points</td>
</tr>
<tr>
<td>$D_A$</td>
<td>Drag of segment $A$</td>
</tr>
<tr>
<td>$D_C$</td>
<td>Diffusion constant for reptation</td>
</tr>
<tr>
<td>$D_A$</td>
<td>Parabolic cylinder function</td>
</tr>
<tr>
<td>$f_o$</td>
<td>Stochastic force in Rouse model</td>
</tr>
<tr>
<td>$G_0$</td>
<td>Plateau modulus</td>
</tr>
<tr>
<td>$G(t)$</td>
<td>Relaxation function</td>
</tr>
<tr>
<td>$G'(\omega)$</td>
<td>Storage modulus</td>
</tr>
<tr>
<td>$G''(\omega)$</td>
<td>Loss modulus</td>
</tr>
<tr>
<td>$k$</td>
<td>Spring constant in Rouse model</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann’s constant</td>
</tr>
<tr>
<td>$\Delta k$</td>
<td>Logarithmic waiting time after arm retraction</td>
</tr>
<tr>
<td>$L_{eq}$</td>
<td>Equilibrium length of a polymer</td>
</tr>
<tr>
<td>$M$</td>
<td>Polymer mass</td>
</tr>
<tr>
<td>$N$</td>
<td>Number of Rouse modes in a polymer</td>
</tr>
<tr>
<td>$N_A$</td>
<td>Avogadro’s number</td>
</tr>
<tr>
<td>$S_A^L$</td>
<td>Initial entanglement number of segment $A$</td>
</tr>
<tr>
<td>$S_A^g$</td>
<td>Entanglement weight of segment $A$</td>
</tr>
<tr>
<td>$R$</td>
<td>Gas constant</td>
</tr>
<tr>
<td>$T$</td>
<td>Absolute temperature</td>
</tr>
<tr>
<td>$t_0$</td>
<td>Start time for arms</td>
</tr>
<tr>
<td>$t_E$</td>
<td>Entanglement time</td>
</tr>
<tr>
<td>$x_e$</td>
<td>Entanglement length</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Friction coefficient in Rouse model</td>
</tr>
<tr>
<td>$\dot{\gamma}$</td>
<td>Initial friction coefficient of one entanglement length</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Dimensionless constant equal to 15/8</td>
</tr>
<tr>
<td>$\sigma^2$</td>
<td>Variance</td>
</tr>
<tr>
<td>$\sigma(t)$</td>
<td>Length of initial tube that still exists at time $t$</td>
</tr>
<tr>
<td>$\tau_R$</td>
<td>Rouse time</td>
</tr>
<tr>
<td>$\tau_E$</td>
<td>Entanglement Rouse time</td>
</tr>
<tr>
<td>$\tau_d$</td>
<td>Reptation time</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Fraction of relaxed material</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>Chain density</td>
</tr>
<tr>
<td>$\Phi_{ST}$</td>
<td>Tube density</td>
</tr>
</tbody>
</table>
1 Introduction

1.1 DSM

DSM started life in 1902 as a state-owned national and regional coal-mining company in the Netherlands. Today, over a century later, it is an advanced biotechnological and chemical company, listed on the stock exchange, and having manufacturing sites and sales offices across the globe.

Originally DSM (Dutch State Mines) was a mining company. In 1930 this changed, as DSM began producing fertilizer. After the second world war, DSM built factories to produce different sorts of plastics. In the seventies of last century, the mines closed, and DSM was dedicated entirely to chemical activities.

From 1989 onwards, DSM is no longer a state-owned company. Lately, DSM has started producing life science products. Nowadays, DSM’s activities can be divided into three clusters:

- Life Science Products,
- Performance Materials,
- Industrial Chemicals.

The activities of the Life Science Products cluster focus on the pharmaceutical and food industries. Products of this cluster are, among others, aspartame, penicillin, medicines based on biotechnology, bakery ingredients, coatings for cheese, flavour enhancers and ingredients for baby food.

The Performance Materials cluster supplies high-performance polymers for electrical equipment, electronics, buildings, cars, paints, boats and clothing. Other products of this cluster are synthetic rubbers, thermoplastic rubbers, bullet-resistant clothing, sports goods, high-heat nylons, coating systems and materials for optical glass fibers.

The Industrial Chemicals cluster produces raw materials, such as raw materials for synthetic fibres and plastics, ammonia and nitric acid. Also the melamine production is part of this cluster.

This project is performed for the Performance Materials cluster. Because polymers are the main material in this cluster, it is no surprise that this project deals with polymers.

1.2 Background of the problem

The Performance Materials cluster is divided into several parts, one of which is the Material Science Centre, MSC. This centre provides solutions for business problems by applying conceptual knowledge of material processes and properties.

Mechanical properties of polymers are the primary properties of this class of materials. A certain balance of stiffness and toughness is needed for every application. Therefore, MSC is looking at deformation and fracture of polymers under a broad range of conditions and with different characterization techniques. Those techniques are ranging from viscoelastic techniques such as dynamic mechanical measurements, creep, relaxation, recovery, hysteresis, fatigue to deformation of materials in tension, bending and compression, and to fracture mechanical tests. Due to a combination of knowledge of mechanical properties and polymer physics, MSC is able to support the development of new materials and the adaption of existing grades to new specifications.
The rheology or flow behavior of materials is of importance for many technological issues varying from polymer processing to process flows in production plants. The rheology group of DSM Research has expertise in the field of rheology, especially the viscoelastic properties of polymeric melts. It is well known that the rheological properties of polymers are intimately related to the details of their molecular structure. Rheology, more specifically dynamic mechanical spectroscopy, is therefore often used as a characterizer for newly developed materials, but also intensively for product quality control and trouble shooting purposes. Within DSM, polymer melts are produced, of which the composition is not fully known. Using other methods, characteristics can be estimated, as the percentage of linear polymers or the average molecular weight. From this information, one could guess the composition of the polymer melt, but there was no easy way to check this guess. If the viscoelastic properties of the guessed composition were known, they could be compared to the measured viscoelastic properties, and this could be a way to check the results. The viscoelastic properties of linear polymers (i.e. without branches) have already been studied extensively in the past fifty years. The result is that linear viscoelastic properties of a linear polymer melt can be predicted reasonably well from its molecular weight distribution. For polymer melts having a more complicated molecular structure, such predictions are not straightforward. However, there has been some research on various structures, such as star polymers, see [1], [2] and [3], H-polymers [4], comb-polymers and pompom-polymers [5]. Although results are promising, no definite model has yet been developed to generalize these results to branched polymers. Recently, theories have become available that incorporate the stress relaxation of the side-arms or branches (the Ball-McLeish approach). A method to use this theory was proposed by Larson [7], but a scheme was only developed for polymers with no higher-order branched structure (in which branches themselves have branches). Larson stated in his article that the scheme could be generalized to consider higher-order branched structures, but that this was beyond the scope of his work. This project will generalize, and improve, Larson’s scheme.

1.3 Project formulation

The basic assignment of this master project is to deliver a software tool for DSM. For a melt modelled as a linear viscoelastic medium, the rheological properties are governed by the relaxation function, or, more practical, by the storage and loss modulus. It is our task to build a model that, given the chemical composition and structural topology, can predict the relaxation function. This must be done by modelling the polymers in a tube model and by incorporating the Ball-McLeish approach for branched polymers in our model. This general model for relaxation of all types of (un)branched polymers must be implemented in a Fortran program that is able to determine numerically the rheological behavior of the polymer melt, more specifically its storage and loss modulus. The results of the program must be validated with known experimental results from either literature or from experiments at DSM. The ultimate aim of this project is thus the development of a software tool. The basics of the Ball-McLeish approach have already been partly implemented in a software code, but up to now this code has not been evaluated extensively. To describe the relaxation of an arbitrary polymer, we distinguish between linear (unbranched) and branched polymers. For linear polymer chains, we will model the relaxation by reptation, whereas for branched polymers, we will consider the retraction of the arms. Thus, we will build a general model that we will implement in the existing software code. This code will be evaluated to yield numerical...
results and these results will be compared with experimental data.

1.4 Overview of report

The structure of the report is as follows: In Chapter 2, we summarize the viscoelastic principles. We introduce the relaxation function and we show why we are interested in it. Chapter 3 describes the tube model, and gives the relation between the relaxation function and the relaxation time. The different ways of relaxation, reptation and arm retraction, are described in this chapter, and the relaxation behavior is expressed in formulae. An improvement for the log(2)-waiting time in Larson [7] is presented. The numerical implementation of this model in Fortran is presented in Chapter 4. The numerical results of this implementation are validated in Chapter 5 by comparison to available experimental data (from literature). Moreover, it is shown how the program can be used to check an assumed structure of a polymer melt from known relaxation moduli; for this experimental data from DSM is used. Chapter 6 contains the conclusions and recommendations.

1.5 Important results and conclusions

The most important result of this project is that we have succeeded in developing a software tool that is able to predict the rheological properties of a polymer melt given its molecular structure. The predicted properties, specifically the storage and loss moduli, show a good correspondence with available experimental data. This validates the numerical simulation. A comparison of the results of our model with those of other models that can be found in literature, shows that our model has at least the same level of correctness, and is, moreover, more general.
2 Viscoelasticity

Polymer melts are described as viscoelastic continua. This section gives a mathematical description of the behavior of viscoelastic media. First the general conservation laws are formulated, and thereafter the material-dependent constitutive equations are given.

2.1 Conservation laws

This is meant to be a very general introduction. Further information can be found in Golden [6].

For a material point \( P \), we define the Lagrange coordinate \( X \) and the Euler coordinate \( x \) as the position of \( P \) in the undeformed, reference, state and the deformed, momentary, state at time \( t \), respectively. The displacement \( u \) is defined by

\[
\mathbf{u} = \mathbf{x} - \mathbf{X} = \mathbf{u}(\mathbf{x}, t),
\]

(2.1)

if we consider \( x \) and \( t \) as the fundamental variables. The velocity \( \mathbf{v} = \mathbf{v}(\mathbf{x}, t) \) of \( P \) is denoted by

\[
\mathbf{v} = \dot{\mathbf{u}} = \frac{\mathrm{d}\mathbf{u}}{\mathrm{d}t},
\]

(2.2)

where \( \mathrm{d}/\mathrm{d}t \) denotes the material time derivative.

For further reference we introduce the linear deformation tensor \( \mathbf{E} \) with components \( e_{ij}, \ (i, j = 1, 2, 3) \) by

\[
e_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i}), \quad i, j \in (1, 2, 3),
\]

(2.3)

and the rate of deformation tensor \( \mathbf{D} \) with components \( D_{ij} \),

\[
D_{ij} = \frac{1}{2}(v_{i,j} + v_{j,i}),
\]

(2.4)

where the subscript \( , j \) is short for \( \partial/\partial x_j \). The stress tensor \( \mathbf{T} \) with components \( t_{ij}, \) is defined as the component of the force per unit of area in the \((\mathbf{x}-\text{state})\) in the \(\mathbf{e}_i\)-direction, acting on a surface element with normal in the \(\mathbf{e}_j\)-direction.

The following equations hold universally:

- conservation of mass or equation of continuity,

\[
\frac{\partial \rho}{\partial t} + \rho \div \mathbf{v} = 0,
\]

(2.5)

- conservation of momentum or equation of motion,

\[
\div \mathbf{T} + \rho \mathbf{b} = \rho \frac{\partial \mathbf{v}}{\partial t} + \rho L \mathbf{v},
\]

(2.6)

- conservation of energy, (here, \( \cdot \) stands for material time derivative)

\[
\rho \dot{\theta} = -\rho \dot{\eta} \dot{\theta} + \text{tr}(\mathbf{T} \mathbf{D}) - \rho \dot{\psi} + \rho \dot{r} + \div \mathbf{q},
\]

(2.7)
where \( \rho \) is the density and \( \mathbf{b} \) is a body force acting on \( P \). The velocity gradient tensor \( \mathbf{L} \) is defined as \( \text{grad} \mathbf{v} \), such that \( L_{ij} = (\text{grad} \mathbf{v})_{ij} = v_{i,j} \). Further, \( \theta \) is the absolute temperature, \( \eta \) is the entropy, \( \psi \) is the free energy density, \( \rho r \) is a heat source and \( \mathbf{q} \) is the heat flux. Finally, \( \text{tr}(\cdot) \) stands for the trace (i.e. \( \text{tr}(T D) = T_{ij} D_{ij} \), where we have used the summation convention).

In this report, we consider quasi-stationary creeping flows and we neglect thermal effects, so the only relevant equation is the equilibrium equation, or the quasi-static equation of motion,

\[
\text{div} \ T + \rho \mathbf{b} = 0, \tag{2.8}
\]

or in index notation (using summation convention)

\[
t_{ij,j} + \rho b_i = 0. \tag{2.9}
\]

Because \( T \) is symmetric, we have nine unknowns \((t_{11}, t_{12}, t_{13}, t_{21}, t_{22}, t_{33}, u_1, u_2 \text{ and } u_3)\) and only three equations, so we need an extra set of six constitutive equations. These will be introduced in the next section.

### 2.2 Constitutive equations

In this section, we present a very limited introduction of the constitutive theory for linear viscoelastic media, in particular that of so called ”simple fluids”. A more detailed review can be found in [6].

The basic concept of the simple fluid theory is that the stress tensor \( T \) at place \( x \) and time \( t \) is completely determined by the deformation \( \mathbf{E} \) at \( x \) at all earlier times \( \tau \), \( \tau \leq t \). Mathematically spoken:

\[
T(x, t) = C[\mathbf{E}(x, \tau); -\infty < \tau \leq t], \tag{2.10}
\]

where \( C \) is an unknown operator. In the linear theory, \( C \) is a linear 4-tensorial operator. Here, the medium (the polymer melt) is assumed to be homogenous isotropic, so the linear 4-tensor \( C \) can only have two independent components: the stress tensor is fundamentally related to changes in volume and changes in shape. In mathematical terms this is stated as

\[
t_{ij}(x, t) = \delta_{ij} L[e_{kk}(x, \tau); -\infty < \tau \leq t] + 2M[e_{ij}(x, \tau); -\infty < \tau \leq t], \tag{2.11}
\]

where \( L \) and \( M \) are (still unknown) linear operators; \( L \) is responsible for the stress caused by change of volume and \( M \) is responsible for the stress caused by change of shape. Taking the deviatoric part \( \mathbf{S} \) of \( T \), with elements \( s_{ij} = t_{ij} - 1/3 t_{kk} \delta_{ij} \), and the deviatoric part of \( \mathbf{E} \), with elements \( \varepsilon_{ij} = e_{ij} - 1/3 e_{kk} \delta_{ij} \), we find that (2.11) yields

\[
s_{ij}(x, t) = 2M[\varepsilon_{ij}(x, \tau); -\infty < \tau \leq t]. \tag{2.12}
\]

Now, suppose that for some \( i, j \), the deformation is specified as \( \varepsilon_{ij}(x, t) = \dot{\varepsilon}_{ij} H(t) \), where \( H(t) \) is the Heaviside step-function, and \( \dot{\varepsilon}_{ij} \) is a constant uniform strain. Because \( \varepsilon_{ij} \) is independent of \( x \), as a result of (2.12) \( s_{ij} \) is also independent of \( x \), and we can write the resulting \( s_{ij}(t) \) as

\[
s_{ij}(t) = 2\dot{\varepsilon}_{ij} M[H(t); -\infty < \tau \leq t] = 2\dot{\varepsilon}_{ij} G(t), \tag{2.13}
\]

where \( G(t) \) is the relaxation function. Because of the linearity of \( M \), \( G(t) = 0 \) if \( t < 0 \). Moreover, for physical reasons \( G(t) \) for \( t > 0 \) is as many times continuously differentiable as
necessary, and \( G(t) \) is a monotonic non-increasing function of \( t \) if \( t > 0 \). If the jump in \( \varepsilon_{ij} \) did not occur at \( t = 0 \), but at \( t = t_0 \), the stress would have been \( s_{ij}(t) = 2\dot{\varepsilon}_{ij}G(t - t_0) \).

Next, consider a deformation \( \varepsilon_{ij}(t) \) such that \( \varepsilon_{ij}(0) = 0 \) and \( \varepsilon_{ij} \) is continuous for \( t \geq 0 \), and approximate \( \varepsilon_{ij} \) by a sum of \( n \) step functions with increments \( \Delta \varepsilon_{ij}(k) \) at \( t = t_k \), so for \( 0 < t < t_{n+1} \),

\[
\varepsilon_{ij}(t) \approx \sum_{k=1}^{n} H(t - t_k) \Delta \varepsilon_{ij}(k).
\] (2.14)

The corresponding stress \( s_{ij} \) is, using the principle of superposition as is allowed because of the linearity of \( \mathcal{M} \)

\[
s_{ij}(t) \approx 2 \sum_{k=1}^{n} G(t - t_k) \Delta \varepsilon_{ij}(k).
\] (2.15)

If the limit of \( n \) is taken to infinity, the approximation for \( \varepsilon_{ij} \) becomes perfect, and the sum becomes an integral:

\[
s_{ij}(t) = 2 \int_{\varepsilon_{ij}(0)}^{\varepsilon_{ij}(t)} G(t - \tau) \omega \varepsilon_{ij}(\tau) G(t - \tau) d\tau.
\] (2.16)

In exactly the same way we can derive the relation

\[
t_{kk}(t) = \int_{e_{kk}(0)}^{e_{kk}(t)} K(t - \tau) d\varepsilon_{kk}(\tau) = \int_{0}^{t} \dot{\varepsilon}_{kk}(\tau) K(t - \tau) d\tau,
\] (2.17)

where \( K \) is the relaxation function in the case of compression. For \((i,j) \in (1,2,3)\), the set (2.16) presents five independent equations relating \( s_{ij} \) and \( \varepsilon_{ij} \) (note that \( s_{kk} = \varepsilon_{kk} = 0 \)); the sixth equation is given by (2.17). In case of incompressibility, \( \varepsilon_{kk} \to 0, \ K \to \infty \), such that the hydrostatic pressure \( p = t_{kk}/3 \) becomes undetermined and becomes an extra unknown.

Relation (2.17) cancels and the sixth equation is now \( \varepsilon_{kk} = 0 \). With this equation, together with (2.16) and (2.9), the nine unknown displacements and stresses for an incompressible viscoelastic medium are completely determined. Polymer melts, the systems of interest, are viscoelastic media, and, on the timescales we are considering, can be considered incompressible. Therefore, we only consider \( G(t) \) as relaxation function.

In conclusion, the constitutive behavior of a polymeric melt modelled as a linear incompressible viscoelastic medium is known once \( G(t) \) is known. In the rest of the report, we will therefore focus on the relaxation function. The next chapter will show how \( G(t) \) can be found, using a certain model for the interactions between polymers.

In experiments, usually not \( G(t) \) is considered, but \( G'(\omega) \) and \( G''(\omega) \), the storage modulus and loss modulus, which are defined by

\[
i\omega \mathcal{G}(\omega) = G'(\omega) + iG''(\omega),
\] (2.18)

where \( \mathcal{G} \) is the Fourier-transform of \( G \),

\[
\mathcal{G}(\omega) = \int_{0}^{\infty} G(t) e^{-i\omega t} dt.
\] (2.19)

Using the Fourier-transform, we can express (2.16) in an easier form,

\[
\pi_{ij}(\omega) = 2\mathcal{G}_{ij}(\omega) \mathcal{G}(\omega).
\] (2.20)
One reason to use the storage and loss modulus instead of the relaxation function is that the storage and loss modulus can be measured directly. For this, a piece of viscoelastic material is loaded by a periodic stress with frequency $\omega$, so

$$t_{ij}(t) = \sigma_0 \sin(\omega t), \quad (2.21)$$

for some $i,j$, and for a constant stress amplitude $\sigma_0$. The resulting deformation $e_{ij}$ will be periodic too, but with some phase difference $\delta$, depending on the frequency $\omega$, and an amplitude $e_0$, depending on $\omega$ too, so

$$e_{ij}(t) = e_0(\omega) \sin(\omega t - \delta(\omega)). \quad (2.22)$$

This deformation can be measured, and using (2.20), we see that

$$\frac{\sigma_0}{4\omega} = 2e_0(\omega) \frac{\sin(\delta(\omega)) - i \cos(\delta(\omega))}{4} G(\omega), \quad (2.23)$$

so

$$i\omega G(\omega) = \frac{\sigma_0}{2e_0(\omega)} \left( - \cos(\delta(\omega)) + i \sin(\delta(\omega)) \right), \quad (2.24)$$

and as a result of (2.18) we see that

$$G'(\omega) = -\frac{\sigma_0}{2e_0(\omega)} \cos(\delta(\omega)), \quad G''(\omega) = \frac{\sigma_0}{2e_0(\omega)} \sin(\delta(\omega)). \quad (2.25)$$

Because rheological tests, giving results in terms of the moduli $G'$ and $G''$, are used to validate the model, the numerical results of the model will be the moduli $G'(\omega)$ and $G''(\omega)$ instead of the relaxation function $G(t)$. The next chapter will give a model to determine the moduli $G'(\omega)$ and $G''(\omega)$ from the molecular structure.


3 Tube model

A polymer melt typically consists of many entangled polymers. Therefore, the motion of a single polymer is highly constrained. The polymers surrounding a given polymer prevent certain displacements. The effect of the surrounding polymers is similar to that of a surrounding tube. Because of that, in the tube model, each polymer is modelled as a chain surrounded by a constraining tube; see Figure 1.

![Figure 1: A polymer segment with its entangling neighbors, which are modelled as a tube. The entanglement length $a$ is indicated by the dotted line.](image)

The average distance at time $t$ between two entangling polymers in the tube is called $a(t)$, the time dependent entanglement length. This entanglement length, which will change over time as polymers, forming the tube, are removed, will turn out to be a useful distance in terms of which several lengths in the problem can be expressed. For example, the total length of the polymer, $L_{eq}$, can be expressed in the entanglement length. In this way, we can define $S_a^l(t)$, the number of entanglements at time $t$. However, we follow Doi and Edwards [10], defining the dimensionless time dependent entanglement number $S_a^t(t)$ as

$$S_a^t(t) := \frac{4L_{eq}}{5a(t)},$$

where the factor $4/5$ indicates that the polymer is not a straight line, and the effective length is $4/5L_{eq}$. We also define the constants $a$ and $S_a^l$, independent of time, as

$$a := a(t = 0), \quad S_a^l := S_a^l(t = 0),$$

so from (3.1) we have the relation

$$S_a^l = \frac{4L_{eq}}{5a}.$$  

Because of their definitions, we call $a$ the initial entanglement length and $S_a^l$ the initial entanglement number, but we will often omit the word 'initial'. Most of the time, we will deal with the initial entanglement length and number; if we use the time-dependent length
or number, we will say so explicitly.

In this report, we restrict ourselves to noncyclic polymers. This means that the polymers can be described, in graph theoretic terms, by a tree. Each edge in the graph is named a polymer segment. The vertices of the graphs are named either end points or branch points; end points being points only connected by one edge and branch points being all the others. Branch points always connect three or more segments, otherwise the branch point could be removed. If a polymer has no branch points, so it is just two end points connected by one segment, we name it linear. All the other polymers are named branched. A segment from a branched polymer that contains an end point is named an arm, the other segments are named backbone segments.

To determine the relaxation function as introduced in Chapter 2, we consider a polymer melt that undergoes a sudden unit deformation at \( t = 0 \). According to (2.13), the resulting stress caused by this deformation is proportional to the relaxation function. Because the plateau modulus \( G_0 = G(0) \), the initial value of the relaxation function, is a material constant that can be directly measured, \( G(t) \) is completely known if the fraction of remaining stress for all \( t \) is known. Immediately after the onset of deformation, every polymer is in an unrelaxed nonequilibrium state. The stress can only disappear if the polymers relax, so we are interested in the different ways of relaxing.

Since the chains cannot move perpendicular to the tube axis, the only way of relaxing is by diffusing out of their tube. A linear polymer (a polymer without branch points) can escape out of its tube by a translational diffusion process along the tube, called reptation. This process will be discussed in Section 3.1. Reptation is prevented for branched polymers because each arm is essentially fixed at one end by the branch point. However, arms can renew their configuration if the arms retract along their tube axes pushing out unentangled loops into the surrounding matrix. This process, called arm retraction, will be discussed in Section 3.2. Once arm retraction is completed, the arm is relaxed and so the structure changes, and this leads to a waiting time for the segments close to the retracted arm; this is investigated in Section 3.3. Knowing the relaxation due to reptation and retraction, the chain density (fraction of unrelaxed polymers) can be given directly, but special attention is needed for the tube density (fraction of unrelaxed tube). This is done in Section 3.4. Knowing these densities, we show in Section 3.5 how to calculate the relaxation function, the function we want to know according to Chapter 2.

The theory presented in this chapter is based on the paper of Larson [7], with some extensions.

### 3.1 Reptation

In this section, we describe the reptation of a linear polymer. The motion of a reptating polymer can be described in two ways: by considering the motion of the end points in the Rouse model, and by considering reptation as a pure diffusion process. The Rouse model analysis should include relaxation due to the motion of the end points, where the diffusion process only allows relaxation due to motion of the central point. If the motion of the end points is neglected (the polymer is considered stiff), then both models should give the same result.

#### 3.1.1 Bead-spring model

In this section, we consider a linear polymer; see Figure 2.
If the polymer is in an unrelaxed state, it will relax, and in the case of a linear polymer this will happen by reptation. Reptation is the event that a chain relaxes by diffusing along the tube contour; see Figure 3.

Because the motion with respect to the tube is not possible for branched polymers, having arms fixed at branch points, reptation only happens if the polymer is linear.

To describe the motion of a linear polymer, we use a variant of the Rouse model [8], also called the bead-spring model; see Figure 4. A polymer is modelled as a chain of $N$ beads, numbered from $-N/2$ at the one end to $N/2$ at the other end (for ease of notation we assume $N$ to be even). The distance between bead-centers is called $b$, the Rouse bond length. In fact, we have three lengths in our model: $L_{eq}$, the length of the total polymer in an equilibrium situation, $a$, the initial entanglement length, and $b$, the Rouse bond length. They are connected through (following [10, p.193]; the left-hand side is the mean square length of a random walk of $N$
steps with length $b$, while the right-hand side is the length of the end-to-end vector of a "Gaussian" chain) 

$$N b^2 = a L_{eq}. \quad (3.4)$$

Using this equation, together with (3.3), we are able to express the lengths $a$ and $b$ in terms of $L_{eq}$, $N$ and $S^i_0$.

We only analyze the motion in the direction of the tube, and neglect the transversal motion, the 'wiggling' of the beads in the tube. This 'wiggling', having a high frequency, will only have an effect on the rheological behavior at high frequencies. Because our model neglects these Rouse fluctuations, we expect (and will see in Chapter 5) that the model can not predict the moduli well at higher frequencies.

In the Rouse model, the $N$ beads are connected by springs of stiffness $k$. According to the tube model, the polymer is surrounded by a tube, which imposes a friction with friction coefficient $\gamma$. Due to Brownian motion, a stochastic force is acting on each bead, denoted by $f_n$, $n \in [-N/2, N/2]$.

To describe this stochastic force, we need some elementary notions from probability theory; see [14]. Let $\eta$ be a stochastic variable and $p_\eta$ its density distribution. This means that

$$P(\eta \leq \xi) = \int_{-\infty}^{\xi} p_\eta(\zeta) d\zeta. \quad (3.5)$$

The notation $\langle \cdot \rangle$ for average is introduced as

$$\langle \eta \rangle := \int_{-\infty}^{\infty} \zeta p_\eta(\zeta) d\zeta. \quad (3.6)$$

The stochastic force $f_n$ on the $n^{th}$ bead is normally distributed with zero mean and variance $\sigma^2$ (see [10]). Moreover, $f_n$ is of so-called "white noise" type (the condition for white noise is expressed by relation (3.8)). These two conditions imply that (note that $f_n(t)$ is a stochastic variable for every $t$)

$$\langle f_n(t) \rangle = 0, \quad (3.7)$$

and

$$\langle f_n(t_1) f_n(t_2) \rangle = \sigma^2 \delta(t_1 - t_2), \quad (3.8)$$

where, for fixed $t_1$ and $t_2$, the product $f_n(t_1) f_n(t_2)$ should be seen as a new stochastic variable, and $\delta$ is the Dirac delta function.

We also assume that the forces on two different beads, say $n_1$ and $n_2$, are uncorrelated, meaning that

$$\langle f_{n_1}(t) f_{n_2}(t) \rangle = 0, \quad \text{if} \quad n_1 \neq n_2. \quad (3.9)$$

To proceed, we consider the motion of one bead, say $n$, of a polymer chain of $N$ beads and total mass $M$. Let $s_n$, with $-N/2 < n < N/2$, be the arc length of the $n$-th bead along the chain. On this bead, the following forces are acting:

- the elastic (linear spring) force due to the interaction with the $(n - 1)$-th and $(n + 1)$-th bead, equal to $k(s_{n+1} - 2s_n + s_{n-1})$, where $k$ is the spring constant. Referring to [10], we note that $k$ is given by (in the Rouse-model) $k = 2\nu S^i_a(t) k_B T / L_{eq}^2$, where $\nu$ is a
dimensionless constant equal to $15/8$, $S^l_a(t)$ is the number of entanglements (which in general is time dependent, but we will ignore this time dependence for now), $k_B$ is Boltzmann’s constant, $T$ is the absolute temperature and $L_{eq}$ is the equilibrium length of the arm;

- the friction force, modelled as the viscous friction force $\gamma \dot{s}_n$, where $\gamma$ is the friction coefficient;
- the stochastic force $f_n$, which is a stochastic function of time $t$, $f_n = f_n(t)$, with characteristics given by (3.7)–(3.9).

Taking this together, and realizing that the mass of one bead is $M/N$, we arrive at the equation of motion for the $n$-th bead,

$$
\frac{M}{N} \ddot{s}_n = k(s_{n+1} - 2s_n + s_{n-1}) - \gamma \dot{s}_n + f_n, \quad -N/2 < n < N/2, \quad (3.10)
$$

where $s_n = s_n(t)$, and the $\cdot$ denotes the time derivative.

Because $N$, the number of beads, is in general a large number, we may consider $n$ as a continuous variable, with $n \in (-N/2, N/2)$, and $s$ as a function of $n$ and $t$, i.e. $s_n = s(n, t)$. In this way, (3.10) becomes

$$
\frac{M}{N} \frac{\partial^2 s}{\partial t^2} = k \frac{\partial^2 s}{\partial n^2} - \gamma \frac{\partial s}{\partial t} + f, \quad -N/2 < n < N/2, \quad t > 0, \quad (3.11)
$$

where $f = f(n, t) = f_n(t)$.

Introducing dimensionless variables $\hat{s}$, $\hat{t}$, $\hat{n}$ and $\hat{f}$ by

$$
s \to S\hat{s}, \quad S := \sigma \sqrt{\frac{N}{\gamma k}}, \quad (3.12)
$$

$$
t \to \frac{\gamma N^2}{k} \hat{t}, \quad (3.13)
$$

$$
n \to N\hat{n}, \quad (3.14)
$$

$$
f(n, t) \to \sigma \frac{k}{\gamma N} \hat{f}(\hat{n}, \hat{t}), \quad (3.15)
$$

we get the dimensionless version of (3.11),

$$
\varepsilon \frac{\partial^2 \hat{s}}{\partial \hat{t}^2} = \frac{\partial^2 \hat{s}}{\partial \hat{n}^2} - \frac{\partial \hat{s}}{\partial \hat{t}} + \hat{f}, \quad -\frac{1}{2} < \hat{n} < \frac{1}{2}, \quad \hat{t} > 0, \quad (3.16)
$$

with

$$
\varepsilon := \frac{Mk}{\gamma^2 N^3}. \quad (3.17)
$$

Using $k = 2\nu S^l_a k_B T / L_{eq}^2$ from [10], and the relations

$$
k_B N_A = R, \quad MN_A = m, \quad (3.18)
$$

where $N_A$ is Avogadro’s number, $R$ is the gas constant and $m$ is the mass of one mole, we write $\varepsilon$ as

$$
\varepsilon = \frac{2\nu S^l_a mRT}{\gamma^2 N^3 N_A^2 L_{eq}^2}. \quad (3.19)
$$
We know that (see [10] and [11])

\[ 2\nu \approx 10, \quad S_a^l \approx 10^3, \quad m \approx 10^3 \text{kg}, \quad R \approx 10^{\frac{1}{2}} \text{kg m}^2\text{s}^2\text{K}, \quad T \approx 10^2 \text{K}, \]

\[ \gamma \approx 10^{-12} \text{kg s}^{-1}, \quad N \approx 10^3, \quad N_A \approx 10^{23}, \quad L_{eq} \approx 10^{-6} \text{m}, \quad (3.20) \]

so we have that \( \varepsilon \approx 10^{-9} \). This is very small, so we can neglect the first term. After doing so, and omitting the hats, we find for (3.16) the reduced form

\[ \frac{\partial s}{\partial t} = \frac{\partial^2 s}{\partial n^2} + f, \quad -\frac{1}{2} < n < \frac{1}{2}, \quad t > 0, \quad (3.21) \]

where \( f \) is characterized by

\[ \langle f(n,t) \rangle = 0, \quad \langle f(m,t_1)f(n,t_2) \rangle = \delta(m-n)\delta(t_1-t_2). \quad (3.22) \]

In the equilibrium situation, where \( \frac{\partial}{\partial t} = 0 \) and \( f = 0 \), the position no longer depends on time and this equilibrium position is no longer a stochastic variable. Hence, in this state we can write \( s = s_{eq} = s_{eq}(n) \). In equilibrium, the polymer has its known equilibrium length \( L_{eq} \), the free or unstretched total length of the springs, so in dimensionless form

\[ s_{eq} \left( \frac{1}{2} \right) - s_{eq} \left( -\frac{1}{2} \right) = \frac{L_{eq}}{S}. \quad (3.23) \]

In the equilibrium situation, (3.21) gives

\[ \frac{d^2 s_{eq}}{dn^2} = 0, \quad -\frac{1}{2} < n < \frac{1}{2}, \quad (3.24) \]

and using (3.23), we get

\[ s_{eq}(n) = \frac{L_{eq}}{S} n + s_{eq}(0). \quad (3.25) \]

To obtain boundary conditions, we suppose that a tensile force is acting on the chain ends. There are many ways for the chain end to leave the tube and only one way to retract into the tube, so this imbalance tends to increase the contour length; we model this by this tensile force. This force should be independent of the configuration, equilibrium or not, so from the equilibrium configuration (3.25) we see that we have to impose

\[ \frac{\partial s}{\partial n} \left( \frac{1}{2}, t \right) = \frac{L_{eq}}{S}, \quad \frac{\partial s}{\partial n} \left( -\frac{1}{2}, t \right) = \frac{L_{eq}}{S}. \quad (3.26) \]

The initial position is chosen as the position where the polymer has its equilibrium length, and all springs have the same length, so

\[ s(n,0) = \frac{L_{eq}}{S} n. \quad (3.27) \]

To solve the differential equation (3.21) with boundary conditions (3.26) and initial condition (3.27), we try the following ansatz

\[ s(n,t) = \frac{L_{eq}}{S} n + \sum_{k=0}^{\infty} y_k(t) \cos \left( \frac{k\pi}{2} n + \frac{1}{2} \right). \quad (3.28) \]
This ansatz automatically satisfies the boundary conditions (3.26), and also the initial condition (3.27), provided that \( y_k(0) = 0 \). The new unknown variables are now \( y_k(t), k = 0, 1, 2, \ldots \). Accordingly, we assume that we can write \( f(n, t) \) as
\[
f(n, t) = \sum_{k=0}^{\infty} f_k(t) \cos \left( k\pi \left( \frac{1}{2} + n \right) \right),
\]
(3.29)
where again \( f_k(t), k = 0, 1, \ldots, \) are stochastic functions (see also (3.35)-(3.36)). The inverse of (3.29) states that
\[
f_0(t) = \int_{-1/2}^{1/2} f(n, t) dn, \quad (3.30)
\]
and, for \( k \geq 1 \),
\[
f_k(t) = 2 \int_{-1/2}^{1/2} f(n, t) \cos \left( k\pi \left( \frac{1}{2} + n \right) \right) dn. \quad (3.31)
\]
The corresponding differential equation for \( y_k \) follows now from (3.21) as
\[
\dot{y}_k(t) = -\left( k\pi \right)^2 y_k(t) + f_k(t), \quad t > 0, \quad (3.32)
\]
with initial condition
\[
y_k(0) = 0, \quad k = 0, 1, \ldots \quad (3.33)
\]
The solution of (3.32) with initial condition (3.33) reads
\[
y_k(t) = \int_0^t e^{(k\pi)^2(\tau-t)} f_k(\tau) \, d\tau. \quad (3.34)
\]
From (3.29), and because \( f \) is normally distributed, we infer that \( f_k \) is normally distributed with, according to (3.22) and with use of (3.31),
\[
\langle f_0(t) \rangle = 0, \quad \langle f_0(t_1) f_0(t_2) \rangle = \delta(t_1 - t_2), \quad (3.35)
\]
\[
\langle f_k(t) \rangle = 0, \quad \langle f_k(t_1) f_k(t_2) \rangle = 2\delta_{kl} \delta(t_1 - t_2), \quad k = 1, 2, \ldots, l = 0, 1, 2, \ldots \quad (3.36)
\]
Using this in (3.34), we see that \( y_k \) is normally distributed with (we assume from now on that \( t_1 \geq t_2 \))
\[
\langle y_0(t) \rangle = 0, \quad \langle y_0(t_1) y_0(t_2) \rangle = t_2, \quad \langle y_k(t) \rangle = 0, \quad (3.37)
\]
\[
\langle y_k(t_1) y_l(t_2) \rangle = \frac{\delta_{kl}}{k^2 \pi^2} \left( e^{-k^2\pi^2(t_1-t_2)} - e^{-k^2\pi^2(t_1+t_2)} \right), \quad k = 1, 2, \ldots, l = 0, 1, \ldots \quad (3.38)
\]
For the two ends of the polymer we introduce their displacements \( x_0 \) and \( x_1 \) by
\[
x_0(t) := s\left(-\frac{1}{2}, t\right) - s\left(-\frac{1}{2}, 0\right) = \sum_{n=0}^{\infty} y_n(t), \quad x_1(t) := s\left(\frac{1}{2}, t\right) - s\left(\frac{1}{2}, 0\right) = \sum_{n=0}^{\infty} (-1)^n y_n(t). \quad (3.39)
\]
We again see that these displacements, being the sum of normally distributed variables, are normally distributed, with
\[
\langle x_0(t) \rangle = 0, \quad \langle x_0(t_1) x_0(t_2) \rangle = t_2 + \frac{1}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{n^2} \left( e^{-n^2\pi^2(t_1-t_2)} - e^{-n^2\pi^2(t_1+t_2)} \right), \quad (3.40)
\]
\[
\langle x_1(t) \rangle = 0, \quad \langle x_1(t_1) x_1(t_2) \rangle = t_2 + \frac{1}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{n^2} \left( e^{-n^2\pi^2(t_1-t_2)} - e^{-n^2\pi^2(t_1+t_2)} \right), \quad (3.41)
\]
\[
\langle x_0(t_1) x_1(t_2) \rangle = t_2 + \frac{1}{\pi^2} \sum_{n=0}^{\infty} \frac{(-1)^n}{n^2} \left( e^{-n^2\pi^2(t_1-t_2)} - e^{-n^2\pi^2(t_1+t_2)} \right). \quad (3.42)
\]
So, in particular we can define the variance function $C^2_v(t)$ and the covariance function $C^2_c(t)$ as

\[
\langle x_0^2(t) \rangle = \langle x_1^2(t) \rangle = C^2_v(t) := t + \frac{1}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \left(1 - e^{-2n^2\pi^2t}\right), \tag{3.43}
\]

\[
\langle x_0(t)x_1(t) \rangle = C^2_c(t) := t + \frac{1}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \left(1 - e^{-2n^2\pi^2t}\right). \tag{3.44}
\]

We see that we can describe the motion of the end points as Brownian motion with a time-dependent variance; see Figure 5.

![Figure 5: Example of the Brownian motion for both end points. In the spring-bead model, the length of the polymer is not constant, however the two end points are not independent.](image)

We try to describe this Brownian motion, derived from the spring-bead model, with another model, that might be easier to deal with: the single spring-model. In this model, we have two points, $x_0$ and $x_1$, with zero mass. They are connected by a spring with a time-dependent spring constant $\dot{k}(t)$, and suffer from friction with friction coefficient 1, (we are using dimensionless variables). We also impose independent Brownian motion on both points, denoted by $\eta_0$ and $\eta_1$, with zero mean and time-dependent variance $\sigma^2(t)$. The functions $\dot{k}$ and $\sigma^2$ will be determined later. Altogether, this gives the following mathematical model:

\[
\begin{pmatrix}
\dot{x}_0(t) \\
\dot{x}_1(t)
\end{pmatrix} + \dot{k}(t) \mathbf{B} \begin{pmatrix}
x_0(t) \\
x_1(t)
\end{pmatrix} = \begin{pmatrix}
\eta_0(t) \\
\eta_1(t)
\end{pmatrix}, \quad \begin{pmatrix}
x_0(0) \\
x_1(0)
\end{pmatrix} = \begin{pmatrix}
0 \\
0
\end{pmatrix}, \tag{3.45}
\]

where

\[
\mathbf{B} = \begin{pmatrix}
1 & -1 \\
-1 & 1
\end{pmatrix}. \tag{3.46}
\]

This two-dimensional differential equation is solved by

\[
\begin{pmatrix}
x_0(t) \\
x_1(t)
\end{pmatrix} = \int_0^t \begin{pmatrix}
\cosh(k(t) - k(\tau))\eta_0(\tau) + \sinh(k(t) - k(\tau))\eta_1(\tau) \\
\sinh(k(t) - k(\tau))\eta_0(\tau) + \cosh(k(t) - k(\tau))\eta_1(\tau)
\end{pmatrix} e^{k(\tau) - k(t)} d\tau. \tag{3.47}
\]
We see that $\langle x_0(t) \rangle = \langle x_1(t) \rangle = 0$, the same result as the previous spring-bead model; see (3.40) and (3.41). For equivalence of the spring-bead model and the single-spring model, we also need the variance and the covariance to be the same. Because the processes are so-called Gaussian processes, this is also a sufficient condition. To calculate the variance we evaluate $\langle x_0^2(t) \rangle$ using (3.47), $\langle \eta_0(t_1)\eta_0(t_2) \rangle = \langle \eta_1(t_1)\eta_1(t_2) \rangle = \sigma^2(t)\delta(t_1 - t_2)$, and $\langle \eta_0(t_1)\eta_1(t_2) \rangle = 0$ to find

$$\langle x_0^2(t) \rangle = \left\langle \int_0^t \int_0^t e^{k(\tau_1) + k(\tau_2) - 2k(t)} \left( \cosh(k(t) - k(\tau_1))\eta_0(\tau_1) + \sinh(k(t) - k(\tau_1))\eta_1(\tau_1) \right) \right. \left. \cdot \left( \cosh(k(t) - k(\tau_2))\eta_0(\tau_2) + \sinh(k(t) - k(\tau_2))\eta_1(\tau_2) \right) d\tau_1 d\tau_2 \right\rangle = \int_0^t \sigma^2(\tau) e^{2(k(t) - k(t))} \cosh(2(k(t) - k(\tau))) d\tau. \quad (3.48)$$

In the same way, we calculate $\langle x_0(t)x_1(t) \rangle$ to get the covariance:

$$\langle x_0(t)x_1(t) \rangle = \left\langle \int_0^t \int_0^t e^{k(\tau_1) + k(\tau_2) - 2k(t)} \left( \cosh(k(t) - k(\tau_1))\eta_0(\tau_1) + \sinh(k(t) - k(\tau_1))\eta_1(\tau_1) \right) \right. \left. \cdot \left( \sinh(k(t) - k(\tau_2))\eta_0(\tau_2) + \cosh(k(t) - k(\tau_2))\eta_1(\tau_2) \right) d\tau_1 d\tau_2 \right\rangle = \int_0^t \sigma^2(\tau) e^{2(k(t) - k(t))} \sinh(2(k(t) - k(\tau))) d\tau. \quad (3.49)$$

Comparing (3.43)–(3.44) with (3.48)–(3.49), we can state that the two models are equivalent, provided $\sigma^2(t)$ and $k(t)$ are such that

$$\int_0^t \sigma^2(\tau) e^{2(k(t) - k(t))} \cosh(2(k(t) - k(\tau))) d\tau = C^2_v(t), \quad (3.50)$$

$$\int_0^t \sigma^2(\tau) e^{2(k(t) - k(t))} \sinh(2(k(t) - k(\tau))) d\tau = C^2_c(t). \quad (3.51)$$

Adding and subtracting (3.50) and (3.51), we obtain

$$C^2_v(t) + C^2_c(t) = \int_0^t \sigma^2(\tau) d\tau, \quad (3.52)$$

$$C^2_v(t) - C^2_c(t) = \int_0^t \sigma^2(\tau) e^{4(k(t) - k(t))} d\tau. \quad (3.53)$$

From the first equation we see that

$$\sigma^2(t) = (C^2_v)'(t) + (C^2_c)'(t), \quad (3.54)$$

and, using this, we get from the second equation that

$$\dot{k}(t) = \frac{(C^2_v)'(t)}{2(C^2_v(t) - C^2_c(t))}. \quad (3.55)$$
In conclusion, we state that we can model the motion of the two end points $x_0$ and $x_1$ by the initial value problem

$$
\begin{pmatrix}
\dot{x}_0(t) \\
\dot{x}_1(t)
\end{pmatrix}
+ \dot{k}(t) \mathbf{B} 
\begin{pmatrix}
x_0(t) \\
x_1(t)
\end{pmatrix}
= \begin{pmatrix}
\eta_0(t) \\
\eta_1(t)
\end{pmatrix},
\begin{pmatrix}
x_0(0) \\
x_1(0)
\end{pmatrix} = \begin{pmatrix}
0 \\
0
\end{pmatrix},
$$

(3.56)

where

$$
\mathbf{B} = \begin{pmatrix}
1 & -1 \\
-1 & 1
\end{pmatrix},
$$

(3.57)

and

$$
\dot{k}(t) = \frac{(C_v^2)'(t)}{2(C_c^2(t) - C_v^2(t))},
$$

(3.58)

and

$$
\langle \eta_0^2(t) \rangle = \langle \eta_1^2(t) \rangle = (C_v^2)'(t) + (C_c^2)'(t),
$$

(3.59)

with $\eta_0$ and $\eta_1$ independent and $C_v^2$ and $C_c^2$ given by (3.43) and (3.44). The system (3.56) will be used to determine the properties of $x_0$ and $x_1$.

We see that the solution, whatever it will be, will be determined by $C_v^2$ and $C_c^2$. Therefore, we write them in their dimensionful versions. This gives us

$$
C_v^2(t) = \frac{\sigma^2}{\gamma^2 N t} + \frac{\sigma^2 N}{\pi^2 k} \sum_{n=1}^{\infty} \frac{1}{n^2} \left( 1 - e^{-\frac{2n^2 \sigma^2 k}{\gamma^2 N t}} \right),
$$

(3.60)

$$
C_c^2(t) = \frac{\sigma^2}{\gamma^2 N t} + \frac{\sigma^2 N}{\pi^2 k} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \left( 1 - e^{-\frac{2n^2 \sigma^2 k}{\gamma^2 N t}} \right).
$$

(3.61)

Using, from Doi and Edwards, [10], that $\sigma^2 = 2\gamma k_B T$ and $k = 3k_BT/b^2$, we obtain

$$
C_v^2(t) = \frac{2k_BT}{\gamma N} t + \frac{2N b^2}{3\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \left( 1 - e^{-\frac{3n^2 \sigma^2 k}{\gamma N b^2 T}} \right),
$$

(3.62)

$$
C_c^2(t) = \frac{2k_BT}{\gamma N} t + \frac{2N b^2}{3\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \left( 1 - e^{-\frac{3n^2 \sigma^2 k}{\gamma N b^2 T}} \right).
$$

(3.63)

Now we introduce, using the same names as [10], the Rouse time $\tau_R$ and the reptation time $\tau_d$ as

$$
\tau_R := \frac{\gamma N b^2}{3\pi^2 k_B T}, \quad \tau_d := \frac{\gamma N L_{eq}^2}{\pi^2 k_B T},
$$

(3.64)

so we can write

$$
C_v^2(t) = \frac{2L_{eq}^2}{\pi^2 \tau_d} t + \frac{2L_{eq} \tau_R}{\pi^2 \tau_d} \sum_{n=1}^{\infty} \frac{1}{n^2} \left( 1 - e^{-\frac{2n^2 \sigma^2 k}{\gamma N b^2 T}} \right),
$$

(3.65)

$$
C_c^2(t) = \frac{2L_{eq}^2}{\pi^2 \tau_d} t + \frac{2L_{eq} \tau_R}{\pi^2 \tau_d} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \left( 1 - e^{-\frac{2n^2 \sigma^2 k}{\gamma N b^2 T}} \right),
$$

(3.66)

and we see that the process is determined by two characteristic times, $\tau_R$ and $\tau_d$. The Rouse time $\tau_R$ is characteristic for changes in arm length, while the reptation time $\tau_d$ is characteristic for the motion of the mass centre.
This model is not finished yet, and it will not be so during this project. One should continue this analysis to derive a solution for the expected unrelaxed length of the polymer; this can be done in the same way as will be done further on in Sections 3.2.2 – 3.2.6. Because we need a solution in order to simulate the relaxation, we look at a more simple model in the next section. In this simpler model, the length of the polymer is taken constant.

### 3.1.2 Diffusion model

This subsection is taken from Doi and Edwards, [10, § 6.2.2].

In the initial condition, at time $t = 0$, the chain is in its tube. The tube at that moment will be called the original tube. The contour length $s$ is measured along this original tube. On one end $s = 0$, on the other end $s = L_{eq}$, because $L_{eq}$ is the length of the original tube.

In this model, the chain is moving through the tube by diffusion. If the chain has left a tube segment at a certain moment, this tube segment is forgotten. At each time $t$, a part of the tube, of length $\sigma(t)$, has never been left; see Figure 6. To calculate this length $\sigma(t)$, we consider a tube segment at position $s$. The probability that this tube segment has not been forgotten at time $t$ is called $\psi(s, t)$. Then the average length $\langle \sigma(t) \rangle$ is calculated as

$$ \langle \sigma(t) \rangle = \int_0^{L_{eq}} \psi(s, t) ds. \quad (3.67) $$

![Figure 6: Reptation according to the diffusion model, where the length of the polymer is fixed. The remaining tube length is denoted by $\sigma(t)$.

consider a tube segment at position $s$. The probability that this tube segment has not been forgotten at time $t$ is called $\psi(s, t)$. Then the average length $\langle \sigma(t) \rangle$ is calculated as

$$ \langle \sigma(t) \rangle = \int_0^{L_{eq}} \psi(s, t) ds. \quad (3.67) $$

19
This \( \psi(s, t) \) we can calculate by conditioning on the distance \( \xi \) moved by the chain. So we introduce \( \Psi(\xi, t, s) \), the probability that the ends of the chain have not reached the segment \( s \) of the original tube and the chain moves the distance \( \xi \), and then

\[
\psi(s, t) = \int_{s-L_{eq}}^{s} \Psi(\xi, t, s) d\xi,
\]

(3.68)

because \( \xi \) can only obtain values between \( s - L_{eq} \) and \( s \). Following [10, p. 195], we note that the probability \( \Psi \) satisfies the one-dimensional diffusion equation

\[
\frac{\partial \Psi}{\partial t} = D_c \frac{\partial^2 \Psi}{\partial \xi^2}, \quad s - L_{eq} < \xi < s, \quad t > 0, \quad 0 < s < L_{eq},
\]

(3.69)

with the initial condition

\[
\Psi(\xi, 0, s) = \delta(\xi),
\]

(3.70)

and the boundary conditions

\[
\Psi(s, t, s) = 0,
\]

(3.71)

\[
\Psi(s - L_{eq}, t, s) = 0.
\]

(3.72)

The differential equation (3.69) together with its initial conditions is solved by

\[
\Psi(\xi, t, s) = \frac{2}{L_{eq}} \sum_{p=1}^{\infty} \sin \left( \frac{p \pi s}{L_{eq}} \right) \sin \left( \frac{p \pi (s - \xi)}{L_{eq}} \right) \exp(-p^2 \frac{t}{\tau_d}),
\]

(3.73)

where

\[
\tau_d = \frac{L_{eq}^2}{D_c \pi^2},
\]

(3.74)

and it can be shown that this \( \tau_d \) is the same as the one in (3.64); see [10, p. 196]. Combining (3.68) and (3.73), we see that

\[
\psi(s, t) = \frac{4}{\pi} \sum_{p \text{ odd}} \frac{1}{p} \sin \left( \frac{p \pi s}{L_{eq}} \right) \exp \left( -p^2 \frac{t}{\tau_d} \right),
\]

(3.75)

which, when used in (3.67) yields

\[
\langle \sigma(t) \rangle = L_{eq} \frac{8}{\pi^2} \sum_{p=1}^{\infty} \frac{1}{(2p - 1)^2} \exp \left( -(2p - 1)^2 \frac{t}{\tau_d} \right).
\]

(3.76)

Because \( \langle \sigma(t) \rangle \) is the average length of the tube that has not been forgotten at time \( t \), we infer that, according to the tube model, it must be equal to the length of polymer that has not relaxed at \( t \). Hence, we can give the length of the polymer that has not relaxed at time \( t \), denoted by \( L(t) \), by

\[
L(t) = L_{eq} \frac{8}{\pi^2} \sum_{p=1}^{\infty} \frac{1}{(2p - 1)^2} \exp \left( -(2p - 1)^2 \frac{t}{\tau_d} \right).
\]

(3.77)

In the next section we will show how to use this result to derive the relaxation equation for reptation.
3.1.3 Relaxation equation for reptation

A typical time for the reptation process, in both the bead-spring and the diffusion model, is the reptation time $\tau_d$. As we saw before in (3.64), the reptation time can be estimated by

$$\tau_d = \frac{\gamma N L_{eq}^2}{\pi^2 k_B T}. \quad (3.78)$$

We use (3.3) to express the length $L_{eq}$ as $L_{eq} = 5/4aS_{l}^{l}$. In both models, for simplicity we assumed a uniform chain, meaning that each bead has the same mass and the same friction coefficient. This is not true in general as we will see later, because arm remainders will increase the mass and the friction of the bead they are attached to. We try to incorporate this effect by identifying the term $\gamma N$ as the total friction in our uniform-chain model. As we will see in Section 3.3 furtheron, the total friction is proportional to the total amount of material in the polymer and to the amount of material in the tube. Therefore, we replace the term $\gamma N$ in (3.78) by $\hat{\gamma} S_{w}^{w} A \Phi_{ST}$, where $\hat{\gamma}$ is a friction constant only depending on the chemical properties of the polymer, $S_{w}^{w}$ is the total amount of material, measured in entanglement lengths, and $\Phi_{ST}$ is the tube density, which will be defined in Section 3.4. In the present situation without arm remainders, obviously $S_{b}^{l} = S_{b}^{w}$, but we will encounter situation later in Section 3.3 where they are not equal. Equation (3.78) is, with these changes, written as

$$\tau_d(t) = \frac{25\hat{\gamma} \Phi_{ST}(t) a^2(S_{l}^{l})^2 S_{w}^{w}}{16\pi^2 k_B T}. \quad (3.79)$$

Hence, once the model parameters $\hat{\gamma}$ and $a$ are known the reptation time can be calculated. These parameters, or rather the Rouse relaxation time $\tau_R$, which is already defined in (3.64), but can be rewritten, using $\gamma N = \hat{\gamma} S_{l}^{l}$ (for linear polymers $S_{b}^{l} = S_{l}^{l}$ and at the start of reptation of a linear polymer $\Phi_{ST} = 1$) and the relations (3.3) and (3.4), as

$$\tau_R = (S_{l}^{l})^2 \frac{5\hat{\gamma} a^2}{12\pi^2 k_B T}, \quad (3.80)$$

can be obtained from experiments with linear polymers.

Using the equilibrium time $\tau_E$, defined as

$$\tau_R = (S_{l}^{l})^2 \tau_E, \quad (3.81)$$

we can write (3.79) as

$$\tau_d(t) = 2\nu \tau_E \Phi_{ST}(t) (S_{l}^{l})^2 S_{w}^{w}, \quad (3.82)$$

where $\nu$ is the dimensionless constant $15/8$. Once the reptation time $\tau_d$ is known, our reptation model is ready to be implemented in a numerical code. In the computations presented in Chapter 5, the diffusion model is used. In a later stage the spring-bead model can be implemented.

In the derivation of the diffusion model in Section 3.1.2, we assumed the relaxation time $\tau_d$ to be constant, but we see in (3.82) that it is (slightly) time dependent. However, because $\tau_d$ is only slowly varying in time, when we look at a small time interval, we can take the relaxation time constant. So we can use the results obtained above to develop a local solution, go one step further in time, find a new local solution, etc. To use the results from the diffusion model for $t > 0$, (3.77) is first approximated by its dominant term, i.e. $p = 1$, and after that
transformed to a logarithmic timescale $k = \log(t)$ ($L(t) = L(e^k) = L_d(k)$). For the fraction of relaxed material $f$ we thus obtain

$$f(k) := 1 - \frac{L_d(k)}{L_{eq}} = 1 - \frac{8}{\pi^2} \exp\left(-\frac{1}{\tau_d} e^k\right), \quad (3.83)$$

The unrelaxed fraction of a reptating polymer one timestep later can be calculated by

$$f(k + \Delta k) = f(k) + \Delta f(k) = f(k) + \frac{\Delta k}{\tau_d} (1 - f(k)) e^k. \quad (3.84)$$

With this equation, the relaxation due to reptation can be calculated, as will be done in Chapter 4. However, we will need a similar equation to calculate the relaxation due to arm retraction, the other method of relaxation. This equation will be derived in the next section.

### 3.2 Arm retraction

In this section, we describe the arm retraction of branched polymers. Reptation is impossible for branched polymers, because the branch points are essentially fixed; see Figure 7. For a branched polymer, relaxation is achieved by another mechanism, namely arm retraction. As the branch points are essentially fixed, the only moving segments are the free arms; see Figure 8 for an example.

It is clear that this type of motion is much slower than reptation. Relaxation times due to arm retraction are therefore much larger than relaxation times due to reptation. The arm is only relaxed after it has retracted itself along its entire original tube; a process of which the duration will be shown to be exponential in the arm length. The motion of the end points of a retracting arm is described by the Ball-McLeish equation, which is derived below.

#### 3.2.1 Derivation of the stochastic differential equation

To describe the motion of a polymer arm, we again use the Rouse model. The model is the same as in Subsection 3.1.1, only now the beads are numbered from 0 at the backbone to $N$.

![Figure 7: An example of a branched polymer, surrounded by a tube.](image_url)
at the free end. Doing the same analysis as for the reptation model in Subsection 3.1.1, we arrive, using the same notation at the stochastic partial differential equation

\[ \frac{\partial s}{\partial t} = \frac{\partial^2 s}{\partial n^2} + f, \quad (3.85) \]

where now \( t > 0 \) and \( 0 < n < 1 \), and again

\[ \langle f(t) \rangle = 0, \quad \langle f(n, t_1) f(m, t_2) \rangle = \delta(m - n)\delta(t_1 - t_2). \quad (3.86) \]

Because the first bead is connected to the backbone, we see that \( s(0, t) = 0 \). To get a second boundary condition, we again choose to apply a tensile force acting on the free end. This force should be independent of the configuration, so we look at the equilibrium expected situation, where \( \partial/\partial t = 0 \) and \( f = 0 \), and we write \( \langle s(n, t) \rangle = s_{eq}(n) \). We first notice that the average length of the total chain in equilibrium is equal to \( L_{eq} \), so in our dimensionless variables

\[ s_{eq}(1) = \frac{L_{eq}}{S}. \quad (3.87) \]

Taking averages in (3.85) for the equilibrium state gives

\[ \frac{d^2 s_{eq}}{dn^2} = 0, \quad (3.88) \]

so using (3.87) and \( s_{eq}(0) = 0 \), which follows from \( s(0, t) = 0 \), we get

\[ s_{eq}(n) = \frac{L_{eq}}{S} n, \quad (3.89) \]

so we know that

\[ \frac{ds_{eq}}{dn} = \frac{L_{eq}}{S}. \quad (3.90) \]

Since we assume that this boundary condition for the special equilibrium state is the same as the general boundary condition, we use here as boundary conditions

\[ s(0, t) = 0, \quad \frac{\partial s}{\partial n}(1, t) = \frac{L_{eq}}{S}. \quad (3.91) \]
The initial condition is again chosen as the situation in which the arm has its equilibrium length and all springs have the same length, so

\[ s(n, 0) = \frac{L_{eq}}{S} n. \]  

(3.92)

To solve the differential equation (3.85) with boundary conditions (3.91) and initial condition (3.92), we try the ansatz

\[ s(n, t) = \frac{L_{eq}}{S} n + \sum_{k=1}^{\infty} y_k(t) \sin \left( \frac{\pi(2k-1)n}{2} \right), \]

(3.93)

so

\[ y_k(t) = 2 \int_0^1 \sin \left( \frac{\pi (2k-1)}{2} n \right) \left( s(n, t) - \frac{L_{eq}}{S} n \right) dn, \quad k = 1, 2, \ldots. \]

(3.94)

This ansatz, which is different from (3.28), is chosen such that it automatically satisfies boundary conditions (3.91), and also the initial condition (3.92), provided that \( y_k(0) = 0 \). The equation for motion for \( y_k \), derived from (3.85), becomes

\[ \dot{y}_k(t) = -\frac{(2k-1)^2\pi^2}{4} y_k(t) + f_k(t), \]

(3.95)

where

\[ f_k(t) = 2 \int_0^1 \sin \left( \frac{\pi (2k-1)}{2} n \right) f(n, t) dn, \]

(3.96)

so

\[ \langle f_k(t) \rangle = 0, \quad \langle f_k(t_1) f_l(t_2) \rangle = 2\delta_{kl}\delta(t_1 - t_2). \]

(3.97)

We can express \( y_k \) in the stochastic force \( f_k \) (assuming that \( y_k(-\infty) \) remains finite) as

\[ y_k(t) = \int_{-\infty}^t f_k(\tau) \exp \left( \frac{(2k-1)^2\pi^2}{4}(\tau - t) \right) d\tau, \]

(3.98)

from which we derive that

\[ \langle y_k(t) \rangle = 0, \quad \langle y_k(t)y_l(t + \Delta t) \rangle = \frac{4\delta_{kl}}{(2k-1)^2\pi^2} e^{-\frac{(2k-1)^2\pi^2}{4}\Delta t}. \]

(3.99)

Because for \( L(t) \), the length of the arm, holds

\[ L(t) = S (s(1, t) - s(0, t)) = L_{eq} - S \sum_{k=1}^{\infty} (-1)^k y_k(t), \]

(3.100)

we see that

\[ \langle L^2(t) \rangle = L_{eq}^2 + S^2 \sum_{k=1}^{\infty} \langle y_k^2(t) \rangle = L_{eq}^2 + \sum_{k=1}^{\infty} \frac{4S^2}{(2k-1)^2\pi^2} = L_{eq}^2 + \frac{S^2}{2}. \]

(3.101)

Using \( S^2 = \sigma^2 N/k\gamma \) from (3.12), we arrive at

\[ \langle L^2(t) \rangle = L_{eq}^2 + \frac{\sigma^2 N}{2k\gamma}. \]

(3.102)
We know from [10] that $\sigma^2 = 2\gamma k_B T$ and $k = 3k_B T/b^2$, so

$$\langle L^2(t) \rangle = L^2_{eq} + \frac{N b^2}{3}. \quad (3.103)$$

Summarizing, we have

$$\langle L(t) \rangle = L_{eq}, \quad \langle L^2_{eq}(t) \rangle - \langle L(t) \rangle^2 = \frac{N b^2}{3}. \quad (3.104)$$

After introducing $x(t) = L - L(t)$ and using the relations (3.4) and (3.3), we see that (using the previously introduced dimensionless constant $\nu := 15/8$)

$$\langle x(t) \rangle = 0, \quad \langle x^2(t) \rangle = \frac{L^2_{eq}}{2\nu S^l_a}. \quad (3.105)$$

We identify this motion $x(t)$, following [10], with a Brownian motion of a particle in a harmonic potential, which is defined by

$$\frac{dU}{dx}(x(t)) = -\gamma \dot{x}(t) + \eta(t), \quad (3.106)$$

where $U(x)$ is the potential, $\gamma$ is the friction coefficient as given before, and $\eta(t)$ is a stochastic variable of white noise type, with zero mean and variance $\sigma^2$. Because the potential is harmonic, we write $U(x) = Ax^2$, with $A$ a yet unknown constant, such that (3.106) becomes

$$2Ax = -\gamma \dot{x} + \eta, \quad (3.107)$$

for which we can write down the solution

$$x(t) = \frac{1}{\gamma} \int_{-\infty}^{t} e^{\frac{2\gamma \tau}{4A}} \eta(\tau) d\tau. \quad (3.108)$$

From this we conclude that

$$\langle x \rangle = 0, \quad \langle x^2 \rangle = \frac{\sigma^2}{4\gamma A}. \quad (3.109)$$

For thermodynamical reasons, see [14, p. 264], we know that $\sigma^2 = 2k_B T\gamma$, so to match (3.105) with (3.109) we must require that

$$A = \frac{\nu S^l_a k_B T}{L^2_{eq}}, \quad (3.110)$$

yielding the equation of motion for the end of the arm,

$$\frac{2\nu S^l_a k_B T}{L^2_{eq}} x = -\gamma \dot{x} + \eta, \quad (3.111)$$

where the stochastic force $\eta$ is characterized by

$$\langle \eta(t) \rangle = 0, \quad \langle \eta(t_1) \eta(t_2) \rangle = 2k_B T\gamma \delta(t_1 - t_2). \quad (3.112)$$

Introduce $\tau_e$ and $x_e$ by

$$\tau_e = \frac{\gamma L^2_{eq}}{2\nu S^l_a k_B T}, \quad x_e = \frac{L_{eq}}{\sqrt{2\nu S^l_a}}, \quad (3.113)$$
and replace $t \to \tau \hat{t}$, $x(t) \to x(x \hat{t})$ and $\eta(t) \to \sigma \hat{\eta}(t)/\sqrt{\tau}$ to obtain the dimensionless version of (3.111),

$$\frac{d\hat{x}}{d\hat{t}} = -\hat{x} + \sqrt{2} \hat{\eta}. \quad (3.114)$$

In this dimensionless form, the stochastic force $\hat{\eta}$ is a random variable for each $t$ with a normal distribution, such that

$$\langle \hat{\eta}(t) \rangle = 0, \quad \langle \hat{\eta}(t)\hat{\eta}(t') \rangle = \delta(t - t'). \quad (3.115)$$

Because (3.114) is a stochastic differential equation, its solution will be a stochastic function. In the next section, we will derive an equation for the density distribution of this stochastic function.

### 3.2.2 Derivation of the differential equation for the density distribution

In this subsection, we focus on the probability density that the end of the chain is at position $x$ at time $t$, given that it was originally at $x_0$ at time $t_0$ and that at no time between $t_0$ and $t$ did it move further toward the branch point than $y$. Of course this is only useful if $x_0 < y$. We denote this density by $p(x,t|x_0,t_0,y)$, or if no confusion is possible, by $p(x,t)$.

For this density the Chapman-Kolmogorov [14] equation states for all $t_1 \in \mathbb{R}$,

$$p(x,t|x_0,t_0,y) = \int_{-\infty}^{\infty} p(x,t|x_1,t_1,y)p(x_1,t_1|x_0,t_0,y)dx_1. \quad (3.116)$$

We use this in the next derivation, partly taken from [14], where $R(x)$ is an arbitrary test function with vanishing boundary terms,

$$\int_{-\infty}^{\infty} \frac{\partial p(u,t|x,t',y)}{\partial t} R(u)du$$

$$= \lim_{\tau \to 0} \frac{1}{\tau} \int_{-\infty}^{\infty} (p(u,t+\tau|x,t',y) - p(u,t|x,t',y)) R(u)du$$

$$= \lim_{\tau \to 0} \frac{1}{\tau} \int_{-\infty}^{\infty} \left( \int_{-\infty}^{\infty} p(u,t+\tau|z,t,y)p(z,t|x,t',y)dz - p(u,t|x,t',y) \right) R(u)du$$

$$= \lim_{\tau \to 0} \frac{1}{\tau} \int_{-\infty}^{\infty} \left( \int_{-\infty}^{\infty} p(u,t+\tau|z,t,y)p(z,t|x,t',y)R(u)du \right)dz - \int_{-\infty}^{\infty} p(u,t|x,t',y)R(u)du$$

$$= \lim_{\tau \to 0} \frac{1}{\tau} \left( \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left( R(z) + (u-z)R'(z) + \frac{(u-z)^2}{2}R''(z) + O((u-z)^3) \right) \times \right.$$

$$\left. \times p(u,t+\tau|z,t,y)p(z,t|x,t',y)du \right)dz - \int_{-\infty}^{\infty} p(u,t|x,t',y)R(u)du$$

26
\[ = \lim_{\tau \to 0} \frac{1}{\tau} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left( (u - z)R'(z) + \frac{(u - z)^2}{2} R''(z) + O((u - z)^3) \right) \times \]
\[ \times p(u, t + \tau | z, t, y) p(z, t | x, t', y) du dz \]
\[ = \frac{1}{\tau} \int_{-\infty}^{\infty} R'(z) \int_{-\infty}^{\infty} (u - z)p(u, t + \tau | z, t, y) du + \int_{-\infty}^{\infty} \frac{(u - z)^2}{2} p(u, t + \tau | z, t, y) du + \cdots \]
\[ \cdots + \int_{-\infty}^{\infty} O((u - z)^3) p(u, t + \tau | z, t, y) du \int_{-\infty}^{\infty} p(z, t | x, t', y) dz, \quad (3.117) \]

where we have used a Taylor-expansion for \( R(u) \) around \( u = z \), and \( \int_{-\infty}^{\infty} p(u, \cdot | \cdot) du = 1 \).

We now use the differential equation (3.114) to evaluate the inner integrals. We want to replace \( u \) by \( z + \Delta z \), and use the differential equation to express \( \Delta z \). For this, we integrate (3.114), with \( x \) replaced by \( z \), from \( t \) to \( t + \tau \), to obtain
\[ \Delta z = z(t + \tau) - z(t) = -z(t)\tau + \sqrt{2} \int_{t}^{t+\tau} \eta(t') dt' + o(\tau). \quad (3.118) \]

If we consider the integral as a limiting value of a sum, it is clear that it is a sum of normally distributed random variables, so the integral is also normally distributed. We can determine the mean value,
\[ \langle \int_{t}^{t+\tau} \eta(t') dt' \rangle = \int_{t}^{t+\tau} \langle \eta(t') \rangle dt' = 0, \quad (3.119) \]

and the variance,
\[ \langle (\int_{t}^{t+\tau} \eta(t') dt')^2 \rangle = \int_{t}^{t+\tau} \eta(t'_1) dt'_1 \int_{t}^{t+\tau} \eta(t'_2) dt'_2 = \int_{t}^{t+\tau} \int_{t}^{t+\tau} \langle \eta(t'_1) \eta(t'_2) \rangle dt'_1 dt'_2 \]
\[ = \int_{t}^{t+\tau} \int_{t}^{t+\tau} \delta(t'_1 - t'_2) dt'_1 dt'_2 = \tau. \quad (3.120) \]

So we can replace the integral in (3.118) by \( \sqrt{\tau} \eta_t \), where \( \eta_t \) is a normally distributed random variable with mean 0 and variance 1, leading to
\[ \Delta z = -z\tau + \sqrt{2\tau} \eta_t + o(\tau). \quad (3.121) \]

We return to the integrals in (3.117). Assuming that \( \tau \) is small, such that \( t + \tau \) is close to \( t \), and hence also \( u \) is close to \( z \), we may interpret \( u \) as \( z + \Delta z \), and thus replace \( u - z \) by \( \Delta z \) and use (3.121), to obtain
\[ \int_{-\infty}^{\infty} (u - z) p(u, t + \tau | z, t, y) du = \int_{-\infty}^{\infty} \Delta z p(u, t + \tau | z, t, y) du \]
\[ -z \tau + \sqrt{2 \tau} \int_{-\infty}^{\infty} \eta \eta(u, t + \tau | z, t, y) du + o(\tau). \]  
(3.122)

Taking the expected value, using \( \langle \eta \rangle = 0 \), we get
\[ \langle \int_{-\infty}^{\infty} (u - z) \eta(u, t + \tau | z, t, y) du \rangle = -z \tau + o(\tau). \]  
(3.123)

The second integral is evaluated in the same way, yielding
\[ \int_{-\infty}^{\infty} \frac{(u - z)^2}{2} \eta \eta(u, t + \tau | z, t, y) du + \tau \int_{-\infty}^{\infty} \eta^2(u, t + \tau | z, t, y) du + o(\tau). \]  
(3.124)

Taking the expected value and using \( \langle \eta \rangle = 0 \) and \( \langle \eta^2 \rangle = 1 \), we get
\[ \langle \int_{-\infty}^{\infty} \frac{(u - z)^2}{2} \eta \eta(u, t + \tau | z, t, y) du \rangle = \tau + o(\tau). \]  
(3.125)

The third integral becomes
\[ \int_{-\infty}^{\infty} O((u - z)^3) \eta \eta \eta(u, t + \tau | z, t, y) du = \int_{-\infty}^{\infty} O(\Delta z^3) \eta \eta \eta(u, t + \tau | z, t, y) du = o(\tau). \]  
(3.126)

Using these results, we see that (3.117) changes in the limit \( \tau \to 0 \), when taking expected values of the integrals, into
\[ \int_{-\infty}^{\infty} \frac{\partial p(z, t | x, t', y)}{\partial t} R(z) dz = \int_{-\infty}^{\infty} \left( -R'(z) z + R''(z) \right) p(z, t | x, t', y) dz. \]  
(3.127)

After partial integration with vanishing boundary terms, this becomes
\[ \int_{-\infty}^{\infty} \frac{\partial p(z, t | x, t', y)}{\partial t} R(z) dz = \int_{-\infty}^{\infty} \left( \frac{\partial}{\partial z} [z \ p(z, t | x, t', y)] + \frac{\partial^2}{\partial z^2} p(z, t | x, t', y) \right) R(z) dz, \]  
(3.128)

and because \( R \) is arbitrary, the differential equation for \( p = p(x, t | x_0, t_0, y) = p(x, t) \) is
\[ \frac{\partial p}{\partial t} = p + x \frac{\partial p}{\partial x} + \frac{\partial^2 p}{\partial x^2}, \quad t > 0, \ x < y. \]  
(3.129)

We are interested in the density distribution in the situation where the arm end never moved further towards the branch point than \( y \). Therefore, the boundary conditions are
\[ p(y, t) = 0, \]  
(3.130)
\[ p(-\infty, t) = 0. \]  
(3.131)
At $t = 0$, the arm started at $x_0 = \sqrt{2\nu S_0}$, so the initial condition is

$$p(x, 0) = \delta(x - x_0). \quad (3.132)$$

Next, we construct a solution for the differential equation (3.129), with boundary conditions (3.130) and (3.131), and initial condition (3.132).

### 3.2.3 Solution of the stochastic differential equation

To solve the differential equation (3.129), we try

$$p(x, t) = X(x)T(t),$$

and because the left-hand side only depends on $t$ and the right-hand side only on $x$, both sides should be constant, say $-\lambda$. So we are left with two equations,

$$T'(t) = -\lambda T(t), \quad (3.134)$$

$$X(x) + xX'(x) + X''(x) = -\lambda X(x). \quad (3.135)$$

The first is solved by

$$T(t) = Ae^{-\lambda t}. \quad (3.136)$$

In the second one, we substitute

$$X(x) = F(x)e^{-x^2/4}, \quad (3.137)$$

which gives

$$F''(x) + (\lambda + \frac{1}{2} - \frac{1}{4}x^2)F(x) = 0. \quad (3.138)$$

Two independent solutions of these equation are $D_{\lambda}(-x)$ and $D_{-\lambda-1}(ix)$, where $D$ is the parabolic cylinder function, as introduced in [15, p. 347]. Because the boundary condition (3.131) requires $X(-\infty) = 0$, we have

$$F(x)e^{-x^2/4} \to 0, \quad \text{if } x \to -\infty, \quad (3.139)$$

and as, according to [15],

$$D_{\lambda}(-x) \sim e^{-x^2/4}, \quad D_{-\lambda-1}(ix) \sim e^{x^2},$$

we see that the only allowable solution is

$$F(x) = D_{\lambda}(-x). \quad (3.140)$$

The boundary condition (3.130) requires

$$D_{\lambda}(-y) = 0, \quad (3.141)$$

which has countable many solutions for $\lambda$, which we denote by $\lambda_0(y), \lambda_1(y), \ldots$, where $\lambda_0(y) < \lambda_1(y) < \ldots$. Moreover, all $\lambda_i$ are positive [15].
At this point, we have found a set of solutions for (3.129) satisfying the boundary conditions (3.130) and (3.131),

\[ p_i(x, t) = e^{-\lambda_i(y)t} e^{-x^2/4} D_{\lambda_i(y)}(-x). \] (3.142)

The complete solution is found by superposition of these solutions,

\[ p(x, t) = \sum_{i=0}^{\infty} a_i e^{-\lambda_i(y)t} e^{-x^2/4} D_{\lambda_i(y)}(-x). \] (3.143)

The functions \( D_{\lambda_i(y)}(-x) \) form an orthogonal set on the domain \((-\infty, y)\) for \( i = 0, 1, \ldots \),

\[ \int_{-\infty}^{y} D_{\lambda_i(y)}(-x) D_{\lambda_j(y)}(-x) dx = \delta_{ij} B_i(y) = \delta_{ij} \sqrt{2\pi} \Gamma(\lambda_i(y) + 1). \] (3.144)

The values of \( a_i \) are determined by the initial condition,

\[ p(x, 0) = \delta(x - x_0). \] (3.145)

Multiplying the left- and right-hand side of (3.145) by \( e^{x^2/4} D_{\lambda_i(y)}(-x) \), using (3.143) for \( p(x, 0) \), and integrating this over \((-\infty, y)\) gives

\[ \sum_{i=0}^{\infty} a_i \int_{-\infty}^{y} D_{\lambda_i(y)}(-x) D_{\lambda_j(y)}(-x) dx = B_j(y) a_j = e^{x_0^2/4} D_{\lambda_j(y)}(-x_0). \] (3.146)

So the complete solution for the probability density function \( p(x, t|x_0, 0, y) \), the probability that the end of the arm is at place \( x \) at time \( t \), given that it started at \( x_0 \) at time \( t_0 = 0 \), and that it never moved further towards the branch point than \( y \), is

\[ p(x, t|x_0, 0, y) = e^{-(x^2 - x_0^2)/4} \sum_{i=0}^{\infty} \frac{1}{B_i(y)} D_{\lambda_i(y)}(-x_0) D_{\lambda_i(y)}(-x) e^{-\lambda_i(y)t}, \] (3.147)

where

\[ B_i(y) = \int_{-\infty}^{y} D_{\lambda_i(y)}^2(-x) dx = \sqrt{2\pi} \Gamma(\lambda_i(y) + 1), \] (3.148)

and the \( \lambda_i(y) \) are the solutions of

\[ D_{\lambda}(-y) = 0. \] (3.149)

Now that we found the probability density of the position of the end point, we will use this density in the next sections to find certain probabilities for the end point.

### 3.2.4 Chain end probability

In this subsection, we consider \( F(y, t) \), the probability that the chain end has not penetrated to \( y \) at time \( t \). This can be expressed in the probability density function \( p \) as

\[ F(y, t) = \int_{-\infty}^{y} p(x, t|x_0, 0, y) dx. \] (3.150)

Because for small \( y \) the probability will approach 0 even for small \( t \), we are only interested in \( y \gg 1 \). To get an expression for this probability, we integrate (3.129) on the domain \((-\infty, y)\) to get (using (3.130) and (3.131))

\[ \frac{\partial F}{\partial t} = \frac{\partial p}{\partial x}(y, t). \] (3.151)
Combining this with
\[ F(y, 0) = \int_{-\infty}^{y} p(x, 0)dx = \int_{-\infty}^{y} \delta(x - x_0)dx = 1, \tag{3.152} \]
using that \(x_0 < y\), we conclude that
\[ F(y, t) = 1 + \int_0^t \frac{\partial p}{\partial x}(y, \tau)d\tau. \tag{3.153} \]

Because we are only interested in \(y \gg 1\), we see that we only require the solution for \(p\) if \(x \gg 1\). The dimensionless length of the arm is \(L \gg 1\), with
\[ L = \frac{L_{eq}}{x_e}. \tag{3.154} \]
The probability that the end of the arm is still at its original place is \(F(0, t)\), while the probability that it has reached the backbone is \(1 - F(L, t)\). The average relaxed length of the arm \(L_r\), at time \(t\), therefore is
\[ L_r(t) = \int_0^L \frac{\partial F(y, t)}{\partial y} ydy + L(1 - F(L, t)), \tag{3.155} \]
or, after partial integration,
\[ L_r(t) = L - \int_0^L F(y, t)dy. \tag{3.156} \]
The average fraction of relaxed material at time \(t\), denoted by \(f(t)\), is
\[ f(t) = 1 - \frac{1}{L} \int_0^L F(y, t)dy = 1 - \frac{1}{L} \int_0^L \left( 1 + \int_0^t \frac{\partial p}{\partial x}(y, \tau)d\tau \right) dy = - \frac{1}{L} \int_0^t \frac{\partial p}{\partial x}(Ly, \tau)d\tau dy. \tag{3.157} \]

Although this is an exact solution to the problem, it is not useful, because of the infinite sum in (3.76). In the next section, we will therefore approximate the average fraction \(f(t)\).

### 3.2.5 Approximation of the density distribution

In the preceding subsection, we have seen that we are interested in the solution of the density distribution \(p\) for \(x, y \gg 1\) and \(t > 0\). For \(y \gg 1\), the asymptotic form of \(D_{\lambda}\) can be used to determine an asymptotic expression for the eigenvalues \(\lambda_i(y)\); see Miller & Good [16],
\[ \lambda_0(y) \approx \frac{y}{\sqrt{2\pi}} e^{-\frac{y^2}{4}}, \tag{3.158} \]
\[ \lambda_n(y) > n, \quad n = 1, 2, \ldots. \tag{3.159} \]

Hence, for \(y \gg 1\) and \(t \gg 1\), in the sum in (3.147), containing terms as \(\exp(-\lambda_i(y)t)\), only the \(i = 0\) term is significant. After neglecting the other terms, (3.147) becomes
\[ p(x, t|x_0, 0, y) \approx \frac{1}{B_0(y)} D_{\lambda_0(y)}(-x) D_{\lambda_0(y)}(-x_0) e^{\frac{x^2-x_0^2}{4}} e^{-\lambda_0(y)t}. \tag{3.160} \]
If \( x \gg 1 \), which will be our region of interest, we have according to [1],

\[
D_{\lambda_0(y)}(-x) \approx e^{-\frac{x^2}{4}} (1 + O(x^{-2})),
\]

and

\[
B_0(y) \approx \sqrt{2\pi},
\]

so

\[
p(x, t | x_0, 0, y) \approx \frac{1}{\sqrt{2\pi}} \exp(-\frac{x^2}{2} - \frac{yt}{\sqrt{2\pi}} e^{-\frac{y^2}{2}}).
\]

If we use this approximation in (3.157), we get

\[
f(t) = \int_0^t \int_0^t \frac{L y}{\sqrt{2\pi}} \exp(-\frac{L^2 y^2}{2} - \frac{Ly \tau}{\sqrt{2\pi}} e^{-\frac{\tau^2 y^2}{2}}) d\tau dy = 1 - \int_0^t \exp(\frac{Ly t}{\sqrt{2\pi}} e^{-\frac{\tau^2 y^2}{2}}) dy.
\]

Because we are not interested in short arms, we take \( L \gg 1 \), and investigate the integrated function. We first introduce a new variable \( k \), defined by

\[
t = \frac{A}{L} \exp(\frac{L^2}{2} k),
\]

where \( A \), the retraction constant, is a positive constant (that will be eliminated further on), so

\[
\exp(-\frac{Ly t}{\sqrt{2\pi}} e^{-\frac{\tau^2 y^2}{2}}) = \exp(-\frac{yA}{\sqrt{2\pi}} e^{\frac{L^2(k-y^2)}{2}}).
\]

We see that in the limit \( L \to \infty \),

\[
\exp(-\frac{yA}{\sqrt{2\pi}} e^{\frac{L^2(k-y^2)}{2}}) \to \begin{cases} 1 & \text{if } k < y^2, \\ 0 & \text{if } k > y^2. \end{cases}
\]

Therefore, the integral can be approximated for \( L \gg 1 \) by

\[
\int_0^1 \exp(-\frac{yA}{\sqrt{2\pi}} e^{\frac{L^2(k-y^2)}{2}}) dy = \begin{cases} 1 & \text{if } k < 0, \\ 1 - \sqrt{k} & \text{if } 0 \leq k < 1, \\ 0 & \text{if } 1 \leq k. \end{cases}
\]

The result of this approximation is depicted in Figure 9.

Hence, the average fraction of relaxed material, \( f(t) \), is

\[
f(t) = 1 - \int_0^1 \exp(-\frac{Ly t}{\sqrt{2\pi}} e^{-\frac{\tau^2 y^2}{2}}) dy = \begin{cases} 0 & \text{if } t < \frac{A}{L}, \\ \sqrt{\frac{2\log(\frac{A}{L})}{L^2}} & \text{if } \frac{A}{L} \leq t < \frac{A}{L} e^{\frac{L^2}{2}}, \\ 1 & \text{if } \frac{A}{L} e^{\frac{L^2}{2}} \leq t. \end{cases}
\]

The starting time for relaxation therefore is \( t = \frac{A}{L} e^{\frac{L^2}{2} f^2} \), \( 0 < f < 1 \).
Returning to the dimensional variable $\tilde{t}$, this relation reads
\[
\tilde{t} = \frac{A\tau_e}{L} \exp\left(\frac{L^2_{eq} f^2}{2x_e^2}\right) = \frac{A\gamma L^2_{eq}}{2(\nu S_l)^{3/2} k_BT} e^{\nu S_l f^2}.
\] (3.171)

This is usually written as a differential equation for $k = \log(\tilde{t})$, the logarithmic time,
\[
\frac{\partial f}{\partial k} = \frac{1}{2\nu S_l f'},
\] (3.172)

with initial condition
\[
f(k_0) = 0, \quad k_0 = \log\left(\frac{A\gamma L^2_{eq}}{2(\nu S_l)^{3/2} k_BT}\right).
\] (3.173)

Using (3.3), we can write (3.173) as
\[
f(k_0) = 0, \quad k_0 = \log(t_0) + \log(\frac{\gamma}{\gamma}) + \frac{1}{2} \log(S_l^t),
\] (3.174)

where $\gamma$ is the friction coefficient of a piece of polymer with one entanglement length, and
\[
t_0 = \frac{5A a^2 \dot{\gamma}}{12\nu^{1/2} k_BT}.
\] (3.175)

is the starting time. It is this starting time, that can be found from experiments. Using $\tau_E$ as defined in (3.81), we can write this as
\[
t_0 = \frac{\pi^2}{\nu^{1/2} A\tau_E} \approx 7.2A\tau_E.
\] (3.176)

The material-independent retraction constant $A$ can be determined from experiments. In the examples in Chapter 5, we will use (3.176) with $A = 1$ (which gives acceptable results) to determine $t_0$, unless the value is given in literature.
3.2.6 Dynamic dilution

In the derivation presented here, \( S_a^i \) is assumed to be constant. In reality, we should be considering the time dependent \( S_a^i(t) \) instead of the constant initial entanglement number \( S_a^i \). It appears, according to [2], that the time dependence in \( S_a^i(t) \) is determined by the tube density \( \Phi_{ST} \) (which will be defined properly in Section 3.4). If the arms of polymers are partially relaxed, this must have an effect on the tube, consisting of arms. Due to this relaxation of arms, the tube density, and therefore the time-dependent entanglement number, changes. This is called dynamic dilution. Dynamic dilution leads to predictions that can differ from measurements up to a factor 3 in the exponent, according to [2]. To compensate for the effect of dynamic dilution, usually (3.172) is changed into

\[
\frac{\partial f}{\partial k} = \frac{1}{2\nu S_a^i(\Phi_{ST})f},
\]

where usually

\[
S_a^i(\Phi_{ST}) = \Phi_{ST} S_a^i,
\]

if \( S_a^i = S_a^i(0) \), the initial amount of entanglements. Written in this form, (3.177) is known as the Ball-McLeish equation.

To use (3.177) in the numerical computation, we write it as

\[
\frac{\partial f^2}{\partial k} = \frac{1}{\nu S_a^i(\Phi_{ST})},
\]

to arrive at

\[
f(k + \Delta k) = \sqrt{f^2(k) + \frac{\Delta k}{\nu \Phi_{ST} S_a^i}}.
\]

This equation gives the retraction of an arm. Together with the reptation behavior of linear polymers derived in Section 3.1, this can be used to find the relaxation function of a polymer melt. Before this is done, first some minor questions have to be answered, for example what happens if \( f = 1 \), when an arm has completely retracted? This will be answered in the next section.

3.3 Waiting time

When an arm end has reached the branch point, the arm retraction is completed. If afterwards there are more than two (partially) unrelaxed segments left attached to the branch point, the branch point is still restricted to move, and the relaxed arm is equivalent to extra drag on the branch point (which has no immediate effect). But, if only two (partially) unrelaxed segments are attached to the branch point, then the branch point is free to move. The two remaining segments are combined into one larger segment. At the position of the branch point, there will be an arm remainder, which increases the drag. If the new larger segment happens to be an arm and can retract, then a waiting time, due to the sudden increase in drag, appears.

3.3.1 Simplest situation

Consider the situation sketched in Figure 10, where arm \( A \) is relaxing. Segment \( B_2 \) is a backbone segment that does not relax, while segment \( B_1 \) is an arm that completes its relaxation
Figure 10: The most simple situation: $B_2$ is a backbone segment, $A$ is the arm that relaxes first and $B_1$ is the other arm.

at a later time than arm $A$ does.

If we assume that the friction of an arm is proportional to its entanglement length $S_a$, such that $\gamma = \hat{\gamma} S_a$, we see from (3.174) that the starting logarithmic times for arms $A$ and $B_1$ are (with $S_A = (S_a)_A$, etc.)

$$k^A_0 = \log(t_0) + \frac{3}{2} \log(S_A), \quad (3.181)$$

$$k^{B_1}_0 = \log(t_0) + \frac{3}{2} \log(S_{B_1}). \quad (3.182)$$

We now consider $k^*$ to be the time at which segment $A$ has completely relaxed. We define $f^* = f(k^*)$, the average fraction of relaxed material at time $k^*$. First, suppose that segment $A$ did never exist, so there was only one segment $B$ (where $B = B_1 + B_2$), and that the density $\Phi_{ST}$ at times before $k^*$ was constant. Then the relaxation process according to the Ball-McLeish equation (3.177) could be followed backwards from $f = f^*$ to $f = 0$ to get the starting time for segment $B$, which, because the friction coefficient would be $\hat{\gamma} S_B$, would have been

$$k^*_B = \log(t_0) + \log(S_B) + \frac{1}{2} \log(S_B). \quad (3.183)$$

Next, suppose that the remainder of arm $A$ was always there, so segment $B$ always would have had an extra drag, and assume that the tube density $\Phi_{ST}$ at times before $k^*$ was constant. In this case, again the Ball-McLeish equation could be followed backwards from $f = f^*$ to $f = 0$ to get the starting time for segment $B$. If the extra drag of the remainder of arm $A$ is denoted by $D_A$, we get

$$k^B_0 = \log(t_0) + \log(S_B + \frac{D_A}{\hat{\gamma}}) + \frac{1}{2} \log(S_B). \quad (3.184)$$

The extra waiting time $\Delta k$ at the start $f = 0$, caused by $D_A$, therefore is equal to

$$\Delta k = k^0_B - k^*_B = \log \left( 1 + \frac{D_A}{\hat{\gamma} S_B} \right). \quad (3.185)$$

Because the Ball-McLeish equation (3.177) is independent of time (the chain density $\Phi$ is assumed constant here), this time difference is kept until $f = f^*$. So the waiting time, caused by the extra drag of segment $A$, is equal to $\Delta k$.  

35
A reasonable assumption is that the drag, corresponding to the remainder of arm $A$, is the same as the drag when arm $A$ was still active, so $D_A = \hat{\gamma} S_A$. This gives
\[
\Delta k = \log \left( 1 + \frac{S_A}{S_B} \right).
\] (3.186)
This leads to the acceptable result that relaxed short arms ($S_A \ll S_B$) lead to a short waiting time, and relaxed long arms ($S_A \gg S_B$) lead to a long waiting time. We also see that if the arm lengths are approximately equal, the waiting time reduces to $\Delta k \approx \log(2)$, the result used in Larson’s article [7].

### 3.3.2 Backbones relaxing

In the previous section, segments $A$ and $B_1$ were both pure arms; they did not contain any remainders of other relaxed arms. A more general approach allows segments $A$, $B_1$ and $B_2$ to contain remainders, as visualized in Figure 11, where the remainders are indicated by black dots.

![Figure 11: Arms $A$ and $B_1$ relaxing on a backbone, $B_2$, both containing extra drag due to arm remainders (visualised by black dots).](image)

We suppose these remainders cause extra drags, $D_B$ and $D_A^*$. We follow the same procedure as in the preceding section. First suppose that segment $A$ did never exist and $\Phi$ was constant at times before $k^*$. The starting time for segment $B$ then would have been
\[
k_B^* = \log(t_0) + \log \left( S_B + \frac{D_B}{\hat{\gamma}} \right) + \frac{1}{2} \log(S_B).
\] (3.187)
Next, suppose that the remainder of segment $A$ was always there, so segment $B$ always would have had the extra drag $D_A$, and that $\Phi$ at times before $k^*$ was constant. In this case the starting time for segment $B$ would have been
\[
k_B^0 = \log(t_0) + \log \left( S_B + \frac{D_A + D_B}{\hat{\gamma}} \right) + \frac{1}{2} \log(S_B).
\] (3.188)
The extra waiting time $\Delta k$ at the start $f = 0$, caused by $D_A$, therefore is equal to
\[
\Delta k = k_B^0 - k_B^* = \log \left( 1 + \frac{D_A}{\hat{\gamma} S_B + D_B} \right).
\] (3.189)
Based on the same argument as in the preceding section, this time difference is kept until \( f = f^* \). So the waiting time, caused by the extra drag of segment \( A \), is equal to \( \Delta k \).

Another reasonable assumption is that the drag, corresponding to the remainder of segment \( A \), is the same as the drag when segment \( A \) was still active. This gives the result that the drag is equal to

\[
D_A = \hat{\gamma} S_A + D_A^*,
\]

(3.190)

The drag due to the remainders on segments \( A \) and \( B \) also originates from relaxed arms, so

\[
D_A^* = \hat{\gamma} \sum_i S_A^{c_i},
\]

(3.191)

\[
D_B = \hat{\gamma} \sum_j S_B^{c_j},
\]

(3.192)

where \( S_A^{c_i} \) are the entanglement numbers of the arms that already have relaxed onto segment \( A \), and \( S_B^{c_j} \) those that have relaxed onto segment \( B \). This gives

\[
\Delta k = \log \left( 1 + \frac{S_A + \sum_i S_A^{c_i}}{S_B + \sum_j S_B^{c_j}} \right).
\]

(3.193)

After defining the entanglement weight \( S^w_A \),

\[
S^w_A = S_A + \sum_i S_A^{c_i},
\]

(3.194)

and analogous for \( S^w_B \), we can write

\[
\Delta k = \log \left( 1 + \frac{S^w_A}{S^w_B} \right).
\]

(3.195)

Hence, the waiting times can be calculated by keeping track of the sum of the entanglement numbers of the arms that have relaxed onto a segment.

### 3.3.3 Multiple relaxing arms

We proceed with the case of two branch points; see Figure 12. In this situation, we assume that the arms \( A_1 \) and \( A_2 \) are relaxed completely before arm \( B_1 \) relaxes.

After the first arm, arm \( A_1 \), has relaxed, we know there will be a waiting time. If arm \( A_2 \) relaxes after this waiting time, we know, from the preceding section, what happens. But what if arm \( A_2 \) relaxes during the waiting time?

The waiting time due to arm \( A_1 \) is, according to (3.195), (consider here only the part \( B_1 B_2 A_1 \))

\[
\Delta k = \log \left( 1 + \frac{S^w_{A_1}}{S^w_{B_1} + S^w_{B_2}} \right).
\]

(3.196)

Suppose that at a certain moment, when this waiting time still has \( \Delta k^* \) to last, arm \( A_2 \) relaxes.

Focussing on the moment at which arm \( A_2 \) completes its relaxation, we see that this situation
Figure 12: A backbone, consisting of $B_2$ and $B_3$, with two branch points.

is completely equivalent to the situation in which an arm of length $(1-\delta)S_{A_1}$ relaxes, and
arm $B_1$ has an extra drag of $\delta S_{A_1}$, where $\delta$ is specified by

$$
\Delta k^* = \log \left( 1 + \frac{(1-\delta)S_{A_1}^w}{S_{B_1}^w + S_{B_2}^w + \delta S_{A_1}^w} \right),
$$

so

$$
\delta = e^{-\Delta k^*} \left( 1 + \frac{S_{B_1}^w + S_{B_2}^w}{S_{A_1}^w} \right) - \frac{S_{B_1}^w + S_{B_2}^w}{S_{A_1}^w}.
$$

A way to visualize this, is by considering the waiting time as a time in which the relaxed arm
aligns itself in its new tube.

The two situations are equal because the waiting time is equal, and the drag on the arm after
the waiting time is equal. We can therefore transform the situation where arm $A_2$ relaxes
during the waiting time due to the completed retraction of arm $A_1$ into the situation where
arm $A_1$ (with remaining drag $(1-\delta)\gamma S_{A_1}^w$) and $A_2$ (with drag $S_{A_2}^w$) relax simultaneously, and
$B_1$ has an extra drag of $\delta\gamma S_{A_1}^w$. The remaining waiting time $\Delta k^{**}$ therefore is according to

$$
\Delta k^{**} = \log \left( 1 + \frac{(1-\delta)S_{A_1}^w + S_{A_2}^w}{\delta S_{A_1}^w + S_{B_1}^w + S_{B_2}^w + S_{B_3}^w} \right),
$$

which, with use of (3.198), can be written as

$$
\Delta k^{**} = \Delta k^* + \log \left( \frac{S_{A_1}^w + S_{A_2}^w + S_{B_1}^w + S_{B_2}^w + S_{B_3}^w}{\delta S_{A_1}^w + S_{B_1}^w + S_{B_2}^w + e^{\Delta k^*} S_{B_3}^w} \right).
$$

We can check (3.200) by looking at two special cases. First suppose that the arms relax
simultaneously, so $\delta = 0$. The sudden increase in drag of $\gamma(S_{A_1}^w + S_{A_2}^w)$ on the backbone drag
of $\gamma(S_{B_1}^w + S_{B_2}^w + S_{B_3}^w)$ results in a waiting time of (according to (3.195))

$$
\Delta k^{**} = \Delta k^* + \log \left( \frac{S_{A_1}^w + S_{A_2}^w + S_{B_1}^w + S_{B_2}^w + S_{B_3}^w}{S_{B_1}^w + S_{B_2}^w + S_{B_3}^w} \right).
$$

38
whereas (3.199) gives
\[ \Delta k^{\ast\ast} = \log \left( 1 + \frac{S_{wA_1} + S_{wA_2}}{S_{wB_1} + S_{wB_2} + S_{wB_3}} \right), \] (3.202)
so this is validated.

The second case is \( \delta = 1 \); so arm \( A_2 \) relaxes at the moment the waiting time for arm \( A_1 \) has just collapsed. The extra waiting time due to arm \( A_2 \) is just its regular waiting time, so (3.195) yields
\[ \Delta k^{\ast\ast} = \log \left( \frac{S_{wA_1} + S_{wA_2} + S_{wB_1} + S_{wB_2} + S_{wB_3}}{S_{wA_1} + S_{wB_1} + S_{wB_2} + S_{wB_3}} \right), \] (3.203)
whereas (3.199) gives
\[ \Delta k^{\ast\ast} = \log \left( 1 + \frac{S_{wA_2}}{S_{wA_1} + S_{wB_1} + S_{wB_2} + S_{wB_3}} \right). \] (3.204)
Hence, this is also validated.

To obtain a general result, we first rewrite (3.198) into
\[ \delta = e^{-k^*} \left( 1 + \frac{S_{wB}}{S_{wA}} \right) - \frac{S_{wB}}{S_{wA}}, \] (3.205)
where \( S_{wA} \) is the entanglement weight of the arm that has relaxed, \( S_{wB} \) is the entanglement weight of the newly formed arm, and \( k^* \) is the remaining waiting time. We know the alignment as a function of the remaining waiting time, but we want to know the alignment as a function of the time itself. Therefore, we write \( k = k^0 + k^{tot} - k^* \), where \( k^0 \) is the time at which the arm reached the backbone, and \( k^{tot} \) is the total time needed to align. We can determine \( k^{tot} \) from (3.205), because it is equal to the remaining waiting time when \( \delta = 0 \),
\[ e^{-k^{tot}} \left( 1 + \frac{S_{wB}}{S_{wA}} \right) - \frac{S_{wB}}{S_{wA}} = 0, \] (3.206)
so
\[ k^{tot} = \log \left( \frac{S_{wA}}{S_{wB}} + 1 \right). \] (3.207)
If we use this in (3.205), we see that
\[ \delta(k) = e^{-(k^0 + k^{tot})} \left( 1 + \frac{S_{wB}}{S_{wA}} \right) - \frac{S_{wB}}{S_{wA}} = \frac{S_{wB}}{S_{wA}} \left( e^{k-k^0} - 1 \right), \] (3.208)
the result we were looking for.

To implement the waiting time into a hierarchical model, we derive a different formulation for it, by making the entanglement weight time dependent. If, \( S_{wB}(k) \) is the entanglement weight of the backbone at logarithmic time \( k \), and \( S_{wA}(k) \) is the entanglement weight of the arm at logarithmic time \( k \), and the arm reached the backbone at \( k^0 \), (3.208) gives
\[ \delta(k) = \frac{S_{wB}(k^0)}{S_{wA}(k^0)} (e^{k-k^0} - 1). \] (3.209)
Thus, at time $k$, the entanglement weight of the backbone is

$$S_{B}^{w}(k) = S_{B}^{w}(k^0) + S_{A}^{w}(k^0)\delta(k) = S_{B}^{w}(k^0)e^{k-k^0},$$

so after one timestep $\Delta k$, we have

$$S_{B}^{w}(k + \Delta k) = S_{B}^{w}(k)e^{\Delta k}.$$  \hfill (3.211)

Consequently, $S_{A}^{w}$, the entanglement weight of the arm, can be described as

$$S_{A}^{w}(k + \Delta k) = (1 - \delta(\Delta k))S_{A}^{w}(k) = S_{A}^{w}(k) + S_{B}^{w}(k)(1 - e^{\Delta k}),$$

where we have used (3.209).

### 3.3.4 Initial waiting times

The equations (3.211)–(3.212) offer the opportunity to implement the initial waiting times (3.176), using the alignment. In the implementation of the theory, we find a numerical solution by integration over time. We start the integration at a still arbitrary time $k_l$, the moment that (hypothetical) arms with length $S_{l}^{s}$, start retracting. The relation between $k_l$ and $S_{l}^{s}$ is, according to (3.174), (because in the initial situation there are no arm remainders, and we can say $\gamma = S_{l}^{s}$)

$$k_l = \log(t_0) + \frac{3}{2}\log(S_{l}^{s}).$$  \hfill (3.213)

Another arm, with length $S_{l}^{t}$, will have an extra waiting time of

$$\Delta k = \frac{3}{2}\log(\frac{S_{l}^{t}}{S_{l}^{s}}).$$  \hfill (3.214)

We try to replace this initial waiting time by an equal waiting time due to alignment. A fraction of the arm, say $\delta_{a}S_{l}^{a}$, will be already aligned at the start of the integration, while the rest, $(1 - \delta)S_{l}^{a}$, will still have to align. Using (3.211) with $k = k_l$, we see that

$$S_{B}^{w}(k_l + \Delta k) = S_{B}^{w}(k_l)e^{\Delta k}.$$  \hfill (3.215)

Because we want the retraction to start after $\Delta k$, we want $S_{B}^{w}(k_l + \Delta k) = S_{l}^{t}$, and we know that $S_{B}^{w}(k_l) = \delta_{a}S_{l}^{a}$. Combining this gives

$$\delta_{a} = \left(\frac{S_{l}^{t}}{S_{l}^{a}}\right)^{3/2}.$$  \hfill (3.216)

Using this $\delta_{a}$ for each arm gives us the right initial waiting time. We still have the freedom to choose $k_l$ (with its associated $S_{l}^{s}$), as the time at which our integration starts. We choose $k_l$ to be at or before the time when the arms start retracting, so we know the position of the arms. This means that we have to choose $S_{l}^{t}$ in (3.213) to be equal to or shorter than the shortest arm in the polymer melt, $S_{-}$, so

$$k_l \leq \log(t_0) + \frac{3}{2}\log(S_{-}).$$  \hfill (3.217)
Furthermore, if the polymer melt contains linear polymers, the reptation before $k_0$ should be negligible, say $0.001$. Solving (3.83) for $\phi = 0.001$, we see that

$$k_1 \leq \log(\tau_d \log(\frac{1}{0.999})),$$

(3.218)

and using (3.82), with $S^w_B = S^l_B$ because the polymer is linear, and $\Phi_{ST} = 1$ because we assume there is not yet any relaxation, we get, where $S^l_{-}$ is the length of the shortest linear polymer,

$$k_1 \leq \log\left(\frac{12}{5} (S^w_{l-})^3 \tau_E \log(\frac{1}{0.999})\right) \approx \log(\tau_E) + 3 \log(S^w_{l-}) - 6,$$

(3.219)

so to be sure we start the integration at a moment when the relaxation is negligible, we start at $k = k_{l0}$, with

$$k_{l0} = \min\{\log(\tau_E) + 3 \log(S^w_{l-}) - 6, \log(t_0) + \frac{3}{2} \log(S^w_{w-})\},$$

(3.220)

where $S^w_{l-}$ is the number of entanglements in the shortest linear polymer, and $S^w_{w-}$ is the number of entanglements in the shortest arm.

### 3.3.5 Three-arm star

When only three arms are left and one arm reaches the branch point, the resulting polymer is effectively linear; see Figure 13.

![Figure 13: A three-armed star that transforms into a linear polymer by arm retraction.](image)

Because the polymer is linear, it will relax by reptation as described in Section 3.1. In the diffusion model, which we use in our implementation, the length of the polymer is considered to be constant, but this is not so in reality. Relaxation actually goes faster due to length fluctuations. To account for these length fluctuations, we treat the linear polymer as a two-armed star, and we let the two arms have extra relaxation due to arm retraction, next to the relaxation due to reptation. If a three-armed star retracts one arm, we introduce a virtual branch point in the middle, such that both sides have equal length and equal drag.
Once the bead-spring model is being used, this will also model the length fluctuations of a linear polymer, so a linear polymer no longer has to be treated as a two-armed star.

### 3.4 Supertube

In Section 3.1, we have introduced the tube density, $\Phi_{ST}$. This is the density of the tube surrounding the chain. Because the tube consists of unrelaxed chains, this density is related to the unrelaxed chain density $\Phi(t)$. For a melt consisting of $M$ polymers, the latter density is defined by

$$\Phi(t) = \sum_{i=1}^{M} \sum_{j=1}^{n_{a}(i)} \phi_{ij}(1 - f_{ij}(t)),$$  \hspace{1cm} (3.221)

where $f_{ij}$ is the relaxed fraction of arm $j$ of polymer $i$, $n_{a}(i)$ the number of segments of polymer $i$, and $\phi_{ij}$ the volume fraction of segment $j$ for polymer $i$.

At $t = 0$, the tube density and the chain density will both be equal to 1 because nothing has happened yet, so

$$\Phi(0) = \Phi_{ST}(0) = 1.$$  \hspace{1cm} (3.222)

If $t > 0$, the segments start relaxing, by reptation and/or retraction, so the chain density $\Phi$ will decrease; there are less chains. Because the tube is made out of chains, a change in the chain density will cause a change in the tube density. This will, however, not always happen at the same time. To illustrate this, consider the situation in Figure 14, just before $t = t_0$.

![Figure 14](image-url)

Figure 14: A polymer and its nearest other polymers. The polymer of interest is the black line, the circles are the other polymers. The tube is visualized by the dotted lines.

In this situation, the tube surrounding the central polymer reaches as far as the nearest other polymers. The width of the tube is completely determined by the other chains, which implies that $\Phi(t_0^-) = \Phi_{ST}(t_0^-)$.

If, at $t_0$, other (parts of) polymers suddenly disappear, by reptation or relaxation, the space available for the tube widens, as can be seen in Figure 15. Because some polymers have disappeared, the chain density $\Phi$, defined by (3.221) decreases. But the width of the tube will not increase instantaneously, because in the model the width of the tube is determined by the average sideward motion of the chain. From $t = t_0$ on, the chain has the place to move further sidewards, but this needs time also. This causes the tube density $\Phi_{ST}$ to decrease slower than the chain density, so $\Phi(t_0^+) \neq \Phi_{ST}(t_0^+)$. This is called the supertube principle; see Milner [17], or Viovy et al. [18].

This supertube event will last until the segment has rediscovered its tube, see Figure 16; from that moment on the tube density $\Phi_{ST}$ and chain density $\Phi$ will be equal again, until a new supertube event occurs.
Figure 15: The same polymer as in Figure 14, directly after some of the nearest polymers have disappeared. The tube did not have the time to widen yet.

Figure 16: The situation of Figure 15, after the chain has had some time to explore its environment, or equivalently, the tube has had some time to widen.

The speed at which a chain discovers its environment when there are no constraints, as in a supertube event, is proportional to $t^{-1/2}$; see [17]. Therefore, the tube density during a supertube event is equal to

$$\Phi_{ST}(t) = \Phi_{ST,0} \sqrt{\frac{t_0}{t}},$$

where $t_0$ is the time at which the supertube event started, and $\Phi_{ST,0} = \Phi_{ST}(t_0)$ is the density at that moment. We have seen that this supertube event only happens if the decrease in $\Phi_{ST}$ is less than the decrease in $\Phi$, so (both are negative) if

$$\frac{d\Phi(t)}{dt} < \frac{d\Phi_{ST}(t)}{dt},$$

and the process stops if the densities $\Phi(t)$ and $\Phi_{ST}(t)$ are equal to each other, because then the chain has rediscovered its tube.

### 3.5 Relaxation function

The relaxation function $G(t)$ is, as stated at the start of this chapter, equal to the plateau modulus $G_0$ multiplied by the relative amount of unrelaxed entanglements at $t$. The plateau modulus can be obtained from observing linear polymers, and is considered to be known here. Because an entanglement is made of a given polymer and a polymer in the tube of the first polymer, the relative density of unrelaxed entanglement can be approximated by the product of the chain density $\Phi$ and the tube density $\Phi_{ST}$. Therefore, the simple relation

$$G(t) = G_0 \Phi(t) \Phi_{ST}(t),$$
seems logical, and it is given by [1] and [17]. However, literature (for example [1], [2], [3], [4], [5], [7], [12], [17] and [19]) more often suggests to use the relation

\[ G(t) = G_0 \int_0^1 e^{-(t/\tau)} d(\Phi(\tau)\Phi_{ST}(\tau)), \]  

(3.226)

and we will follow this too.

Because in the numerical calculation, described in the former sections, \( \Phi \) and \( \Phi_{ST} \) are calculated for every \( \tau \), this allows a calculation of \( G(t) \). However, a problem is that reptation can cause a jump in \( \Phi \). Certain values of \( \Phi_{ST} \) are not reached then. The integral therefore should be interpreted as restricted to the values that \( \Phi(\tau)\Phi_{ST}(\tau) \) takes.

For a numerical calculation, the integral is changed into

\[ G(t) = -G_0 \int_{t_{\text{start}}}^{t_{\text{end}}} e^{-(t/\tau)} \frac{d(\Phi(\tau)\Phi_{ST}(\tau))}{d\tau} d\tau. \]  

(3.227)

The jumps in \( \Phi_{ST} \) are changed into delta-functions in the derivative. If the reptations happen at \( t_i, i = 1, 2, \ldots, n - 1 \), and cause a jump in \( \Phi_{ST} \) of \( \Delta\Phi_i \), this changes (3.227) into

\[ G(t) = -G_0 \sum_{i=0}^{n-1} \left( \int_{t_i}^{t_{i+1}} e^{-(t/\tau)} \frac{\partial(\Phi(\tau)\Phi_{ST}(\tau))}{\partial\tau} d\tau \right) - G_0 \sum_{i=1}^{n-1} e^{-(t/t_i)} \Delta\Phi_i, \]  

(3.228)

and here the derivative is continuous on each interval. Partial integration is then allowed, yielding

\[ G(t) = G_0 \sum_{i=0}^{n-1} \left( \int_{t_i}^{t_{i+1}} e^{-(t/\tau)} \frac{\Phi(\tau)\Phi_{ST}(\tau)}{\tau^2} d\tau \right) + G_0 e^{-(t/t_0)}. \]  

(3.229)

Equation (3.226) can also be converted to expressions for \( G' \) and \( G'' \), which gives

\[ G'(\omega) = G_0 \int_0^1 \frac{\omega^2}{1 + \omega^2} \frac{\tau^2}{\tau^2} d(\Phi(\tau)\Phi_{ST}(\tau)), \]  

(3.230)

\[ G''(\omega) = G_0 \int_0^1 \frac{\omega\tau}{1 + \omega^2} \frac{\tau^2}{\tau^2} d(\Phi(\tau)\Phi_{ST}(\tau)). \]  

(3.231)

It is possible to prove the next inequalities, where \( t_{\text{start}} \) is the time at which the relaxation begins and \( t_{\text{end}} \) is the time at which relaxation has finished:

\[ e^{-\frac{1}{t_{\text{start}}}} \leq \frac{G(t)}{G_0} \leq e^{-\frac{1}{t_{\text{end}}}}, \]  

(3.232)

\[ \frac{\omega^2 t_{\text{start}}^2}{1 + \omega^2 t_{\text{start}}^2} \leq \frac{G'(\omega)}{G_0} \leq \frac{\omega^2 t_{\text{end}}^2}{1 + \omega^2 t_{\text{end}}^2}; \]  

(3.233)

\[ \frac{\omega t_{\text{start}}}{1 + \omega^2 t_{\text{start}}^2} \leq \frac{G''(\omega)}{G_0} \leq \frac{\omega t_{\text{end}}}{1 + \omega^2 t_{\text{end}}^2}. \]  

(3.234)

The tube model does not model the very short time behavior of the polymers. We can therefore expect that especially \( G''(\omega) \) is incorrect for large \( \omega \).

At this point, we have all the ingredients to calculate the relaxation moduli for arbitrary polymer melts. This will be implemented in Chapter 4. In the next section, we will recapitulate the results of this chapter.
3.6 Summary of the tube model

Using the tube model, we can calculate the relaxation function. This is done using

\[ G(t) = -G_0 \int_{t_{\text{start}}}^{t_{\text{end}}} e^{-\frac{(t-T)}{\tau}} \frac{\partial (\Phi(\tau) \Phi_{ST}(\tau))}{\partial \tau} d\tau, \quad (3.235) \]

and the complex moduli \( G' \) and \( G'' \) can be calculated using

\[ G'(\omega) = G_0 \int_{0}^{1} \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} d(\Phi(\tau) \Phi_{ST}(\tau)), \quad (3.236) \]
\[ G''(\omega) = G_0 \int_{0}^{1} \frac{\omega \tau}{1 + \omega^2 \tau^2} d(\Phi(\tau) \Phi_{ST}(\tau)). \quad (3.237) \]

The densities used in this formulas, the chain density \( \Phi \) and the tube density \( \Phi_{ST} \) can also be calculated. The chain density \( \Phi \) is calculated by

\[ \Phi(t) = \sum_{i=1}^{N} \sum_{j=1}^{n_{\alpha}(i)} \phi_{ij}(1 - f_{ij}(t)), \quad (3.238) \]

while the tube density \( \Phi_{ST} \) can be calculated as described in Section 3.4. We can calculate the relaxed fraction \( f \) in the case of reptation by

\[ f(k + \Delta k) = f(k) + \frac{\Delta k}{\tau_d} (1 - f(k)) e^k, \quad (3.239) \]

and in the case of arm retraction by the Ball-McLeish equation

\[ f(k + \Delta k) = \sqrt{f^2(k) + \frac{\Delta k}{\nu \Phi_{ST}(k) S_a}}, \quad (3.240) \]

where arm retraction starts at logarithmic time \( k_0 \) with

\[ k_0 = \log(t_0) + \log \left( \frac{\gamma}{\hat{\gamma}} \right) + \frac{1}{2} \log(S_a^b). \quad (3.241) \]

The reptation time \( \tau_d \) and start time \( t_0 \) can be expressed in the equilibrium time \( \tau_E \) as

\[ \tau_d = 2\nu \Phi_{ST}(S_b^0)^2 S_b^2 \tau_E, \quad t_0 = \frac{\pi^2}{\sqrt{\nu}} \tau_E. \quad (3.242) \]

After an arm \( A \) has retracted completely, it has to align on its backbone \( B \) according to

\[ S_{AB}^B(k + \Delta k) = S_{AB}^B(k) e^{\Delta k}, \quad (3.243) \]
\[ S_{AB}^A(k + \Delta k) = S_{AB}^A(k) + S_{AB}^B(k)(1 - e^{\Delta k}). \quad (3.244) \]

In the next Chapter, this will all be implemented in a Fortran-program.
4 Implementation

The tube model defined in the previous chapter is almost ready to be implemented. However, a few things still need to be done first. These are described in the next sections.

4.1 Sieving

The input data the program requires are the polymer structures. They are generated by another program, and contain for each polymer the number of arms, places of arms/backbones, length of arms and density. Some polymers may be very small, so small that entanglements are not possible. If polymers are not entangled, the processes of reptation and arm retraction will not occur, so these polymers do not need to be included in our model. The sieving procedure removes these small molecules, and replaces them by solvent.

4.2 Coarsegraining

If the polymers are large enough, they still may have arms that are not entangled. The coarsegrain procedure checks all molecules to see if they contain such arms, and removes them. The amount of removed arms, together with the amount of small molecules removed in the sieving procedure, is calculated, because they act as solvent. After the coarsegrain procedure, some initially different molecules could have been changed into the same molecule. Therefore, all molecules are checked to see if there are any doubles.

4.3 Relax

Once all the molecules left are entangled molecules, the relaxation process can be simulated. As input, the program uses the files parameters.txt, topology.txt and number.txt. In the file parameters.txt, the parameters are set, all in one line, in the following order: 

\[ G_0, \tau_E, t_0, Nt, Nlogs, w_0, w_1, Nw \]

- \( G_0 \) is the plateau modulus, the same as used in Chapter 3,
- \( \tau_E \) is the equilibrium time for reptation, defined in (3.81),
- \( t_0 \) is the starting time for arm retraction, defined in (3.175),
- \( Nt \) is the number of different polymers in the melt,
- \( Nlogs \) is the maximum number of time steps the algorithm uses,
- \( w_0, w_1 \) and \( Nw \) are explained in the next section.

In the file topology.txt, the topology of the melt is defined. Because there are \( Nt \) different polymers, this is done in \( Nt \) different blocks. Each block starts with the line

\[ 0 \ Ns \ 0 \ 0, \]

where \( Ns \) is the number of segments in the polymer. The zeroes are only there to make sure the line has four columns. The next \( Ns \) lines consist of the segment information:

\[ p1 \ p2 \ length \ arm/backbone, \]

where
• $p_1$ and $p_2$ denote the begin and end point of the segment,
• \textit{length} is $S^l_a$, the length of the segment, measured in the initial entanglement length,
• \textit{arm/backbone} indicates whether the segment is an arm or a backbone. If it is 0, the segment is a backbone, if it is 1, the segment is an arm.

As an example, a possible topology file for a melt consisting of a mixture of linear and $H$-polymers is, see Figure 17:

0 2 0 0  
1 2 10 1  
1 3 10 1  
0 5 0 0  
1 2 15 0  
1 3 8 1  
1 4 8 1  
2 5 8 1  
2 6 8 1

Figure 17: A topology for a polymer melt, consisting of linear polymers (the left) and $H$-polymers (the right). The labelled circles correspond to branch/end points; the numbers next to the segment denote the length (the initial number of entanglements) of the segment.

Finally, in the file \texttt{number.txt}, the weight fractions of each of the $N_t$ polymers are set. Using these input files, the program can simulate the relaxation, making use of the theory as summarized in Section 3.6. After each timestep, every arm that still has to be aligned in its tube is aligned. After that, the relaxations due to reptation and retraction are calculated. If there are arms that have completely retracted during this timestep, they are removed according to the theory, and the process can start all over again, until every polymer has relaxed, or the maximum number of timesteps, $N_{logts}$, is reached. The output of the program is the file \texttt{relax.txt}, together with the file \texttt{tree.lts}. The file \texttt{tree.lts} contains some uninteresting values needed for further calculation, while the file \texttt{relax.txt} contains the densities $\Phi$ and $\Phi_{ST}$ after every timestep. These data can be used to determine the moduli.
4.4 Modulus

After the simulation of the relaxation, the relaxation function \( G(t) \) and the storage and loss modulus \( G'(\omega) \) and \( G''(\omega) \) can be calculated. This is done in the modulus procedure, which uses the chain density \( \Phi \) and the tube density \( \Phi_{ST} \), calculated by the relax procedure.

The input of the modulus program consists of the files relax.txt and tree.lts generated by the relax program, together with the parameter file parameters.txt already partially explained, with

- \( w_0 \) is the minimal frequency,
- \( w_1 \) is the maximal frequency,
- \( N_w \) is the number of frequencies generated.

The modulus program performs, for \( N_w \) different frequencies from \( w_0 \) to \( w_1 \), a direct calculation of \( G'(\omega) \) and \( G''(\omega) \), according to (3.236) and (3.237). The result is the output file result.txt, containing \( N_w \) lines each of the form \( \omega, G'(\omega), G''(\omega) \).

So the file could begin with

\[
\begin{align*}
1.288249551693134E-005 & \quad 7.1042770E-04 & \quad 1.2899688E-02 \\
1.659586907437561E-005 & \quad 1.1764318E-03 & \quad 1.6583502E-02 \\
2.137962089502233E-005 & \quad 1.9453136E-03 & \quad 2.1290321E-02 \\
2.75422870338167E-005 & \quad 3.2091162E-03 & \quad 2.7271928E-02 \\
3.548133892335756E-005 & \quad 5.2735033E-03 & \quad 3.4806270E-02 \\
4.570881896148752E-005 & \quad 8.6115608E-03 & \quad 4.4158772E-02 \\
5.88843655355893E-005 & \quad 1.3921665E-02 & \quad 5.5494096E-02 \\
7.585775750291843E-005 & \quad 2.1538866E-02 & \quad 6.8710580E-02
\end{align*}
\]

which means that for a frequency \( \omega = 1.288 \cdot 10^{-5}s^{-1} \), the storage and loss moduli are \( G'(\omega) = 7.104 \cdot 10^{-4}\text{Pa s} \) and \( G''(\omega) = 1.290 \cdot 10^{-2}\text{Pa s} \), et cetera.

These procedures have all been implemented, using Fortran. This implementation is used to compute the results shown in the next chapter.
5 Testing

To check the quality of the developed model, we compare its predictions to measured data.

5.1 Literature data

To test the theory, described in Chapter 3 and implemented in Chapter 4, we compare its results to literature data. Because there are three important mechanisms involved in the theory, arm retraction, reptation and the waiting times, we try to analyze them separately.

5.1.1 Retraction data

The first mechanism we analyze is arm retraction, as described in Section 3.2. This is done for a symmetrical star polymer. A symmetrical star polymer is a polymer with one branch point, where all arms (≥ 3) have equal length; see Figure 18. Because of this structure, all arms start moving at the same time and reach the branchpoint at the same time. The polymer is never linear, and no waiting times are involved, so the only mechanism is arm retraction.

We use the experimental data from Park & Larson [12] to compare it to our results, and we choose the same parameters ($\tau_E = 9.5 \cdot 10^{-7}s$, $t_0 = 6.8 \cdot 10^{-6}s$, $G_0 = 1.15 \cdot 10^6Pa$). The result is shown in Figure 19.
Figure 19: Simulation and measurements of dynamic moduli of star polymers. The colored lines denote the simulations by the model developed in this project, the other symbols denote the measurements from [12]. From right to left, the initial arm entanglements are 5.136 (triangles), 13.75 (circles) and 18.41 (squares). The open symbols and blue lines correspond to $G''$, the filled symbols and the red lines correspond to $G'$. We see that the model gives correct predictions over a large frequency range. Because we neglected high-frequency Rouse contributions (see Section 3.1.1), we see that the predicted high-frequency behavior deviates substantially from the measurements for the loss modulus $G''$. Apart from this, the agreement between model and experiment is essentially perfect, so we conclude that arm retraction is described well by the theory, for frequencies less than 1000Hz.

5.1.2 Reptation data

The second mechanism is reptation, as described in Section 3.1. We check the predictions of the theory for linear polymers. With linear polymers, the only relaxation mechanism is reptation, and there are no waiting times. Again, we make use of data from Park & Larson [12], with the same parameters ($\tau_e = 9.5 \cdot 10^{-7}$s, $t_0 = 6.8 \cdot 10^{-6}$s, $G_0 = 1.15 \cdot 10^6$Pa). The model and the measurements are compared in Figure 20.

We see again that the predictions for reptation compare well to the measurements over a large frequency domain, again except for the loss modulus $G''$ for higher frequencies. Hence, our simulation of reptation seems correct.

5.1.3 Waiting times data

The third important aspect of the model is the waiting time, as described in Section 3.3. To analyze the effect of waiting times, we look at $H$-polymers. The four arms of the $H$-polymer relax by arm retraction, followed by a waiting time, and after this waiting time, the center segment relaxes by reptation. We compare predicted results from our model to data from
Figure 20: Simulation and measurements of dynamic moduli of linear polymers. The colored lines denote the simulations by the model developed in this project, the other symbols denote the measurements from [12]. From right to left, the initial entanglement lengths of the linear polymers are 9.41 (diamonds), 20.05 (squares), 44.09 (triangles) and 91.36 (circles).

McLeish et al. [4]. The result is shown in Figure 21. McLeish et al. suggest that this melt consists of $H$-polymers with a backbone of entanglement length 28.9 and arms of entanglement length 5.2, whereas we use $H$-polymers with a backbone of length 28.9 and arms of length 9.7. This could indicate several things: the melt could in reality not be monodisperse ([4] gives a polydispersity of 0.13, whereas the samples from Sections 5.1.1 and 5.1.2 were given polydispersities of around 0.01), the structures could be slightly more branched than $H$-polymers, or the waiting times derived in this project are underestimated. It is not clear what the real reason for this difference in arm length is; further research should provide the answer.

5.2 Laboratory data

Now that the correctness of the model has been shown on the basis of literature data, we continue to see if the model can be used in a practical situation.
At DSM Research, polymer melts are prepared and characterised. The topology of the melt
is known to a certain extent: it is known which monomers are used, but it is not fully known how these monomers react.

To determine the parameters needed in the model, a melt consisting of only linear polymers (which can be made with more certainty about the composition) is made, and the rheological properties \( G' \) and \( G'' \) are determined. From this, the reptation equilibrium time \( \tau_E \) and the plateau modulus \( G_0 \) are determined. The values obtained are \( \tau_E = 5 \cdot 10^{-8} \text{s} \) and \( G_0 = 2 \cdot 10^6 \text{Pa} \). For the arm retraction starting time \( t_0 \) we use (3.176) with \( A = 1 \) (which is comparable to literature), so \( t_0 = 4 \cdot 10^{-7} \text{s} \).

The laboratory claimed that for some sample polymer melts (with the same monomers) the melt was a 100% star-polymer melt. With a different technique, a polymer molecular weight of 240kg/mol was found. It is also known (from former experiments with linear polymers) that the entanglement weight is 1.7kg/mol, so that each polymer has 140 entanglements. Knowing this, we assume that the melt is built from a combination of linear polymers of entanglement length 140, and star polymers with 3 arms, each of entanglement length 46.7. To verify this assumption, and to determine the fraction of star polymers, we used the program, implemented in Chapter 4, to produce rheological predictions for different mixtures of these two ingredients. The results are shown in Figures 22 and 23, together with the rheological measurements of the polymer melt. It shows that the laboratory measurements correspond to a linear component of about 40%, which is comparable to the result of \( \pm 35\% \), given by an analysis proposed by Crosby [20].
Figure 22: The simulated and measured storage modulus ($G'$). The measurements are denoted by the black line, the simulations are denoted by red lines. The lowest red line stands for simulation of a star polymer, volume percentage of 20%, the middle red line of 40%, and the highest red line for 60%.

Figure 23: The simulated and measured loss modulus ($G''$). The measurements are denoted by the black line, the simulations are denoted by blue lines. The lowest blue line stands for simulation of a star polymer, volume percentage of 20%, the middle blue line of 40%, and the highest blue line for 60%.
6 Results, conclusion and recommendations

6.1 Model

In this report, the relaxation of polymer melts is analyzed, both for linear and branched polymers. This is done in three steps: Reptation, arm retraction and waiting times.

6.1.1 Reptation

The effect of reptation on linear polymers is modelled in two ways. The first model, the spring-bead model, is a very general model that also allows for changes in polymer length. However, the model was not fully solved, so it is not used in any calculation. The other model, the diffusion model, is less correct because it assumes that the polymer length is constant in the reptation process, and all length fluctuations arise from hypothetical arm retraction. The diffusion model is incorporated in the final Fortran program.

6.1.2 Arm retraction

The other mechanism for relaxation is arm retraction. To find an equation for arm retraction, first the arm is seen as a spring-bead-system. Then the motion of the end point is modelled as Brownian motion in a harmonic potential, from which a solution for the probability density distribution for the position of the end point is obtained. From this, an equation for the motion of the end point, the Ball-McLeish-equation, is derived. This equation is used in the final Fortran program to simulate arm retraction.

6.1.3 Waiting times

After arm retraction is completed, there is an increase in drag on the remaining segments. This results in a waiting time for the remaining arms, before retraction can start again. This waiting time is modelled as a period in which the retracted arm aligns itself into its new tube, and an equation for this alignment is derived. The initial waiting times for arm retraction, coming from the Ball-McLeish-equation, are handled using this equation.

6.2 Conclusions

The research leading to this report has produced several general conclusions; the most important are:

- The linear viscoelastic behavior of polymer melts is completely determined by the relaxation function.
- Using the tube model, this relaxation function can be determined by knowing the fraction of relaxed material in the melt. Linear polymers can only relax by reptation, while branched polymers also use arm retraction.
- After an arm has completed its retraction, the remaining segments have a waiting period in which the arm aligns itself to its new tube.
- The model developed in this report has been validated with data taken from literature. The results obtained by us have at least the same level of correctness as models that are found in literature. Moreover, the model developed in this report is more general.
The model developed in this report can be used to compare the measured viscoelastic properties of a melt with the viscoelastic properties of its proposed structure. In this way one can check whether this supposed structure is appropriate.

It is possible to model the reptation of linear polymers with a more general model, the spring-bead model, in which length fluctuations are directly incorporated in the resulting equation. This is however not completed yet, but we strongly recommend to finish the solution of this problem.

Although the simulated waiting time gives a correct result, the test, in which we did the simulation, needs longer arms as input than literature suggests. We recommend to do further research on this, to see if this is due to misinterpreted measurements or a wrong implementation.
References


