Van harte nodig ik U uit tot het bijwonen van de openbare verdediging van mijn proefschrift

Computational Polymer Melt Rheology

op maandag 5 november 2001 om 16:00 in zaal 4 van het Auditorium van de Technische Universiteit Eindhoven
alsmede voor de receptie die aansluitend zal plaatsvinden.

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Computational Polymer Melt Rheology

The processing of polymer materials has a large influence on the mechanical and optical properties of the end product. For instance, dimensional stability in precision injection moulding or yield strength and Young’s modulus during film blowing are affected by the viscoelastic properties of the polymer melt. In turn, the rheological behaviour is related to specific molecular structures and molecular weight distribution. Therefore, the design of new polymers and processing devices would benefit from predictive modelling of the viscoelastic behaviour of polymer melts at realistic processing conditions. This requires robust numerical analysis tools and reliable constitutive models which are able to quantitatively capture the polymer melt rheology. In this thesis, constitutive models for, primarily, commercial polyethylene melts are analyzed. After implementation of these models in a finite element program, a combined numerical/ experimental analysis is carried out. A quantitative agreement between experimental data and numerical results is obtained, both in well-defined rheological experiments as well as two- and three-dimensional inhomogeneous prototype industrial flows.
Computational Polymer Melt Rheology
Verbeeten, Wilco M.H.

Computational polymer melt rheology / 
Proefschrift. - ISBN 90-386-3022-0 
NUGI 841 
Trefwoorden: polymere smelten / reologie / karakterisering van polymere smelten / 
constitutieve vergelijkingen in differentiaalvorm / eindige-elementenmethode / 
complexe stromingsgeometriën 
Subject headings: polymer melts / rheology / polymer melt characterisation / 
differential constitutive equations / finite element method / complex flow geometries


This research was financed by the Commission of the European Union through the BRITE- 
EuRAM III project ART (BE96-3490).
Computational Polymer Melt Rheology

Proefschrift

ter verkrijging van de graad van doctor
aan de Technische Universiteit Eindhoven,
op gezag van de Rector Magnificus, prof.dr. R.A. van Santen,
voor een commissie aangewezen door het College voor Promoties
in het openbaar te verdedigen op
maandag 5 november 2001 om 16.00 uur

door

Wilco Martinus Hendrikus Verbeeten

geboren te Haps
Dit proefschrift is goedgekeurd door de promotoren:

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en
prof.dr.ir. H.E.H. Meijer

Copromotor:

dr.ir. G.W.M. Peters
Sólo el amor resistirá
mientras caen como torres dinamitadas
los días, los meses, los años.

Sólo el amor resistirá
alimentando silencioso la lámpara encendida,
el canto anudado a la garganta
la poesía anudado a la garganta,
la poesía en la caricia del cuerpo abandonado.

Algún día,
cualquier día,
doblará otra vez el recodo del camino
lo veré alto y distante,
acercándose,
oiré su voz llamándome,
sus ojos mirándome
y sabrás que el amor ha resistido
mientras todo se derrumbaba.

Gioconda Belli, Sólo el amor resistirá.
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Summary

Processing of polymer materials has a large influence on the resulting mechanical and optical properties of the end product. For instance, dimensional stability in precision injection moulding or yield strength, Young’s modulus and even tear strength of blown films are affected by the viscoelastic properties of the polymer melt. In turn, the rheological behaviour is related to specific molecular structures and the molecular weight distribution. The design of new polymers and processing devices would, therefore, benefit from predictive modelling of the viscoelastic behaviour of polymer melts at realistic processing conditions. This requires robust numerical analysis tools and reliable constitutive models which are able to quantitatively capture the polymer melt rheology. This thesis is a contribution to this predictive modelling of viscoelastic materials, restricted to isothermal flows in confined two- and three-dimensional prototype industrial flow geometries using differential constitutive models.

To be able to predict the rheological behaviour of commercial polymer melts, multiple relaxation times are necessary, since single-mode models are able to only qualitatively predict the rheology, but not quantitatively. The single-mode models show incorrect slopes in both start-up at small time scales as well as in steady state at high shear and strain rates. Furthermore, the non-linear parameters in constitutive models are in general more sensitive in elongational flow than in shear. Elongational data are thus indispensable for the determination of the non-linear parameters.

The main problem in constitutive modelling of the rheology of polymer melts is to describe the correct non-linear behaviour in both elongation and shear. Most well-known conventional models, such as the Phan-Thien Tanner (PTT) and Giesekus models, are unable to overcome this difficulty. The Giesekus model shows a wrong behaviour in steady state elongation, while the PTT model is too strain thinning at high strain rates. Schoonen (1998) introduced the Feta model, which shows an enhanced flexibility in controlling shear and elongational properties. An improved prediction of the stresses in a stagnation flow for polymer solutions is accomplished. However, the model overpredicts the first normal stress difference in shear, lacks an overshoot in start-up shear flow, and does not predict an equibiaxial viscosity. The Pom-Pom model, introduced by McLeish and Larson (1998), can be considered as a breakthrough in the field of viscoelastic constitutive equations, since it does not suffer from these deficiencies. The original differential version has been adapted to overcome three drawbacks: steady state elongational viscosities showed discontinuities, the equation for orientation was unbounded for high strain rates, and the model did not have a second normal stress difference in shear. The resulting eXtended Pom-Pom (XPP) model can quantitatively describe the experimental data over a wide range of rheological experiments.
Summary

for both low density and high density polyethylene melts.

Besides in rheological experiments, the PTT, Giesekus and XPP models are also tested in flows with a combination of shear and elongation: inhomogeneous complex flows, or prototype industrial flows. For three typical examples of these flows, a planar contraction flow, a planar flow around a confined cylinder, and a planar flow in a cross-slot device, computations are compared to experimental data. Velocities are measured with particle tracking velocimetry and stresses with field-wise flow induced birefringence. As a numerical method, the Discrete Elastic Viscous Stress Splitting (DEVSS) technique in combination with the Discontinuous Galerkin (DG) method is used. This is an accurate and robust numerical tool for viscoelastic flow simulations that efficiently handles multiple relaxation times. Calculations for both two- and three-dimensional geometries are performed. Although this technique is known to have a temporal stability problem for high elasticities, more stable numerical methods using Streamline Upwind/Petrov Galerkin (SUPG) techniques have in general more trouble solving non-smooth flows. The DEVSS/DG method does encounter convergence problems depending on (the structure of) the constitutive model, its rheological behaviour invoked by the parameters, the mesh, and the time step. For the eXtended Pom-Pom model, a small change in the structure, as suggested by Van Meerveld (2001), resulted in a more stable combination of numerical method and constitutive model and converged results were found even for the contraction flow problem.

The eXtended Pom-Pom model shows the best overall agreement with experimental data in all three prototype industrial flows, especially in regions with strong elongation. In that respect, the planar contraction flow is not a discriminating prototype industrial flow for testing constitutive models. In that particular geometry, only a mild excursion into the non-linear elongational regime is obtained in the experimentally accessible regions. The flow in a cross-slot device is the more ideal complex flow geometry.

In general, a good basic ground is laid for predictive modelling of commercial polymer melts; a reliable constitutive model and an accurate, robust and efficient numerical technique are available, still keeping room for improvement on both sides.
Chapter 1

Introduction

1.1 Background

The commodity plastics market, involving polymer materials such as polyethylene (PE), polypropylene (PP) and polystyrene (PS), would benefit widely from predictive modelling of the viscoelastic behaviour of polymer melts at realistic processing conditions. It would aid to design and optimize new polymers and processing devices. The mechanical and optical properties of the end products depend to a large extent on the deformation history of the material and therefore on its rheological behaviour. For instance, the yield strength, Young’s modulus, and elongation at break during film blowing or dimensional stability in precision injection moulding are affected by the viscoelastic properties of the flowing polymer melt. In turn, the melt rheology is related to specific molecular structures and molecular weight distribution. Therefore, predictive modelling requires reliable constitutive equations and associated material parameters in combination with sophisticated numerical analysis tools. The constitutive models should be able to quantitatively describe the complex viscoelastic behaviour of polymer melts in both well-defined rheological experiments as well as inhomogeneous prototype industrial flows, while the numerical techniques should be sufficiently efficient, accurate and robust.

Industrial processing of polymer materials is essentially three-dimensional, non-isothermal, and contains areas with free surfaces. Moreover, processing speeds are in general high, which exhibits high strain and shear rates well into the non-linear regime of the viscoelastic material behaviour. Several studies are conducted on non-isothermal [Baloch et al. (1992), Peters and Baaijens (1997)] and free surface flows [Baaijens (1993), Wagner et al. (1998b), Rasmussen and Hassager (1999), Liang (2001)]. This thesis is a contribution to predictive modelling of viscoelastic materials, restricted to isothermal flows in confined two- and three-dimensional prototype industrial flow geometries.

1.2 Constitutive models

An important issue in predictive modelling is the proper choice of a constitutive equation to describe the rheology of polymer melts. Over the years, various constitutive models have been proposed [Larson (1988), Bird and Wiest (1995)], but until recently, most of them failed
to correctly predict the nonlinear behaviour in both elongation and shear.

The Feta model, as discussed in chapter 2, introduces an enhanced flexibility between shear and elongation. Improvement is gained by fixing the viscosity in shear (hence its acronym: Fixed eta), while still being able to control the elongational behaviour with a nonlinear parameter. Since this is a purely phenomenological model, it lacks a sound physical background and fails to predict an equibiaxial viscosity. Recently, a new class of constitutive models has been introduced, based on the tube model of Doi and Edwards (1986), which is a major step forward in the field of viscoelastic constitutive modelling. Examples are the Pom-Pom model by McLeish and Larson (1998), which exists of an integral version and an approximated differential form, and the Molecular Stress Function (MSF) model by Rubio et al. (2001). Other reptation models, i.e. the Marrucci-Greco-Ianniruberto (MGI) model by Marrucci et al. (2001), concentrate on the physics of Convective Constraint Release (CCR). In chapter 3, the differential Pom-Pom model is investigated. In its original form, that model lacks a second normal stress difference in shear and no convective constraint release is included. In this thesis, modifications of the Pom-Pom model are proposed for better rheological performance, inclusion of a second normal stress difference in shear, and avoiding numerical problems (see chapters 3 and 5).

Multiple relaxation times within the relaxation spectrum are necessary to satisfactorily describe the linear and non-linear behaviour of commercial polymers. Single-mode models can qualitatively describe the behaviour of polymer melts and therefore contribute to understand polymer processing. However, a quantitative description with single-mode models is still not possible. They predict incorrect slopes in both transient start-up as well as steady state behaviour.

Along with a reliable constitutive model, an adequate parameter identification is crucial for a correct rheological description of the characterized material. Linear viscoelastic parameters are determined from dynamic shear experiments. They form the basis for the non-linear behaviour. The chosen relaxation times determine where the non-linear start-up curves will deviate from the linear viscoelastic viscosity, depending on the strain and shear rates imposed. Non-linear parameters especially depend on the elongational behaviour of the material, and are significantly less sensitive in shear. Although materials are mostly characterized by performing linear viscoelastic and viscometric experiments, elongational data contains more information about the non-linear material behaviour. Contrary to the relatively easy viscometric, i.e. simple shear, experiments, it is very difficult to obtain reliable, accurate and reproducible shear-free data [Walters (1992), Hudson and Jones (1993), Meissner and Hostettler (1994), Zahorski (1995), Schulze et al. (1999)]. Most elongational experiments are inhomogeneous and time dependent in a Lagrangian sense. Furthermore, it is questionable if a real constant strain rate is applied and if true steady state is reached [Schulze et al. (1999), McKinley and Hassager (1999)]. Nevertheless, a lot of progress has been made in obtaining reliable rheological data for increasingly more materials and different flows, including second normal stress difference in shear and planar elongation, reversed flow and exponential shear [Meissner (1975), Münstedt and Laun (1979), Laun (1986), Hachmann (1996), Kraft (1996), Kalogrianitis and Van Egmond (1997), Wagner et al. (1998a,c), Venerus (2000), Rubio et al. (2001)].
1.3 Prototype Industrial Flows

After testing the constitutive models in pure shear or elongational flows, the question remains how well the material behaviour is captured in a flow with a combination of shear and elongation: an inhomogeneous complex flow. After all, the rheological flows are only limiting cases of complex flows. A combined experimental/numerical analysis of these complex flows is a method to evaluate constitutive models and their adequacy to describe the rheological behaviour of polymer melts and solutions. Furthermore, it may aid to understand the influence of certain geometries on the material behaviour and thus gain knowledge about industrial processes. As a consequence, complex flow problems are usually chosen as simplification of the concerning industrial processes, hence the name Prototype Industrial Flows (PIF).

The choice of a suitable Prototype Industrial Flow for evaluating constitutive equations depends on the following criteria: accessibility for experiments; maximum strain and strain rates; interplay between shear and elongation; numerical convenience. Considering these criteria, the most extensively investigated PIF, i.e. the benchmark problem of the planar abrupt contraction flow, is not really suitable. Although it has a deceptively simple geometry and mimics very well a basic industrial process, it does have some disadvantages for the evaluation of constitutive models. The sharp re-entrant corner creates a geometrical singularity, imposes high stress gradients and a thin stress boundary layer along the downstream channel wall which complicates numerical calculations (see chapter 5). Moreover, the elongational strains on the material are relatively low compared to, for example, another benchmark problem of the planar flow around a confined cylinder. The latter flow is free of geometrical singularities. In the wake of the cylinder, steady state in elongation is almost reached. However, it does have a thin stress boundary layer along the cylinder wall, causing numerical and experimental problems (see chapter 4). The third PIF investigated in this thesis is the stagnation flow in a cross-slot device. In its stagnation point, a true steady state is reached. Furthermore, it is an experimentally and numerically friendly geometry, and thus ideal for evaluating constitutive models. The three Prototype Industrial Flows are shown in figure 1.1.

![Figure 1.1: Selection of Prototype Industrial Flows.](image-url)
Other Prototype Industrial Flows that impose different deformation histories on the material are the planar contraction/expansion flow for a reversed flow effect [Wapperom and Keunings (2000, 2001)], and the axi-symmetric flow around a piston for equibiaxial elongational behaviour [Burghardt et al. (1999), Li et al. (2000), Harrison et al. (2001)].

Recent advances in experimental techniques have helped to gain point- and field-wise data. Macroscopic, integrated quantities, e.g. vortex size and pressure drop for contraction flows, and drag or friction coefficient for the flow around a confined cylinder, are only global parameters and do not reflect the local material behaviour. The present availability of non-invasive optical techniques for measuring velocities with Laser Doppler Anemometry (LDA) and stresses using Flow Induced Birefringence (FIB) makes local, quantitative comparison with computations possible. In this thesis, calculations are compared with experimental results in PIF's from Schoonen (1998). Velocities were measured using Particle Imaging Velocimetry (PIV), while stresses were obtained by Flow Induced Birefringence. More stable experimental data with a significantly higher resolution was realized by introducing a gear pump in the experimental set-up and using a laser beam as a light source [Schoonen (1998)]. The flow cells were designed to have nominally two-dimensional geometries for a comparison with two-dimensional computations. To link the experimental FIB light intensities (which is an integrated effect over the depth of the flow cell) to the calculated stresses, the empirical Stress Optical Rule (SOR) is used. This rule is temperature dependent and it is not always certain if it holds. Besides the SOR, also Mueller calculus is needed if three-dimensional results are compared. In chapter 2, a full three-dimensional numerical/experimental comparison is carried out for a solution flowing through a cross-slot device. At the time, only three-dimensional experimental results for a solution were available.

1.4 Numerical methods

Although significant progress has been made in the last decades on numerical tools, they are still not able to provide accurate results at processing conditions in a fully coupled manner. Decoupled techniques, i.e. first solving the kinematic variables with a generalized Maxwell model and then calculating stresses over stream lines, can resolve problems for higher speeds. However, the velocities and velocity gradients may differ significantly from those calculated by coupled methods, i.e. velocities and stresses influence each other, resulting in very different numerical predictions as shown in chapter 4.

Different numerical techniques have been proposed over the years to resolve the problems involved in calculating viscoelastic flows. Chapter 2 gives a short overview and a more elaborate review on mixed finite element methods is given in Baaijens (1998b). Most of these methods employ differential type constitutive models. Although the newly developed deformation fields method by Peters et al. (2000a) is an attractive way to calculate models of the integral type, finite element methods using the differential models are still more efficient in CPU time and computational memory.

The stability of numerical methods is still a major issue, which involves elaborate investigation [Bogaards et al. (1999a), Smith et al. (2000), Bogaards et al. (2001), Sureshkumar (2001)]. Loss of convergence may be due to the numerical method used, the constitutive model, or its parameters, see for example Bogaards et al. (2001) or chapter 5. In
general, single-mode models are more liable to numerical problems than multi-mode models [Bishko et al. (1999), Bogaerds et al. (2001)].

Throughout this thesis, the Discrete Elastic Viscous Stress Splitting (DEVSS) technique in combination with the Discontinuous Galerkin (DG) method is used. Although it is known to have a temporal stability problem for flows which invoke high elasticities [Bogaerds et al. (1999a)], it is more robust towards non-smooth flows than Streamline Upwind Petrov-Galerkin (SUPG) methods. Furthermore, it has proven to be an accurate method which is able to efficiently handle multiple relaxation times.

The chapters 2 to 5 in this thesis are separate articles, resulting in overlap and recurrence between the chapters.
Chapter 2

3D viscoelastic analysis of a polymer solution in a complex flow*

A mixed low-order finite element technique based on the DEVSS/DG method has been developed for the analysis of three dimensional viscoelastic flows in the presence of multiple relaxation times. In order to evaluate the predictive capabilities of some established nonlinear constitutive relations like the Giesekus and the Phan-Thien Tanner model results of 3D calculations are compared with experimental results in a cross-slot flow geometry. Moreover, the performance of a new viscoelastic constitutive equation that provides enhanced independent control of the shear and elongational properties is investigated. Steady shear flows and a combined shear/elongational flow are analyzed for a polyisobutylene solution. A general method is introduced to compare calculated stresses along the depth of the flow with birefringence measurements using the stress optical rule.

In particular at and downstream of the stagnation point in the cross-slot flow geometry, the numerical/experimental evaluation shows that the multi-mode Giesekus and the PTT model are unable to describe the stress related experimental observations. The new viscoelastic constitutive relation proves to perform significantly better for this stagnation flow.

2.1 Introduction

Most present research on calculations of steady viscoelastic flows has been performed on 2D benchmark problems like the falling sphere in a tube problem (e.g. Lunsmann et al. (1993), Baaijens (1994a), Sun and Tanner (1994), Yurun and Crochet (1995), Baaijens et al. (1997)) or the four-to-one contraction problem (e.g. Yurun and Crochet (1995), Guénette and Fortin (1995), Azaiez et al. (1996), Baaijens et al. (1997)). Also periodic flows such as the corrugated tube flow (e.g. Pilitsis and Beris (1989), Pilitsis and Beris (1991), Van Kemenade and Deville (1994), Talwar and Khomami (1995b), Szady et al. (1995)) and the flow past an array of cylinders (e.g. Khomami et al. (1994), Talwar and Khomami (1995a), Souvaliotis

*This chapter is largely based on: Bogaards et al. (1999b)
and Beris (1996)) have been extensively investigated. These flows are generally characterized by steep stress gradients near curved boundaries and geometrical singularities, which require the use of highly refined meshes. Accurate flow analysis of both polymer solutions and melts compels the use of multiple relaxation times. When using mixed finite element methods this results in a very large number of degrees of freedom and solution efficiency, both in terms of CPU time and memory requirement, is an important issue.

Over the last decade, a lot of research has been performed on solving the governing equations in an accurate and stable manner and yet still being able to efficiently handle the multitude of stress unknowns. For a recent review on mixed finite element methods for viscoelastic flow analysis, see Baaijens (1998b). Two basic problems needed resolution: i) the presence of convective terms in the constitutive equation whose relative importance grows with increasing Weissenberg number and ii) the choice of discretisation spaces of the independent variables (velocity, pressure, extra stresses and auxiliary variables). Several techniques have been proposed to overcome these problems and some of the most effective mixed finite element methods presently available either employ the Streamline Upwind Petrov Galerkin (SUPG) method of Marchal and Crochet (1987) or the Discontinuous Galerkin (DG) method of Fortin and Fortin (1989) based on the ideas of Lesaint and Raviart (1974) to handle the convective terms, while the lack of ellipticity of the momentum equation is resolved by using the Explicitly Elliptic Momentum Equation (EEME) formulation introduced by King et al. (1988), the Elastic Viscous Stress Split (EVSS) formulation of Rajagopalan et al. (1990), or, more recently, the Discrete Elastic Viscous Stress Splitting (DEVSS) method of Guénette and Fortin (1995).

Marchal and Crochet (1987) used the inconsistent SU method and emphasized that in a mixed velocity-pressure-stress formulation interpolation of the deviatoric stress cannot be chosen independent and has to satisfy a compatibility condition. In order to fulfill this condition they used a four-by-four bi-linear subdivision for the stresses on each bi-quadratic velocity element. This however leads to a very high number of degrees of freedom of the stresses, especially when multiple relaxation times are considered. The EEME method has been shown to give accurate and stable results by introducing a second-order elliptic operator to the momentum equation. This method however, is restricted to UCM-like nonlinear constitutive equations and excludes the use of a solvent viscosity. The EVSS method is obtained by splitting the deviatoric stress into a viscous and an elastic contribution. An adaptive strategy in combination with a modified SUPG method as proposed by Sun et al. (1996) has given stable results for the falling sphere in a tube benchmark problem. A disadvantage of all of these methods is the continuous interpolation of the extra stress and the subsequent large sets of global unknowns upon discretisation. The Discontinuous Galerkin method on the other hand employs a discontinuous interpolation of the stress variables which leads to a more easily satisfied inf-sup condition for stress and velocity and a substantial reduction of global degrees of freedom when an implicit/explicit scheme is used. In this work, the numerical method applied to the viscoelastic flow simulations is basically a modified formulation of the DG method. The DG method has been extended with the DEVSS formulation for which a change of variable leads to an extra stabilizing equation. Furthermore, using an implicit/explicit handling of the advective part of the constitutive equation, this leaves the DEVSS/DG method which has been introduced to the calculation of viscoelastic flows by Baaijens et al. (1997) and has recently been successfully used by Béraudo et al. (1998).
In this work, an efficient numerical scheme, based on the DEVSS/DG method, is developed for the analysis of 3D multi-mode viscoelastic flows. Also, a numerical/experimental evaluation is presented for both steady shear flows as well as a steady inhomogeneous flow in a cross-slot device to study the behavior of different constitutive models under such circumstances. To achieve this, a method based on Mueller calculus is implemented to retrieve measurable optical quantities from computed stress fields by assuming the stress optical rule to hold. Two of the more popular constitutive relations of differential type (the Giesekus and the Phan-Thien Tanner model) are applied together with a recently proposed model by Peters et al. (1999) that provides enhanced control of shear and elongational properties. Although the computational procedure allows for transient calculations, only steady flows will be investigated using a time-marching scheme to reach the steady state solution.

2.2 Problem definition

Here, only steady incompressible, isothermal and inertia-less flows are considered. In the absence of body forces, these flows can be described by a reduced equation for conservation of momentum (2.1) and conservation of mass (2.2):

$$\nabla \cdot \sigma = 0 ,$$  \hspace{1cm} (2.1)

$$\nabla \cdot \vec{u} = 0 ,$$  \hspace{1cm} (2.2)

with $\nabla$ the gradient operator, and $\vec{u}$ the velocity field. The Cauchy stress tensor $\sigma$ is defined as:

$$\sigma = -pI + \tau ,$$  \hspace{1cm} (2.3)

with pressure $p$ and the extra stress tensor $\tau$. For most realistic viscoelastic fluids it is often necessary to approximate the relaxation spectrum with a discrete set of viscoelastic modes. The total extra stress for these so called multi-mode applications can be expressed as the sum of the stresses belonging to the separate viscoelastic modes, hence:

$$\tau = \sum_{i=1}^{M} \tau_i ,$$  \hspace{1cm} (2.4)

where $M$ denotes the total number of different modes. Within the scope of this work, a sufficiently general way to describe the constitutive behavior of one individual mode is obtained by using a constitutive equation of the differential form:

$$\nabla \tau + f_c(\tau, D) + \frac{f_d(\tau)}{\lambda} = 2GD ,$$  \hspace{1cm} (2.5)

with $\lambda$ and $G$ the relaxation time and the modulus of this mode and $D$ the rate of deformation tensor defined as $D = \frac{1}{2}(\nabla \vec{u} + (\nabla \vec{u})^c)$ with $(\cdot)^c$ denoting the conjugate of a second order...
The upper convected time derivative of the extra stress tensor is defined as:

\[ \nabla \tau = \frac{\partial \tau}{\partial t} + \mathbf{u} \cdot \nabla \tau - \mathbf{L} : \mathbf{\tau} - \mathbf{\tau} : \mathbf{L}^c, \]  

(2.6)

with \( \mathbf{L} \) the velocity gradient tensor \( \mathbf{L} = (\nabla \mathbf{u})^c \). Both functions \( f_c(\tau, \mathbf{D}) \) and \( f_d(\tau) \) depend upon the chosen constitutive model. Notice that for \( f_c(\tau, \mathbf{D}) = 0 \) and \( f_d(\tau) = \tau \) the Upper Convected Maxwell (UCM) model is obtained. Some conventional nonlinear models that are applied in this work for the rheological characterization of the viscoelastic fluid, are the Giesekus model which is defined as:

\[ f_c = 0, \quad f_d = \tau + \frac{\varepsilon}{G} \tau : \mathbf{\tau}, \]  

(2.7)

and the linear Phan-Thien Tanner (PTT) model:

\[ f_c = \xi (\mathbf{D} : \mathbf{\tau} + \mathbf{\tau} : \mathbf{D}), \quad f_d = (1 + \frac{\varepsilon}{G} I_\tau) \mathbf{\tau}, \]  

(2.8)

with \( I_\tau \) the first invariant of \( \mathbf{\tau} \) (i.e. \( I_\tau = \text{tr}(\mathbf{\tau}) \)) and \( \varepsilon \) and \( \xi \) adjustable parameters. More detailed information on the rheological behavior of the constitutive equations can be found in Tanner (1985), Bird et al. (1987) and Larson (1988).

A new class of viscoelastic constitutive relations that incorporate more flexibility was recently proposed by Peters et al. (1999) and Schoonen et al. (1998). Their method involves a generalization of the UCM model by allowing both the relaxation time and the modulus to be a function of the extra stress, i.e. \( \lambda(\tau) \) and \( G(\tau) \). Both \( \lambda(\tau) \) and \( G(\tau) \) are chosen such that in the limit of infinitesimal strains the linear Maxwell model is recovered. For steady planar shear flows, with shear rate \( \dot{\gamma} \), it holds that:

\[ \tau = G \lambda \dot{\gamma}, \]  

(2.9)

with \( \tau \) the shear stress. To obtain the simple shear viscosity function \( (\eta = G\lambda) \), the empirical Cox-Merz rule is approximated by a modification of the Ellis-model [Schoonen (1998)], hence:

\[ G\lambda = \left\{ \frac{G_0 \lambda_0}{1 + A \left[ \frac{H_\tau}{G_0} \right]^a} \right\}^b \]  

(2.10)

with \( H_\tau = \frac{1}{2}(I_\tau^2 - \text{tr}(\mathbf{\tau} : \mathbf{\tau})) \) the second invariant of the extra stress tensor and \( G_0, \lambda_0 \) initial linear material parameters. Since only the viscosity function is determined, a choice remains to be made for the relaxation time (or the modulus). A suitable choice can be:

\[ \lambda = \frac{\lambda_0}{1 + \frac{\lambda_0}{G_0} I_\tau}, \]  

(2.11)

which is the same function as is used in the linear PTT model. This model has been introduced as the Feta-PTT model for its shear viscosity is fixed by equation 2.10 (hence the prefix Fixed eta) and thus not sensitive to variations of the nonlinear parameter \( \varepsilon \). While the first normal stress coefficient only slightly depends on \( \varepsilon \), the elongational viscosity proves to be significantly more sensitive to variations of this parameter. As a result, shear and elongational properties can be controlled more independently.
2.3 Computational method

The modeling of polymer flows gives rise to some considerable characteristic problems. Looking more closely at the governing equations (eq. 2.1, 2.2 and 2.5) it is obvious that the use of multiple relaxation times inevitably leads to a very large system of equations when the extra stress variables are considered as global degrees of freedom. Another problem and a challenging field of investigation is the loss of convergence of the numerical algorithm for increasing elasticity in the viscoelastic flow.

There are several computational methods available today that are more or less capable of efficiently handling the above problems. The method used in this report is known as the Discrete Elastic Viscous Stress Splitting Discontinuous Galerkin method (DEVSS/DG). It is basically a combination of the Discontinuous Galerkin method that was developed by Lesaint and Raviart (1974) and the Discrete Elastic Viscous Stress Splitting technique of Guénette and Fortin (1995). The DEVSS/DG was first applied to 2D viscoelastic flows in Baaijens et al. (1997) and can be stated as:

**Problem DEVSS/DG:** Find $\tau_i$, $\vec{u}$, $D$ and $p$ such that for all admissible test functions $S_i$, $\vec{v}$, $G$ and $q$,

\[
\left( S_i, \nabla \tau_i + f_c(\tau_i, D_u) + \frac{f_d(\tau_i)}{\lambda_i} - 2G_i D_u \right) - \sum_{i=1}^{K} \int_{\Gamma^\text{inflow}} S_i : \vec{u} \cdot \vec{n} \left( \tau_i - \tau_i^\text{ext} \right) d\Gamma = 0 \quad \forall \ i \in \{1, 2, \ldots, M\},
\]

\[
\left( D_u, 2\eta \left( D_u - D \right) + \sum_{i=1}^{M} \tau_i \right) - \left( \nabla \cdot \vec{v}, p \right) = 0,
\]

\[
\left( G, D - D_u \right) = 0,
\]

\[
\left( q, \nabla \cdot \vec{u} \right) = 0,
\]

where $(.,.)$ denotes the $L_2$-inner product on the domain $\Omega$, $\tau_i^\text{ext}$ the extra stress tensor of the neighboring element, $\vec{n}$ the unit vector pointing outward normal on the boundary of the element ($\Omega^e$) and $D_\varphi = \frac{1}{2} \left( \nabla \varphi + \left( \nabla \varphi \right)^t \right)$ with $\varphi = \vec{u}, \vec{v}$.

As proposed by Guénette and Fortin (1995) a stabilization term has been added to the momentum equation (2$\eta(D_u - D)$, eq. 2.13) in combination with an $L_2$ projection of the rate of deformation tensor to yield a discrete approximation of $D$ (eq. 2.14). The stabilizing parameter $\bar{\eta}$ in equation 2.13 can be varied in order to give optimal results. Following Guénette and Fortin (1995) and Baaijens et al. (1997), $\bar{\eta} = \sum_{i=1}^{M} G_i \lambda_i$ is chosen and found to give satisfactory results.

Based on the ideas of Lesaint and Raviart (1974), a discontinuous interpolation is applied to the extra stress variables which are now considered as local degrees of freedom and can
be eliminated at the element level. Upwinding is performed on the element boundaries by adding integrals on the inflow boundary of each element and thereby forcing a step of the stress at the element interfaces (eq. 2.12). Time discretisation of the constitutive equation is attained using an implicit Euler scheme, with the exception that $\tau_{\text{ext}}$ is taken explicitly (i.e. $\tau_{\text{ext}}^{i} = \tau_{\text{ext}}^{i}(t_{n})$). Hence, the term $\int_{S_{i}}: \vec{u} \cdot \vec{n}(-\tau^{\text{ext}}_{i})d\Gamma$ has no contribution to the Jacobian which allows for local elimination of the extra stress.

In order to obtain an approximation of problem DEVSS/DG, the 3D domain is divided into $K$ hexahedral elements. A choice remains to be made about the order of the interpolation polynomials of the different variables with respect to each other. As is known from solving Stokes flow problems, velocity and pressure interpolation cannot be chosen independently and has to satisfy the Ladyzenskaya-Babuska-Brezzi condition. Likewise, interpolation of velocity and extra stress has to satisfy a similar compatibility condition in order to obtain stable results. Baaijens et al. (1997) have shown that for 2D problems, discontinuous bi-linear interpolation for extra stress, bi-linear interpolation for discrete rate of deformation and pressure with respect to bi-quadratic velocity interpolation gives stable results. Hence, extrapolating this approach to a third dimension and satisfying the LBB condition, spatial discretisation is performed using tri-quadratic interpolation for velocity, tri-linear interpolation for pressure and discrete rate of deformation while the extra stresses are approximated by discontinuous tri-linear polynomials (figure 2.1). Integration of equation 2.12 to 2.15 over an element is performed using a quadrature rule common in finite element analysis ($3 \times 3 \times 3$-Gauss rule).

To obtain the solution of the nonlinear equations, a one step Newton-Raphson iteration process is carried out. Consider the iterative change of the nodal degrees of freedom ($\delta_{\tau}, \delta_{u}, \delta_{\bar{D}}, \delta_{p}$) as variables of the algebraic set of linearized equations. This linearized set is given by:

\[
\begin{pmatrix}
Q_{\tau\tau} & Q_{\tau u} & 0 & 0 \\
Q_{u\tau} & Q_{uu} & Q_{uD} & Q_{up} \\
0 & Q_{D u} & Q_{D D} & 0 \\
0 & Q_{p u} & 0 & 0
\end{pmatrix}
\begin{pmatrix}
\delta_{\tau} \\
\delta_{u} \\
\delta_{\bar{D}} \\
\delta_{p}
\end{pmatrix}
=
\begin{pmatrix}
f_{\tau} \\
f_{u} \\
f_{\bar{D}} \\
f_{p}
\end{pmatrix},
\]

where $f_{\alpha}$ ($\alpha = \tau, \vec{u}, \bar{D}, p$) correspond to the residuals of eq. 2.12-2.15, while $Q_{\alpha\beta}$ follow from linearisation of these equations. Due to the fact that $\tau_{\text{ext}}$ has been taken explicitly in eq. 2.12, matrix $Q_{\tau\tau}$ has a block diagonal structure which allows for calculation of $Q_{\tau\tau}^{-1}$ on

Figure 2.1: Mixed finite element, $\vec{u} \rightarrow$ tri-quadratic, $p, \bar{D} \rightarrow$ tri-linear, $\tau \rightarrow$ discontinuous tri-linear.
the element level. Consequently, this enables the reduction of the global DOF’s by static condensation of the extra stress. Despite this approach, still a rather large number of global degrees of freedom remains per element as it is depicted in figure 2.1 (137 DOF/element). A further reduction of the size of the Jacobian is obtained by decoupling problem 2.16. First, the ‘Stokes’ problem is solved (\(u, p\)) after which the updated solution is used to find a new approximation for \(D\). The following problems now emerge:

**Problem DEVSS/DG\(a\):** Given \(\tau, \bar{u}, D\) and \(p\) at \(t = t_n\), find a solution at \(t = t_{n+1}\) of the algebraic set:

\[
\begin{pmatrix}
Q_{uu} - Q_{up}Q_{\tau}^{-1}Q_{\tau u} & Q_{up} \\
Q_{pu} & 0
\end{pmatrix}
\begin{pmatrix}
\delta u \\
\delta p
\end{pmatrix}
= -
\begin{pmatrix}
f_u - Q_{up}Q_{\tau}^{-1}f_{\tau} \\
f_p - f_{p}\end{pmatrix},
\]  

(2.17)

and **Problem DEVSS/DG\(b\):** Given \(D\) at \(t = t_n\) and \(\bar{u}\) at \(t = t_{n+1}\), find \(\delta D\) from:

\[
Q_{DD} \delta D = -f_D.
\]

(2.18)

Notice that \(f_D\) is now taken with respect to the new velocity approximation, i.e. \(f_D(\bar{u}^{n+1}, D^n)\) rather than \(f_D(\bar{u}^n, D^n)\). The nodal increments of the extra stress are retrieved element by element following:

\[
\delta \tau = -Q_{\tau}^{-1}f_{\tau},
\]

(2.19)

with \(f_{\tau}\) also taken with respect to the new velocity approximation \((f_{\tau}(\tau^n, \bar{u}^{n+1}))\).

Using the above procedure, still a substantial number of unknowns remain per element. Although direct solvers often prove to be more stable in comparison to iterative solvers, they soon become impractical for 3D viscoelastic calculations due to excessive memory requirements which inevitably leads to the application of iterative solvers. To solve the non-symmetrical system of problem DEVSS/DG\(a\) an iterative solver has been used based on the Bi-CGSTAB method of Van der Vorst (1992). The symmetrical set of algebraic equations of problem DEVSS/DG\(b\) has been solved using a Conjugate-Gradient solver. Incomplete LU preconditioning has been applied to both solvers. It was found that solving the coupled problem (hence, solving for \(\delta u, \delta D, \delta p\) at once) led to divergence of the solver while significantly better results were obtained for the decoupled system. In order to enhance the computational efficiency of the Bi-CGSTAB solver, static condensation of the center-node velocity variables results in filling of the zero block diagonal matrix in problem DEVSS/DG\(a\) and, in addition, achieves a further reduction of global degrees of freedom.

Finally, to solve the above sets of algebraic equations, both essential and natural boundary conditions must be imposed on the entrance and exit of the flow channels. At the entrance and the exit of the flow channels the velocity unknowns are prescribed. Also, at the entrance, the known shear rates enable the calculation of the ‘steady state’ stresses by solving the constitutive equation which are then prescribed along the inflow boundary.

### 2.4 Rheological characterization

The polymer solution consists of 2.5% Polyisobutylene (Oppanol B200, BASF) dissolved in tetrade cane (2.5% PIB/C14). This solution has been extensively characterized and
Table 2.1: Material parameters of 2.5% polyisobutylene dissolved in tetradecane (2.5% PIB/C14) at \( T = 20 \, ^\circ\text{C} \), obtained from Schoonen et al. (1998).

<table>
<thead>
<tr>
<th>Mode</th>
<th>Maxwell</th>
<th>Giesekus</th>
<th>PTT (set 1)</th>
<th>PTT (set 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.3 \times 10^{11}</td>
<td>3.6 \times 10^{-3}</td>
<td>0.30</td>
<td>0.80</td>
</tr>
<tr>
<td>2</td>
<td>3.6 \times 10^{10}</td>
<td>3.1 \times 10^{-2}</td>
<td>0.00</td>
<td>0.42</td>
</tr>
<tr>
<td>3</td>
<td>1.8 \times 10^{10}</td>
<td>1.6 \times 10^{-1}</td>
<td>0.42</td>
<td>0.07</td>
</tr>
<tr>
<td>4</td>
<td>5.1 \times 10^{-4}</td>
<td>3.6 \times 10^{-1}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

documented by Schoonen et al. (1998). Results of the material characterization are listed in table 2.1. The fluid has been characterized by the Giesekus model and the linear PTT model (once with a nonzero parameter \( \xi \) and once with \( \xi \) set to zero). The moduli and the relaxation times are obtained from dynamic measurements and the nonlinear parameters \( (\varepsilon, \xi) \) have been fitted on steady shear data only. Figure 2.2 shows the rheological behavior of both the Giesekus and the linear PTT model in simple shear together with the measured shear data. It can be seen that the PTT model (set 1) agrees very well with experimental observations of steady shear viscosity. Because of the limited range covered by the relaxation times, deviations from measured data start at shear rates of approximately \( \dot{\gamma} > 2 \times 10^2 \, [\text{s}^{-1}] \). Predictions for the different models in extension are depicted in figure 2.3. As can be seen from this figure the Giesekus model and, to a lesser degree, the PTT model with the nonzero \( \xi \) parameter, show an elongational thickening behavior for increasing extension rates whereas the PTT model with the zero \( \xi \) parameter shows an elongational thinning behavior.

Determination of the parameters of the Feta-PTT model is more troublesome. Parameters of the modified Ellis model can easily be determined from measured viscosity data (figure 2.4(left), \( A, a, b = 16, 2, 0.45 \)). However, since the nonlinear parameter \( \varepsilon \) only slightly influences the shear properties of the model, additional elongational data is required to obtain a fit for this parameter. Figure 2.4(right) shows the influence of variations of \( \varepsilon \) on the first normal stress coefficient whereas figure 2.5 shows the sensitivity of the elongational

Figure 2.2: Steady shear viscosity (left) and first normal stress coefficient (right) of 2.5% PIB/C14 together with experimental data, --- Giesekus, \( \cdots \) PTT \((\xi=0)\), \( - - \) PTT \((\xi\neq0)\).
3D viscoelastic analysis of a polymer solution in a complex flow

Figure 2.3: Predictions for 2.5% PIB/C14 in uniaxial (left) and planar elongation (right), —— Giesekus, ···· PTT (ξ=0), —— PTT (ξ≠0).

Figure 2.4: Material functions for increasing nonlinear parameter ε of the Feta-PTT model (ε = 0.04, 0.06, 0.08, 0.10, 0.12). Steady shear viscosity (left) and first normal stress coefficient (right).

Figure 2.5: Uniaxial (left) and planar (right) elongational viscosity for increasing nonlinear parameter ε of the Feta-PTT model (ε = 0.04, 0.06, 0.08, 0.10, 0.12).
viscosities towards $\varepsilon$. Additional information on the behavior of the fluid in elongation is obtained from Schoonen et al. (1998) who was able to estimate the planar elongational viscosity at a number of elongational rates from the stagnation flow described in this work. It can be seen that $\varepsilon = 0.06$ yields the best fit of the elongational data whereas a reasonable fit of the first normal stress coefficient is obtained.

### 2.5 Flow induced birefringence

The experimental data of the flows described in this work consists of two parts. First, point-wise velocity measurements have been carried out using Laser Doppler Anemometry (LDA) and second, Flow Induced Birefringence (FIB) has been used to measure the stresses over the depth of the flow. Generally, the stress state will not be constant over the depth of the flow cell due to the influence of both confining walls. Therefore, in order to present a valid comparison between measured and computed stress related quantities, the flow induced birefringence measurements need some further attention.

#### 2.5.1 General Mueller/Stokes approach

Physically, the change of polarization of light traveling through the flow cell is caused by refractive gradients induced by the alignment of the polymeric molecules. Hence, upon emerging from the flow cell, the relative phase difference (retardation angle) of the extraordinary and ordinary component of the light differs from its initial value. Figure 2.6 shows the change of polarization within a small detail of the flow cell. The two principal electro-magnetic components will move differently along the optical path which causes a relative phase difference. The optical axis of this detail of the flow is rotated (rotation angle $\chi$) relative to a fixed axis.

Mathematically, the state of polarization and the change of polarization caused by a retarder can be described by the Stokes vector and the Mueller matrix ($4 \times 4$) characteristic for this retarder [Hecht (1987)]. Hence, the change of polarization of light traveling through
the total flow cell can be expressed as:

\[ S_{\text{out}} = M^{fc} S_{\text{in}}, \]

(2.20)

with \( M^{fc} \) the Mueller matrix of the flow cell and \( S_{\text{in}}, S_{\text{out}} \) the Stokes vectors of respectively the incoming and outgoing light beam.

The Stokes vector consists out of four Stokes parameters: \( S_0, S_1, S_2, \) and \( S_3 \). They can be formulated out of directly measurable quantities. \( S_0 \) is the incident irradiance, while \( S_1, S_2, \) and \( S_3 \) specify the state of polarization in the following way:

\[
S_0 = 2I_0, \\
S_1 = 2I_1 - 2I_0, \\
S_2 = 2I_2 - 2I_0, \\
S_3 = 2I_3 - 2I_0.
\]

(2.21) \( (2.22) \) \( (2.23) \) \( (2.24) \)

Here, \( I_0 \) is the total irradiance, \( I_1 \) denotes the irradiance transmitted by a horizontal linear polarizer, \( I_2 \) equals the irradiance transmitted by a linear polarizer at 45°, and \( I_3 \) is the irradiance transmitted by a right circular polarizer.

A general differential method to calculate \( M^{fc} \) was developed by Azzam (1978). For the viscoelastic flows described in this work, the change of polarization of light traveling through the optical anisotropic medium with continuously varying properties along the optical path is approximated by a discrete set of 2-dimensional optical elements (figure 2.7). Thus, the Mueller matrix of the flow cell is now given by multiplication of the subsequent Mueller matrices of these 2-dimensional optical elements:

\[ M^{fc} = M_N M_{N-1} \ldots M_2 M_1, \]

(2.25)

where \( N \) is taken equal to the number of numerical elements along the optical path. Each optical element is characterized by a phase retardation (\( \delta \)) and an orientation angle (\( \chi \)) which leads to the following Mueller matrix:

\[
M_i(\delta, \chi) = \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & c_\phi^2 + s_\phi^2 s_\chi^2 & (1 - c_\phi)s_\phi s_\chi c_\chi & -s_\phi s_\chi c_\phi \\
0 & (1 - c_\phi)s_\phi s_\chi c_\chi & s_\phi^2 c_\chi^2 + c_\phi^2 s_\chi^2 & s_\phi c_\phi c_\chi \\
0 & s_\phi s_\chi c_\phi & -s_\phi c_\chi s_\phi & c_\phi^2 + s_\phi^2 s_\chi^2 \\
\end{pmatrix},
\]

(2.26)

where \( c_\phi = \cos \varphi \) and \( s_\varphi = \sin \varphi \) (\( \varphi = \delta, 2\chi \)). Mechanical and optical properties can be coupled by means of the empirical stress optical rule, which relates the deviatoric part

Figure 2.7: Flow through a rectangular duct (flow direction perpendicular to the paper), optical properties are represented by \( N \) optical elements with \( N \) equal to the number of elements along the depth of the duct in the numerical simulation.
of the refractive index tensor \( (n) \) to the extra stress tensor by a characteristic stress optical coefficient \( (C) \):

\[
n = C\tau .
\]

(2.27)

Now, consider only the projection of the birefringence tensor in the plane perpendicular to the optical path, say for example the \( xy \)-plane, the empirical stress optical rule for one optical element leads to:

\[
\sin 2\chi \delta = 2k_0dC\tau_{xy} ,
\]

(2.28)

\[
\cos 2\chi \delta = k_0dCN_1 ,
\]

(2.29)

with \( k_0 \) the initial propagation number \( (k_0 = 2\pi/\lambda_0) \), \( d \) the thickness, \( \tau_{xy} \) the mean plane shear stress and \( N_1 = \tau_{xx} - \tau_{yy} \) the mean first normal stress difference of the \( i^{th} \) element. Application of equation 2.28 and 2.29 to the Mueller matrix of a single element layer \( (M_i) \), enables the calculation of a discrete approximation of the Mueller matrix of the total flow cell \( (M_{fc}) \) and hence, allows for a numerical/experimental evaluation of the optical properties.

### 2.5.2 FIB measurements for polymer solutions

The setup, used for the 2.5% PIB/C14 solution, gathers point-wise optical data and is shown in figure 2.8. Here, only a short outline of the experimental setup is presented, for a detailed description on the FIB experiments see Schoonen et al. (1998). Unpolarized monochromatic light from a source with intensity \( I_{in} (\lambda_0=632.8 \text{ [nm]}) \) travels through the total setup. Using standard expressions for the Mueller matrices of the optical elements [Hecht (1987)], the intensity of the transmitted light can be described by:

\[
I_{out} = \frac{I_{in}}{4} \left( 1 + M_{42} \cos (4\omega t) + M_{43} \sin (4\omega t) \right) ,
\]

(2.30)

with \( \omega \) the rotating frequency of the half wave plate and \( M_{42} \), \( M_{43} \) the \((4,2)\) and the \((4,3)\)-component of the Mueller matrix of the flow cell. For low-viscosity viscoelastic flows that induce little retardation upon the transmitted light, it can be shown that \( M_{42} \) and \( M_{43} \) reduce to integrals along the optical path:

\[
M_{42} = 2k_0C \int \tau_{xy} \, dz ,
\]

(2.31)

\[\text{Figure 2.8: Experimental (FIB) setup for 2.5\% PIB/C14 solution, light travels through a linear polarizer (p) at } 0^\circ, \text{ a rotating half-wave plate (r), a collimating lens (l), the flow cell (fc), a quarter-wave plate (q) at } 45^\circ \text{ and again through a linear polarizer at } 0^\circ.\]
This approximation has, for instance, been used in Li et al. (1998) and Schoonen et al. (1998).

\[ M_{43} = -k_0 C \int N_1 \, dz \]  \hfill (2.32)

2.6 Flows of a polyisobutylene solution

A comparison is presented between numerical and experimental results for a steady 3D shear flow in a rectangular tube (slit flow), figure 2.9 (left), and a steady combined complex flow, figure 2.9 (right), through a cross-slot device. For the cross-slot flow, due to its non-homogeneous nature (material near the center will experience a much higher strain rate than near the in- or outlet), the behavior of the constitutive models can be evaluated for complex flows. The aspect-ratio of both main axes of the rectangular cross section of the channel has been chosen close to unity and thus, a full 3D flow field is obtained.

2.6.1 Slit flow

Numerical investigations of a steady shear flow have been performed on a rectangular channel with a depth to height ratio of 2. Figure 2.10 shows the geometry and mesh used to analyze this flow. For reasons of symmetry only one-quarter of the total channel has been modeled.
Figure 2.11: Calculated and measured fully developed velocity profile along $y$-axis (left) and $z$-axis (right) ($\bar{u}_{20} = 26 \cdot 10^{-2} \text{ [m/s]}$), — Giesekus, ⋯ PTT ($\xi = 0$), —— PTT ($\xi \neq 0$).

Figure 2.12: Calculated fully developed velocity profile and stress components for the Giesekus model ($\bar{u}_{20} = 26 \cdot 10^{-2} \text{ [m/s]}, |\tau| = 18.9 \text{ [Pa]}$).
3D viscoelastic analysis of a polymer solution in a complex flow

At the entrance and the exit, initially, a fully developed Newtonian velocity profile [Shah and London (1978)] is prescribed with a 2D mean velocity ($\bar{u}_{2D}$) at symmetry plane $z = 0$. This characteristic mean 2D flow follows from experimental observations and was determined at $\bar{u}_{2D} = 26 \cdot 10^{-2}$ [m/s]. As a next step, the converged solution at the middle of the flow cell is taken as boundary conditions for a recurring computation. In this way the slit flow is iterated until the non-Newtonian steady state solution is obtained, usually two or three iteration steps suffice. An alternative to this procedure (but one that has not been implemented in our code yet) is the application of periodical boundary conditions for the in- and outflow unknowns. In this way fully developed flows may be obtained in a more natural way by prescribing a flow rate rather than velocities. A dimensionless flow strength for this shear flow can be obtained by means of the Weissenberg number:

$$\text{We} = \frac{\bar{\lambda} \bar{u}_{2D}}{H} = 2.54,$$  \hspace{0.5cm} (2.33)

with $\bar{\lambda}$ a viscosity averaged relaxation time ($\bar{\lambda} = \sum_{i=1}^{M} (\lambda_i G_i) / \sum_{i=1}^{M} (\lambda_i G_i)$).

Results of calculated fully developed velocity profiles along the $y$-axis and the $z$-axis for the different established constitutive models are shown in figure 2.11 together with the measured values. As can be seen from this figure, both the Giesekus and the PTT model with the nonzero $\xi$ parameter fit the measured velocity data reasonably well.

Figure 2.12 shows the calculated fully developed stresses at a cross section of the slit for the Giesekus model. The, in principle, discontinuous stresses are averaged over the nodes and scaling is performed following $|\tau| = \sum_{i=1}^{M} (\lambda G_i) \bar{u}_{2D} / H$. It can be seen from this figure that both confining walls have a large influence on the calculated stress field. Especially the stress components relevant for birefringence measurements, i.e. $N_1$ and to a lesser degree $\tau_{xy}$, are influenced by these walls. Rather than simple extinction near the upper and lower walls, as is observed for $\tau_{xy}$, additional nonzero values of $N_1$ are observed due to the shear rate perpendicular to the $xy$-plane. Thus, large deviations can be expected for these integrated stresses along the depth of the flow compared to 2D calculations. This is also confirmed in figure 2.13 where integrated stresses are compared to stresses at the mid plane ($z = 0$).

Figure 2.13: Integrated principal stress difference ($N_1$) (left) and shear stress ($\tau_{xy}$) (right) over the depth of the slit for the Giesekus model (---) compared to 2D stresses (- -) ($|\tau| = 18.9$ [Pa]).
Hence, this flow has to be treated as truly 3D and cannot be compared using 2D viscoelastic calculations.

Comparison of the point-wise optical data with the calculated stresses is performed by means of the empirical stress optical coefficient. This material constant has been determined by Schoonen et al. (1998) which is adopted here \( C = 2.505 \cdot 10^{-9} \, \text{[m}^2/\text{N}] \). The calculated optical properties for the different models are presented in figure 2.14 together with measured values of the optical signal. It can be seen that all models predict shear stresses that are in good agreement with experimental observations. Predictions of the first normal stress difference, on the other hand, are best for the Giesekus model while the PTT model underpredicts and the Feta-PTT overpredicts the shear induced normal stresses.

### 2.6.2 Cross-slot flow

Flow of the PIB/C14 solution through a cross-slot device has been analyzed. The geometry and the mesh used for this flow are depicted in figure 2.15. Again, due to symmetry, only a fraction of the total flow is modelled (1/8). Nonzero boundary conditions for the velocity at the in- and outlet are obtained from the previously described slit flow. Using \( R \) as a typical length scale rather than \( H \) yields \( \text{We} = 1.27 \).

As, for the slit flow, the best overall agreement with experiments was observed for the Giesekus model, this model, together with the new Feta-PTT model, is used for calculations of the cross-slot flow. Figure 2.16 shows the velocity profiles at outflow cross section \( x/R = 1.5 \) calculated with the Giesekus model. Obviously the predicted maximum velocity is in good agreement with experimentally observed values. However, along the \( y \)-axis a more flattened velocity profile has been measured. For comparison, added to this figure are the steady state velocity profiles, as obtained from slit flow calculations. It can be seen that the velocity at this cross section still exhibits extensional effects. This is also confirmed in figure 2.17 which shows the calculated and measured velocity as well as the calculated strain rate \( (\dot{\varepsilon}_{xx}) \) along the inflow axis towards the stagnation point and from there along the outflow axis.

Velocity, strain rate and principal stress difference along the same axes and over the depth of the flow are shown in figure 2.18. Along the inflow planes, elongational rates increase
3D viscoelastic analysis of a polymer solution in a complex flow

Figure 2.15: FE mesh of cross-slot device \((D/H = 2)\), inflow along \(y\)-axis, outflow along \(x\)-axis, \#elements=2835, \#nodes=25631, \#DOF(\(u, p\))=71988, \#DOF(\(D\))=21600, \#DOF(\(\tau\)) = 4 \times \#elements \times 48 = 544320.

Figure 2.16: Calculated and measured velocity profile along \(y\)-axis (left) and \(z\)-axis (right) at outflow cross-section \(x/R = 1.5\) (\(u_{20} = 26 \cdot 10^{-2} [m/s]\), Giesekus model). For comparison the fully developed velocity profiles, obtained from slit flow calculations, are added (---).

Figure 2.17: Calculated and measured velocity along positive \(y\)-axis (inflow) towards the stagnation point and along positive \(x\)-axis (outflow) (left) and strain rate (\(\dot{\varepsilon}_{xx}\)) along the same axes (right) (\(u_{20} = 26 \cdot 10^{-2} [m/s]\), \(|\gamma| = u_{20}/R = 13.0 [s^{-1}]\)).
from zero towards a local maximum at approximately \( y/R = 0.8 \). A maximum is reached at the stagnation point (\( \dot{\varepsilon}_{xx} = 22.9 \text{ [s}^{-1}] \)). At the outflow planes, rather than a local maximum, a small plateau is observed after which the elongational rates rapidly decrease towards a negative value. Thus, the fluids elasticity causes the velocity to reach a maximum value where the channel straightens again (\( x = R + H/2 \)). The influence of both confining walls on the first normal stress difference can clearly be observed in this figure. Just like slit flow calculations, a typical parabolic, shear induced, shape is observed near the inlet and outlet of the flow. The stress field near the stagnation line is mainly dominated by planar elongation with a maximum at the stagnation point.

Comparison of the calculated stress with experiments is performed using the approach described in section 2.5.1. Again, the stress optical coefficient is taken at \( C = 2.505 \cdot 10^{-9} \text{ [m}^2/\text{N}] \). Figure 2.19 (left) shows the measured optical data compared to calculated optical data along the the inflow and outflow symmetry planes for both the Giesekus and the \textit{Feta}-PTT model. For the Giesekus model it is seen that along the inflow planes the calculated principal stress difference is accurately described. However along the outflow axes the predicted normal stresses deviate from experimental data. Although the overall shape is
consistent with the experiments, integrated first normal stress difference along the stagnation line is about 30% of experimentally observed values. The Feta-PTT model, on the other hand yields a less exact description of the mainly shear induced normal stresses along the inflow boundaries though a far more accurate fit of the measured data along the relaxation region is obtained. This is also shown in figure 2.19 (right) where at the outflow cross section $x/R = 1.5$ measured and calculated data are shown along the $y$-axis. For comparison with a steady state shear flow, see also figure 2.14. The performance of the new Feta-PTT model is further demonstrated in figure 2.20 where experimental and numerical results are shown for different values of the dimensionless Weissenberg number. Included are measurements which were performed at $\bar{u}_{20} = 13 \cdot 10^{-2}$ [m/s] yielding a Weissenberg number which is half the Weissenberg number of the previously described flow.

**Figure 2.19:** Calculated and measured optical signal ($M_{43}$) along positive $y$-axis towards the stagnation point and along positive $x$-axis (left) and at outflow cross section $x/R = 1.5$ (right), --- Giesekus, - - - Feta-PTT.

**Figure 2.20:** Calculated and measured optical signal ($M_{43}$) along positive $y$-axis towards the stagnation point and along positive $x$-axis (left) and at outflow cross section $x/R = 1.5$ (right) for the Feta-PTT model at different flow rates, --- $\bar{u}_{20} = 13 \cdot 10^{-2}$ [m/s], --- $\bar{u}_{20} = 26 \cdot 10^{-2}$ [m/s].
2.7 Conclusions and discussion

A mixed low-order finite element based on the DEVSS/DG method has been implemented for the calculation of 3D viscoelastic flows. Calculations have been performed on a steady shear flow and a combined shear/elongational flow of a polymer solution. For the evaluation of these flows different constitutive relations have been applied. The flow of the solution through a rectangular duct with a height to depth ratio of 2, has been numerically evaluated using some established nonlinear constitutive models (Giesekus, Phan Thien Tanner) and the, only recently introduced, Feta-PTT model. From point-wise birefringence measurements it follows that shear stresses are fitted reasonably well by all models whereas considerable differences are observed between the different models for the shear induced normal stresses. For the cross-slot flow, it is observed that the normal stresses, predicted with the Giesekus model are far too low, near the stagnation line, compared with experimental data. It is expected from predictions of the models in planar elongation that none of the fits performed with the PTT model is capable to predict the normal stresses induced by the elongational component of the flow due to the elongational thinning (or less elongational thickening) of this model. The Feta-PTT model performed significantly better in the complex stagnation flow than the Giesekus model. Although some accuracy is lost on the shear induced normal stresses, a lot is gained with the prediction of the principal stress difference induced by the elongational component of the flow.
Chapter 3

Differential Constitutive Equations for Polymer Melts: the eXtended Pom-Pom model*

The Pom-Pom model, recently introduced by McLeish and Larson [J.Rheol., 42(1):81-110, 1998], is a breakthrough in the field of viscoelastic constitutive equations. With this model, a correct nonlinear behaviour in both elongation and shear is accomplished. The original differential equations, improved with local branch-point displacement, are modified to overcome three drawbacks: solutions in steady state elongation show discontinuities, the equation for orientation is unbounded for high strain rates, the model does not have a second normal stress difference in shear. The modified eXtended Pom-Pom (XPP) model does not show the three problems and is easy for implementation in Finite Element packages, because it can be written as a single equation. Quantitative agreement is shown with experimental data in uniaxial, planar, equibiaxial elongation as well as shear, reversed flow and step-strain for two commercial low density polyethylene (LDPE) melts and one high density polyethylene (HDPE) melt. Such a good agreement over a full range of well defined rheometric experiments, i.e. shear, including reversed flow for one LDPE melt, and different elongational flows, is exceptional.

3.1 Introduction

A main problem in constitutive modeling for the rheology of polymer melts is to get a correct non-linear behaviour in both elongation and shear. Most well-known constitutive models, such as the PTT, Giesekus and K-BKZ models, are unable to overcome this difficulty. Recently, McLeish and Larson (1998) have introduced a new constitutive model, which is a major step forward in solving this problem: the Pom-Pom model.

The rheological properties of entangled polymer melts depend on the topological structure of the polymer molecules. Therefore, the Pom-Pom model is based on the tube theory and a

*This chapter is largely based on: Verbeeten et al. (2001a)
simplified topology of branched molecules. The model consists of two decoupled equations: one for the orientation and one for the stretch. A key feature is the separation of relaxation times for this stretch and orientation. Both an integral and a differential form are available.

After its introduction, the model has been intensively investigated. Bishko et al. (1999) presented calculations of the transient flow of branched polymer melts through a planar 4:1 contraction. For various LDPE samples, Inkson et al. (1999) showed predictions for a multi-mode version of the Pom-Pom model. Blackwell et al. (2000) suggested a modification of the model and introduced local branch-point withdrawal before the molecules are fully stretched. Investigation of the thermodynamic admissibility of the differential Pom-Pom model was presented by Ottinger (2000). Although the model is found to be thermodynamically admissible, he showed that non-equilibrium thermodynamics strongly suggests several model modifications.

This paper investigates the differential form of the Pom-Pom model. Following the ideas of Blackwell et al. (2000), local branch-point displacement before maximum stretching is introduced by an exponential drop of the stretch relaxation times. Moreover, as adopted from Inkson et al. (1999), the structure is decoupled into an equivalent set of Pom-Pom molecules with a range of relaxation times and arm numbers: a multi-mode approach. However, three problems can still be detected. First, as the orientation equation is UCM-like, it is unbounded for high strain rates. Second, although local branch-point displacement is introduced, solutions in steady state elongation still show discontinuities due to the finite extensibility condition. And finally, this differential version does not have a second normal stress difference in shear. In section 3.2, we will introduce the eXtended Pom-Pom model that overcomes these problems.

Section 3.3 shows the results in a single-mode dimensionless form for both transient and steady state shear as well as elongational deformations. In section 3.4, the multi-mode version is tested for two commercial LDPE melts. Both LDPE melts have been characterized thoroughly [Hachmann (1996), Kraft (1996), Meissner (1972, 1975), Münstedt and Laun (1979)], providing a large set of experimental data. To investigate the ability of the model to predict the rheological behaviour of a melt with a different sort of topology (non-branched), the experimental data of an HDPE melt is compared with the results of the multi-mode Pom-Pom model.

In short, the key objective of this work is to investigate the capabilities of an extended version of the Pom-Pom model to describe a wide range of available rheometric data for three different polyethylene melts.

### 3.2 The Differential Pom-Pom Model

To describe stresses of polymer melts, the Cauchy stress tensor $\sigma$ is defined as:

$$\sigma = -pI + 2\eta_s D + \sum_{i=1}^{M} \tau_i .$$

(3.1)

Here, $p$ is the pressure term, $I$ the unit tensor, $\eta_s$ denotes the viscosity of the purely viscous (or solvent) mode, $D = \frac{1}{2}(L + L^T)$ the rate of deformation tensor, in which $L = (\nabla \vec{u})^T$ is the velocity gradient tensor and $(\cdot)^T$ denotes the transpose of a tensor. The visco-elastic
contribution of the $i^{th}$ relaxation mode is denoted by $\tau_i$ and $M$ is the total number of different modes. A multi-mode approximation of the relaxation spectrum is often necessary for a realistic description of the visco-elastic contributions.

Here, the constitutive behaviour for a single mode of the visco-elastic contribution is described with the differential Pom-Pom model. A schematic structure of the molecule for this model is given in figure 3.1. The model is developed, mainly, for long-chain branched polymers. The multiple branched molecule can be broken down into several individual modes [Inkson et al. (1999)]. Each mode is represented by a backbone between two branch-points, with a number of dangling arms on every end. The backbone is confined by a tube formed by other backbones. For details refer to McLeish and Larson (1998). The original differential form by McLeish and Larson (1998), improved with local branch-point displacement [Blackwell et al. (2000)], is written in two decoupled equations and reads as follows:

\[
\nabla A + \frac{1}{\lambda_{0b}} \left[ A - \frac{1}{3} I \right] = 0, \quad S = \frac{A}{I_A},
\]

\[
\dot{\Lambda} = \Lambda \left[ D : S \right] - \frac{1}{\lambda_s} (\Lambda - 1), \quad \lambda_s = \lambda_{0s} e^{-\nu (\Lambda - 1)} \quad \forall \Lambda \leq q,
\]

\[
\tau = \sigma - G_0 I = G_0 \left( 3 \Lambda^2 S - I \right).
\]

Expression (3.4) for the extra stress, differs (by a constant) from that proposed by McLeish and Larson (1998), but Rubio and Wagner (1999) have shown that for the differential model (3.4) is the correct form. Equation (3.2) and (3.3) are the evolution of orientation tensor $S$ and backbone tube stretch $\Lambda$, respectively. $A$ is an auxiliary tensor to get the backbone tube orientation tensor $S$. $\lambda_{0b}$ is the relaxation time of the backbone tube orientation. It is obtained from the linear relaxation spectrum determined by dynamic measurements. $I_A$ is the first invariant of tensor $A$, defined as the trace of the tensor: $I_A = \text{tr}(A)$. The backbone tube stretch $\Lambda$ is defined as the length of the backbone tube divided by the length.
at equilibrium. $\lambda_{0s}$ is the relaxation time for the stretch, and $\nu$ a parameter which, based on the ideas of Blackwell et al. (2000), is taken to be $\frac{2}{q}$, where $q$ is the amount of arms at the end of a backbone. Alternatively, $\nu$ can also be seen as a measure of the influence of the surrounding polymer chains on the backbone tube stretch. Finally, $G_0$ is the plateau modulus, also obtained from the linear relaxation spectrum. The upper convected time derivative of the auxiliary tensor $A$ is defined as:

$$\nabla A = \dot{A} - L \cdot A - A \cdot L^T = \frac{\partial A}{\partial t} + \vec{u} \cdot \nabla A - L \cdot A - A \cdot L^T. \quad (3.5)$$

The reason for introducing an auxiliary tensor $A$ in equation (3.2) is to obtain an orientation tensor $S$ that mimics the behaviour of the true tube orientation, given by the integral expression (see McLeish and Larson (1998)). For clarification (and also to compare more easily with our model modifications later on), the equation is rewritten in terms of $S$ (see also appendix A):

$$\nabla S + 2 [D \cdot S] S + \frac{1}{\lambda_{0b} I_A} \left[ S - \frac{1}{3} I \right] = 0. \quad (3.6)$$

Notice that this equation is almost identical to equation (30) in McLeish and Larson (1998), i.e. the simplest candidate for the backbone evolution that they ruled out:

$$\nabla S + 2 [D \cdot S] S + \frac{1}{\lambda_{0b}} \left[ S - \frac{1}{3} I \right] = 0. \quad (3.7)$$

In fact, introducing the auxiliary tensor $A$ is equivalent to multiplying the backbone relaxation time with $I_A$ in this simplest candidate. Although the shear-response $S_{12}$ of equation (3.7) does have a maximum as a function of shear rate, it decreases as $\dot{\gamma}^{-2/3}$ rather than as $\dot{\gamma}^{-1}$ which is found for the integral form and equations (3.2) and (3.6). The latter is the shear thinning behaviour in standard Doi-Edwards theory for linear polymers. If local branch-point displacement is not accounted for, the less steep shear-rate dependence does not give the right shear-thinning response. In section 3.3, the positive influence of local branch-point displacement on the shear-thinning behaviour will be shown. In short, equations (3.2) and (3.6) are equivalent and have similar asymptotic forms in extension and shear as the integral version, contrary to equation (3.7). A disadvantage is that equation (3.2) is UCM-like: it runs into numerical problems when trying to solve it for high elongation rates ($\dot{\varepsilon}_{\lambda_{0b}} > 1$). The UCM-type models are unbounded in extension.

Notice, that equation (3.3) holds only if the stretch $\Lambda$ is smaller or equal to the number of dangling arms $q$. In this way, finite extensibility of the backbone tube is introduced. However, this condition causes discontinuities in steady state elongational viscosity curves. Although local branch-point displacement diminishes this discontinuity, it is still present.

Unfortunately, the set of equations (3.2)-(3.4) predicts a zero second normal stress coefficient in shear ($\Psi_2 = 0$). There are several reasons to include a second normal stress difference. First of all, experimental data [Kalogrianitis and Van Egmond (1997)] indicates a non-zero $\Psi_2$. Larson (1992) showed that a non-zero $\Psi_2$ positively influences the stability of viscoelastic flows. Debbaut and Dooley (1999) observed and analyzed the secondary motions due to the non-zero second normal stress difference. Furthermore, during flow-induced crystallization, phenomena have been observed that are assumed to be related to
the second normal stress difference \cite{Jerschow1996}. Doufas et al. \cite{Doufas1999} introduced a model for flow-induced crystallization that incorporates $\Psi_2 \neq 0$.

A number of changes are made to the original differential equations to overcome these disadvantages. The extended model is based on the molecular background of the original Pom-Pom model. In particular the different relaxation processes for stretch and orientation are maintained. However, the requirement that the tube orientation for linear polymers follows the Doi-Edwards theory is relaxed. Moreover, the phenomenological approach of Inkson et al. \cite{Inkson1999} is followed in the sense that the model parameters will not be determined from molecular data directly.

A different starting point is taken. The polymer melt molecules will be represented by connector vectors $\vec{R}_i$, similar to Peters and Baaijens \cite{Peters1997}. Consider a single Pom-Pom molecule as given in figure 3.2. A part of the backbone tube of the molecule is defined as the dimensionless connector vector $\vec{R}_i$, with a dimensionless length or stretch $\Lambda_i$ and direction $\vec{n}_i$:

$$\vec{R}_i = |\vec{R}_i| \vec{n}_i = \Lambda_i \vec{n}_i .$$  \hfill (3.8)

The subscript $i$ is introduced to distinguish between different parts. For convenience, it will be omitted in the rest of the paper. The equation of motion for a vector $\vec{R}$ is postulated as:

$$\dot{\vec{R}} = (L - B) \cdot \vec{R} \implies \dot{\vec{n}} = (L - B) \cdot \vec{n} - (D - B) : (\vec{n} \vec{n}) \vec{n} ,$$  \hfill (3.9)

where the second order tensor $B$ is a yet to be specified function of averaged, thus macroscopic, variables, \textit{i.e.} the stress, strain or strain rate. The level of description is taken in averaged sense. The term $-B : \vec{R}$ represents the slippage of the element with respect to the continuum. Therefore, the tensor $B$ is called the slip tensor.

Now, let us define the orientation tensor $S$ as:

$$S = < \vec{n} \vec{n} > ,$$  \hfill (3.10)

where $< >$ denotes an average over the distribution space. Then its time derivative is taken (which is not trivial as it is a time derivative of an integral over the distribution space):

$$\dot{S} = < \dot{\vec{n}} \vec{n} + \vec{n} \dot{\vec{n}} > .$$  \hfill (3.11)
By using the closure approximation $<\vec{n}\vec{n}\vec{n}\vec{n}> = <\vec{n}\vec{n}> <\vec{n}\vec{n}>$, this gives:

$$\nabla \mathbf{S} + \mathbf{B} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{B}^T + 2 [ (\mathbf{D} - \mathbf{B}) : \mathbf{S} ] \mathbf{S} = 0 .$$  \hspace{1cm} (3.12)

In a similar way, take the evolution in time of the length of an arbitrary averaged connector vector $|\vec{R}|$:

$$|\dot{\vec{R}}| = \dot{\Lambda} = \Lambda (\mathbf{D} - \mathbf{B}) : <\vec{n}\vec{n}> \iff \dot{\Lambda} = \Lambda (\mathbf{D} - \mathbf{B}) : \mathbf{S} ,$$  \hspace{1cm} (3.13)

stating that any local fluctuations in the stretch $\Lambda$ very rapidly equilibrate over the backbone tube [McLeish and Larson (1998)], i.e. $\Lambda_i = \Lambda_j = \Lambda \forall i, j$.

What remains is a choice for the slip tensor $\mathbf{B}$. We choose it to be only a function of the averaged macroscopic stress $\mathbf{\sigma}$ (as defined by equation (3.4)):

$$\mathbf{B} = c_1 \mathbf{\sigma} + c_2 \mathbf{I} - c_3 \mathbf{\sigma}^{-1} = c_1 \dfrac{3}{3} G_0 \Lambda^2 \mathbf{S} + c_2 \mathbf{I} - \dfrac{c_3}{3 G_0 \Lambda^2} \mathbf{S}^{-1} ,$$  \hspace{1cm} (3.14)

with $c_1$, $c_2$ and $c_3$ still to be specified. If equation (3.14) is substituted into equation (3.12), the orientation equation is only a function of $c_1$ and $c_3$. The reptational behaviour of the chains is incorporated by introducing anisotropic forces (drag and Brownian forces), following the ideas of Giesekus. This also gives a non-zero second normal stress coefficient. Therefore, we choose $c_1$ and $c_3$ to be Giesekus-like (see e.g. equation (A10) in Peters and Baaijens (1997)):

$$c_1 = \dfrac{\alpha}{2 G_0 \lambda_0 \xi}, \quad c_3 = \dfrac{G_0 (1 - \alpha)}{2 \lambda_0} .$$  \hspace{1cm} (3.15)

Here, $\alpha$ is a material parameter ($\alpha \geq 0$), defining the amount of anisotropy. To obey exactly the stretch equation (3.3) of McLeish and Larson, $c_2$ can be determined by substituting equation (3.14) into equation (3.13):

$$c_2 = \dfrac{1 - \alpha - 3 \alpha \Lambda^4 I_{\text{ss}}}{2 \lambda_0 \xi \Lambda^2} + \dfrac{1}{\lambda_\xi} [1 - \dfrac{1}{\Lambda}] .$$  \hspace{1cm} (3.16)

The slip tensor $\mathbf{B}$ then reads:

$$\mathbf{B} = \dfrac{3 \alpha \Lambda^2}{2 \lambda_0 \xi} \mathbf{S} + \left( \dfrac{1 - \alpha - 3 \alpha \Lambda^4 I_{\text{ss}}}{2 \lambda_0 \xi \Lambda^2} + \dfrac{1}{\lambda_\xi} [1 - \dfrac{1}{\Lambda}] \right) \mathbf{I} = \dfrac{(1 - \alpha)}{6 \lambda_0 \xi \Lambda^2} \mathbf{S}^{-1} ,$$  \hspace{1cm} (3.17)

giving the evolution equations for orientation and stretch:

$$\nabla \mathbf{S} + 2 [ (\mathbf{D} : \mathbf{S} ) \mathbf{S}$$

$$+ \dfrac{1}{\lambda_0 \xi \Lambda^2} \left[ 3 \alpha \Lambda^4 \mathbf{S} \cdot \mathbf{S} + (1 - \alpha - 3 \alpha \Lambda^4 I_{\text{ss}}) \mathbf{S} - \dfrac{(1 - \alpha)}{3} \mathbf{I} \right] = 0 ,$$  \hspace{1cm} (3.18)

and

$$\dot{\Lambda} = \Lambda [ (\mathbf{D} : \mathbf{S} ) - \dfrac{1}{\lambda_\xi} (\Lambda - 1) , \quad \lambda_\xi = \lambda_0 \xi e^{-\nu (\Lambda - 1)} .$$  \hspace{1cm} (3.19)
For non-zero \( \alpha \), also a non-zero second normal stress coefficient \( \Psi_2 \) is predicted. Moreover, \( \Psi_2 \) is proportional to \( \alpha \). If \( \alpha = 0 \), equation (3.18) simplifies to:

\[
\nabla S + 2 [ D : S ] S + \frac{1}{\lambda_0 \Lambda^2} \left[ S - \frac{1}{3} I \right] = 0 .
\]

(3.20)

Notice, that this equation is equivalent to equation (3.6) of McLeish and Larson, with the only difference that \( I_A \) is replaced by \( \Lambda^2 \). Thus, to end up with the equations (3.2) or (3.3), as was derived by McLeish and Larson (1998), the slip tensor \( B \), to be filled in equations (3.12) and (3.13), reads:

\[
B = \left( \frac{1}{2 \lambda_0 I_A} + \frac{1}{\lambda_s} \left[ 1 - \frac{1}{\Lambda} \right] \right) I - \frac{1}{6 \lambda_0 I_A} S^{-1} .
\]

(3.21)

In this way, we have shown that our approach is consistent with McLeish and Larson (1998), and the same equations can be found.

The orientation equation of McLeish and Larson (1998) is an Upper Convected Maxwell model. For that model, the backbone tube can completely orient in the flow direction for simple shear flows, resulting in a shear-response \( S_{12} \) that decreases as \( \dot{\gamma}^{-1} \) for high enough shear rates. The proposed orientation equation (3.20) is no longer an Upper Convected Maxwell model and the backbone tube can not orient completely in simple shear flows. As a result, our orientation equation does not follow the standard Doi-Edwards theory and the behaviour is less shear thinning as the original Pom-Pom model.

Equations (3.18) and (3.19) may be reformulated into a single equation. For this purpose, the evolution equation for the extra stress tensor \( \tau \) will be written in terms of the slip tensor \( B \). To achieve that, we choose to work with tensor \( \mathbf{c} \), which is the average of all the connector vectors \( \vec{R} \) over the distribution space, also known as the conformation tensor. Now it follows:

\[
\mathbf{c} = \frac{1}{\Lambda^2} \mathbf{S} = \Lambda^2 \Rightarrow I_c = \Lambda^2 .
\]

(3.22)

For the extra stress, it can now be written:

\[
\tau = 3 G_0 \mathbf{c} - G_0 \mathbf{I} = 3 G_0 \frac{\vec{R}}{\Lambda} - G_0 \mathbf{I} = 3 G_0 \Lambda^2 \mathbf{S} - G_0 \mathbf{I} ,
\]

(3.23)

which is similar to equation (3.4). By taking the time evolution of the previous equation, it follows:

\[
\dot{\tau} = 3 G_0 < \vec{R} \dot{R} + \dot{\vec{R}} \vec{R} > .
\]

(3.24)

The stress evolution equation then reads:

\[
\nabla + B \cdot \tau + \tau \cdot B^T + G_0 (B + B^T) = 2 G_0 \mathbf{D} .
\]

(3.25)

Substituting equation (3.17) into equation (3.25) gives the single equation for \( \tau \):

\[
\nabla + \lambda(\tau)^{-1} \cdot \tau = 2 G_0 \mathbf{D} ,
\]

(3.26)

with

\[
\lambda(\tau)^{-1} = \frac{1}{\lambda_0} \left[ \frac{\alpha}{G_0} \tau + f(\tau)^{-1} I + G_0 \left( f(\tau)^{-1} - 1 \right) \tau^{-1} \right] ,
\]

(3.27)
\[ \frac{1}{\lambda_{0b}} f(\tau)^{-1} = \frac{2}{\lambda_s} \left( 1 - \frac{1}{\Lambda} \right) + \frac{1}{\lambda_{0b} \Lambda^2} \left[ 1 - \frac{\alpha I_{r,r}}{3 G_0^2} \right], \]  
(3.28)

and

\[ \Lambda = \sqrt{1 + \frac{I_{r,r}}{3 G_0}}, \quad \lambda_s = \lambda_{0s} e^{-\nu (\Lambda - 1)} \quad \text{and} \quad \nu = \frac{2}{q}. \]  
(3.29)

Notice, that we drop the finite extensibility condition of equation (3.3) \((\Lambda \leq q)\). McLeish and Larson (1998) suggest, that the backbone tube stretch equation only holds if the stretch \(\Lambda\) is smaller than the amount of arms \(q\). The backbone can only maintain a maximum stretch, which is equal to the number of arms \((\Lambda = q)\). However, equation (3.3) is the evolution for the averaged backbone tube stretch. So, some molecules will have reached their maximum stretch before others, giving a maximum stretch distribution. As the finite extensibility condition does not yield a distribution but a discrete condition, it seems to be unphysical, especially if poly-dispersion is involved. Even in case of mono-dispersion, such a discrete behaviour is not seen in data [Blackwell et al. (2000)]. Moreover, the condition produces an unrealistic discontinuity in the gradient of the extensional viscosity [McLeish and Larson (1998), Bishko et al. (1999), Inkson et al. (1999), Blackwell et al. (2000)]. Therefore, the sudden transition from stretch dynamics to a fixed maximum stretch has been taken out. It can also be justified by considering that local branch-point displacement contributes to a larger backbone tube, which again can be stretched further. Taking away the finite extensibility condition results in the removal of the peaks and discontinuities of steady state elongational curves, as will be shown in the next section, while the stretch is not unbounded. This because the exponential in the stretch relaxation time \(e^{-\nu (\Lambda - 1)}\) ensures for high strains, that the stretch relaxes very fast and stays bounded. The parameter \(q\) still denotes a measure for the amount of arms in the molecule for a particular mode. However, \(q\) does not fix the finite extensibility, but only limits it indirectly by influencing the drop in the stretch relaxation time \(\lambda_s\).

Although two effects, stretch and orientation, are combined in one equation, the different parts can still be recognised. Assume the easy case that \(\alpha = 0\). For low strains, \(i.e.\) no stretch \((\Lambda = 1)\), part (b) in equation (3.28) equals zero and the only relaxation time of significance is the one for the backbone tube orientation \(\lambda_{0b}\). In that case, part (a) in equation (3.26) is also equal to zero and this equation reduces to the linear visco-elastic model. For high strains, \(i.e.\) significant stretch \((\Lambda \gg 1)\), part (c) in equation (3.28) reduces to zero and the stretch relaxation time \(\lambda_s\) becomes the most important relaxing mechanism. Physically, it could be interpreted as if the orientation can not relax because it is trapped by the stretching effect, and the stretch has to relax before the orientation is able to relax. Parameter \(\alpha\) only influences the orientation part (c) of the equation.

The set of equations (3.18), (3.19) and (3.4) or equation (3.26) is referred to as the eXtended Pom-Pom (XPP) model, as, by choosing \(\alpha \neq 0\), the model is extended with a second normal stress coefficient \(\Psi_2\). This model overcomes the three problems mentioned above. For convenience, an overview of the model is given in tables 3.1 and 3.2.

Recently, Öttinger (2000) investigated the thermodynamic admissibility of the Pom-Pom model. He focussed on the differential version, as it fits more naturally into the modern framework of non-equilibrium thermodynamics. He proposed a modification for the orientation equation, which also has a quadratic term in the orientation tensor. Similar
as above, the model proposed by Öttinger (2000) can be written in a double-equation or single-equation formulation. (See appendix B for details.)

Table 3.1: Double-equation XPP equation set.

<table>
<thead>
<tr>
<th>Double-equation eXtended Pom-Pom (XPP) model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscoelastic stress:</td>
</tr>
<tr>
<td>( \bm{\tau} = G_0 \left( 3 \Lambda^2 \bm{S} - \bm{I} \right) ).</td>
</tr>
<tr>
<td>Evolution of orientation:</td>
</tr>
<tr>
<td>( \nabla \left[ 2 \left[ \bm{D} : \bm{S} \right] \bm{S} + \frac{1}{\lambda_{0b} \Lambda^2} \left[ 3\alpha \Lambda^4 \bm{S} : \bm{S} + (1 - \alpha - 3\alpha \Lambda^4 I_e) \bm{S} - \frac{(1 - \alpha)}{3} \bm{I} \right] \right] = 0 ).</td>
</tr>
<tr>
<td>Evolution of the backbone stretch:</td>
</tr>
<tr>
<td>( \dot{\Lambda} = \Lambda \left[ \bm{D} : \bm{S} \right] - \frac{1}{\lambda_s} (\Lambda - 1) , \quad \lambda_s = \lambda_{0s} e^{-\nu (\Lambda - 1)} , \quad \nu = \frac{2}{q} ).</td>
</tr>
</tbody>
</table>

Table 3.2: Single-equation XPP equation set.

<table>
<thead>
<tr>
<th>Single-equation eXtended Pom-Pom (XPP) model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscoelastic stress:</td>
</tr>
<tr>
<td>( \nabla \bm{\tau} + \lambda (\bm{\tau})^{-1} \cdot \bm{\tau} = 2 G_0 \bm{D} ).</td>
</tr>
<tr>
<td>Relaxation time tensor:</td>
</tr>
<tr>
<td>( \lambda (\bm{\tau})^{-1} = \frac{1}{\lambda_{0b}} \left[ \frac{\alpha}{G_0} \bm{\tau} + f(\bm{\tau})^{-1} \bm{I} + G_0 \left( f(\bm{\tau})^{-1} - 1 \right) \bm{\tau}^{-1} \right] ).</td>
</tr>
<tr>
<td>Extra function:</td>
</tr>
<tr>
<td>( \frac{1}{\lambda_{0b}} f(\bm{\tau})^{-1} = \frac{2}{\lambda_s} \left( 1 - \frac{1}{\Lambda} \right) + \frac{1}{\lambda_{0b} \Lambda^2} \left[ 1 - \frac{\alpha I_e}{3 G_0^2} \right] ).</td>
</tr>
<tr>
<td>Backbone stretch and stretch relaxation time:</td>
</tr>
<tr>
<td>( \Lambda = \sqrt{1 + \frac{I_e}{3 G_0}} , \quad \lambda_s = \lambda_{0s} e^{-\nu (\Lambda - 1)} , \quad \nu = \frac{2}{q} ).</td>
</tr>
</tbody>
</table>
3.3 Model features

A one mode version of the XPP model derived in the previous section will now be investigated for different simple flows. All variables are made dimensionless with \( G_0 \) and \( \lambda_{0b} \). The parameters are chosen \( q = 5 \) and \( \lambda_{0s} = \frac{150}{\tau_0} \lambda_{0b} \), unless indicated otherwise, i.e. the same choice as McLeish and Larson (1998) and Blackwell et al. (2000). The parameter related to the anisotropy, \( \alpha \), is varied to investigate its influence.

3.3.1 Simple shear

The transient and steady state viscosity, first normal stress coefficient and second over first normal stress coefficient ratio \((\Psi_2 / \Psi_1)\) for simple shear are plotted in figure 3.3.

The influence of \( \alpha \) on \( \eta \) and \( \Psi_1 \) is rather small. Only for \( \alpha = 0.5 \), a small difference can be noted. The parameter \( \alpha \) mostly influences \( \Psi_2 \). For \( \alpha = 0 \), clearly \( \Psi_2 = 0 \) and no line is plotted in that case. Notice that for \( \alpha = 0.5 \) the steady state \(-\Psi_2 / \Psi_1\) shows a 'shoulder' for high shear rates. This is due to a similar 'shoulder' in the third component of the orientation tensor \( S_{33} \), as shown in figure 3.4, and needs further investigation.

The shear orientation \( S_{12} \) decreases as \( \dot{\gamma}^{-1/2} \) for high shear rates, as can be seen in figure 3.5. However, the backbone stretch \( \Lambda \) does not increase dramatically fast, which is due to the local branch-point displacement that decreases the stretch relaxation time \( \lambda_s \). Therefore, shear-thinning behaviour is still accounted for, as is apparent from the steady state shear viscosity plot. The transient backbone stretch in figure 3.5 shows the characteristic overshoot.

3.3.2 Planar elongation

In figure 3.6 the transient and steady state first planar viscosity are shown for the model. The first planar viscosity is defined as:

\[
\eta_{p1} = \frac{\tau_{11} - \tau_{33}}{\dot{\varepsilon}} ,
\]

while the second planar viscosity is given by:

\[
\eta_{p2} = \frac{\tau_{22} - \tau_{33}}{\dot{\varepsilon}} .
\]

The parameter \( \alpha \) has almost no influence on the first planar viscosity, but a significant influence on the second planar viscosity. For \( \alpha = 0.5 \), the steady state second planar viscosity shows a 'shoulder', equal to the one observed in the second over first normal stress difference ratio \((\Psi_2 / \Psi_1)\) in simple shear. This 'shoulder' is also visible in the second component of the orientation tensor, \( S_{22} \), as shown in figure 3.7. It is an artifact of the orientation equation and needs further investigation.

Notice that the steady state planar viscosity is a smooth function with no peaks. This is due to the absence of a finite extensibility condition.

Figure 3.8 shows the transient and steady state backbone stretch. Different from simple shear, the transient backbone stretch shows no overshoot and reaches its steady state value right away. The steady state backbone stretch increases monotonically, but not drastically, due to local branch-point displacement.
Figure 3.3: Transient (a) and steady state (b) dimensionless viscosity $\eta$, transient (c) and steady state (d) first normal stress coefficient $\Psi_1$, and transient (e) and steady state (f) second over first normal stress coefficient ratio $-\Psi_2/\Psi_1$ in simple shear flow for the XPP model. Parameters: $q = 5$; $\lambda_{bn} = \frac{1}{1000} \lambda_{0n}$; $\alpha = 0, 0.1, 0.5$. Transient: $\dot{\gamma} = 10^{-5}, 1, 10$. 
Figure 3.4: Steady state dimensionless orientation components in simple shear flow for the XPP model. Parameters: $q = 5; \lambda_0 = \frac{150}{912} \lambda_0^b; \alpha = 0, 0.1, 0.5$.

Figure 3.5: Transient (a) and steady state (b) dimensionless backbone stretch $\Lambda$ in simple shear flow for the XPP model. Parameters: $q = 5; \lambda_0 = \frac{150}{912} \lambda_0^b; \alpha = 0, 0.1, 0.5$. Transient: $\dot{\gamma} = 10^{-5}, 1, 10$. 
3.3.3 Uniaxial and equibiaxial elongation

The transient and steady state uniaxial viscosities are depicted in the top graphs of figure 3.9. Notice that the parameter $\alpha$ has almost no influence.

The bottom plots of figure 3.9 show the transient and steady state equibiaxial viscosities. For higher elongation rates the curves of the start-up plot first drop under the linear viscoelastic line, and then rise above it. In figure 3.9 it is difficult to see, but in the next section it will be shown, that this is also observed for experimental data. Again, the influence of $\alpha$ is rather small.

3.4 Performance of the multi-modal Pom-Pom model

For three different materials, the performance of the eXtended Pom-Pom model in multimode form is investigated and compared with experimental data. For all materials, the linear parameters, i.e., backbone relaxation time $\lambda_{0b}$ and modulus $G_0$, are determined from dynamic measurements. First, the data for BASF Lupolen 1810H (681 133 256, stabilized...
Figure 3.7: Steady state dimensionless orientation components in planar flow for the XPP model. Parameters: $q = 5; \lambda_{0s} = \frac{15}{912} \lambda_{0b}; \alpha = 0, 0.1, 0.5$.

Figure 3.8: Transient (a) and steady state (b) dimensionless backbone stretch $\Lambda$ in planar flow for the XPP model. Parameters: $q = 5; \lambda_{0s} = \frac{15}{912} \lambda_{0b}; \alpha = 0, 0.1, 0.5$. Transient: $\dot{\varepsilon} =$
Differential Constitutive Equations for Polymer Melts: the eXtended Pom-Pom model

Figure 3.9: Transient (a) and steady state (b) dimensionless uniaxial viscosity $\eta_u$, and transient (c) and steady state (d) equibiaxial viscosity $\eta_e$ for the XPP model. Parameters: $q = 5$, $\lambda_{0b}^0 = \frac{1}{5q^2} \lambda_0^0$; $\alpha = 0, 0.1, 0.5$. Transient: $\dot{\varepsilon} = 10^{-5}, 1, 10$.

with S4918) LDPE melt will be shown in an extensive comparison. This LDPE melt has been characterized by Hachmann (1996) and Kraft (1996). As a second LDPE melt, the IUPAC A melt was investigated, which has been well characterized by Meissner (1972, 1975) and Münstedt and Laun (1979). Finally, the Statoil 870H (85579, stabilized with S5011) HDPE melt has been investigated, also characterized by Hachmann (1996) and Kraft (1996). This last material is chosen to see how the Pom-Pom model, developed for long-chain branched materials, performs for a material with a different molecular structure.

Fitting of the non-linear parameters is done manually. Some physical guidelines are taken into account for that. For a branched molecule, going from the free ends inwards, an increasing number of arms is attached to every backbone of the representative pom-pom. The relaxation time of a backbone segment is determined by the distance to the nearest free end that is able to release it from its tube constraint by retraction. Towards the middle of a complex molecule, the relaxation time is exponentially increasing. So, the parameter $q_i$, denoting the number of arms for every backbone segment, and the orientation relaxation time $\lambda_{0b,i}$ are increasing towards the center of the molecule. The stretch relaxation time $\lambda_{0s,i}$ is physically constrained to lie in the interval $\lambda_{0b,i-1} < \lambda_{0s,i} \leq \lambda_{0b,i}$ [Inkson et al. (1999)].
Table 3.3: XPP parameters for fitting of the Lupolen 1810H melt. \( T_r = 150 \) [\(^\circ C\)]. \( \nu_i = 2/q_i \).
Activation energy: \( E_0 = 58.6 \) [kJ/mol].

<table>
<thead>
<tr>
<th>( i )</th>
<th>( G_{0,i} ) [Pa]</th>
<th>( \lambda_{0,i} ) [s]</th>
<th>( q_i )</th>
<th>ratio: ( \lambda_{0,i} / \lambda_{0,1} )</th>
<th>( \alpha_i )</th>
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<td>1.0000 · 10^{4}</td>
<td>37</td>
<td>1.5</td>
<td>0.005</td>
</tr>
</tbody>
</table>

### 3.4.1 BASF Lupolen 1810H LDPE melt

This LDPE melt has been characterized in elongation by Hachmann (1996). All elongational components have been measured: first and second planar, uniaxial and equibiaxial elongational viscosities. Kraft (1996) characterized the material in shear, both shear viscosity and first normal stress coefficient, and also measured a reversed flow. All measurements, shear and elongation, were carried out at a temperature of \( T = 150 \) [\(^\circ C\)]. The linear parameters \( \lambda_{0b} \) and \( G_0 \) have been calculated from a continuous relaxation spectrum determined by Hachmann (1996). With the given activation energy \( E_0 \), the temperature dependence can be calculated using the following equation [Ferry (1980)]:

\[
\ln \left( \frac{\eta_0(T)}{\eta_0(T_r)} \right) = \ln \left( \frac{\alpha T}{bT} \right) = \frac{E_0}{R} \left( \frac{1}{T} - \frac{1}{T_r} \right). \tag{3.32}
\]

Here, \( R \) is the gas constant, \( T \) is the reference temperature and \( T_r \) the temperature where to shift to, both in Kelvin. The non-linear parameters \( q \) and \( \lambda_{0b} \) are fitted on the uniaxial elongational data only. Since the parameter \( \alpha \) has almost no influence on uniaxial viscosity, shear viscosity and shear first normal stress coefficient, it can solely be used to fit the second normal stress...

Image: (a) Transient uniaxial viscosity, (b) Quasi-steady state uniaxial viscosity

**Figure 3.10:** Transient (a) and quasi-steady state (b) uniaxial elongational viscosity \( \eta_u \) of the XPP model for Lupolen 1810H melt at \( T = 150 \) [\(^\circ C\)]. \( \nu_i = 2/q_i \). \( \dot{\varepsilon}_u = 0.0030, 0.0102, 0.0305, 0.103, 0.312, 1.04 \) [s\(^{-1}\)].
coefficient (if available) or, like with this material, to the second planar viscosity data. We expect the anisotropic behaviour of the forces to decrease from the free ends inwards. Since the middle of the molecule is more strapped in by the rest of the molecule, it can hardly reptate and has to free itself out of the tube by diffusion of the tube, similar as for a Maxwell model. Therefore, relaxation is almost similar in all directions, and the anisotropy parameter $\alpha$ can be zero or almost zero. Towards the free ends, the molecule is more free to reptate and thus is able to have anisotropic relaxation behaviour, denoted by an increased $\alpha$. As can be seen in table 3.3, which gives the linear and non-linear parameters, our expectations are in agreement with the fit. If there is no second normal stress difference or second planar viscosity data available, as a guideline, anisotropy parameter $\alpha$ could be chosen as $0.1$. Since more arms (parameter $q$) are attached to the branch points while going towards the center of the molecule and thus diminishing $\alpha$.

The uniaxial data and fits are plotted in figure 3.10. The model does an excellent job in modelling the experimental data. The final points of the transient experimental data are taken as the steady state data points. As most probably the true steady state values have not been reached yet, these are quasi-steady state data points.

**Figure 3.11:** Transient (a) and quasi-steady state (b) first planar elongational viscosity $\eta_{p1}$, and transient (c) and steady state (d) second planar elongational viscosity $\eta_{p2}$ of the XPP model for Lupolen 1810H melt at $T = 150 \degree C$. $\nu_i = 2/q_i$. $\dot{\varepsilon}_p = 0.0029$, 0.0096, 0.0312, 0.1000 $[s^{-1}]$. 

A more detailed analysis of the model parameters and their implications can be seen in table 3.3. The values of $\nu_i$ and $\dot{\varepsilon}_p$ are obtained from the experimental data and are used to fit the model parameters. The fit is excellent, as seen in figure 3.10, and the model parameters are in agreement with the expectations based on the anisotropic behaviour of the forces.
Figure 3.12: Transient (a) and quasi-steady state (b) equibiaxial elongational viscosity $\eta_e$ of the XPP model for Lupolen 1810H melt at $T = 150 \degree C$. $\nu_i = 2/q_i$. $\dot{\varepsilon}_e = 0.003$, 0.0103, 0.0304, 0.099 [s$^{-1}$].

Figure 3.11 shows the predictions for the transient and quasi-steady state first and second planar viscosity. Again, a good agreement between experiments and calculations is obtained for the first planar viscosity. For the second planar viscosity, quantitative agreement is poorer, although qualitatively a good trend is seen (thinning instead of thickening behaviour). The numerical results underpredict the experimental data. There are three possible reasons for this. First, it is rather difficult to obtain accurate experimental results. Second, better numerical results might be obtained by starting off with more modes. And third, a change in the orientation evolution equation might improve predictions, too. The last two remarks are supported by the unphysically ‘bumpy’ behaviour of the steady state values.

The transient and quasi-steady state equibiaxial experimental data and the calculated results are depicted in figure 3.12. Again, the experimental data is predicted rather well. However, a small delay in time for the upswing can be noticed. A remarkable feature is that the model first predicts a drop under the zero shear rate viscosity line, followed by elongational thickening. This can also be seen in the experimental data.

Figure 3.13 shows the experimental and model results of the shear viscosity and first normal stress coefficient. It is obvious that the model is giving an excellent prediction for the shear viscosity. For the first normal stress coefficient, the model is predicting the experimental data good. Notice, that the overshoot is not so pronounced as for the experimental data. If the transient plots are carefully examined, the different modes can be noted. This is caused by the relaxation times being just a little too far apart.

Figure 3.14 shows the experimental results for a reversed shear flow and the model predictions. In this reversed flow, a strain rate of $\dot{\gamma} = 1$ [s$^{-1}$] is applied in one direction. After a certain amount of time $t^*$, the strain rate is reversed and applied in opposite direction. For details on the reversed flow, see Kraft (1996). The orientation angle plotted in the third picture of the figures, is defined as:

$$\chi = \frac{1}{2} \arctan \left( \frac{2\tau_{12}}{N_1} \right).$$  \hspace{1cm} (3.33)

All features seen in the experiments are predicted. For the shear stress, in case of short reverse
time or pre-shearing, the values change sign and go through a minimum before reaching the steady state value. For higher reverse times or pre-shearing, the curves change sign and then directly reach the steady state value, without going through a minimum first. In case of the first normal stress difference, the curves go through a minimum after pre-shearing and then, as should be, return to the original curve seen if no pre-shearing has occurred. For the predictions, the different modes can be seen as small wiggles just after reversing the flow. We speculate that this might be improved by increasing the amount of modes or a change in the orientation evolution equation. The orientation angle changes sign, just like the shear stress. However, these curves always show a minimum.

In general, a good quantitative agreement is obtained in this reversed flow, and only the first normal stress difference shows some deviations. Notice however, that in this case the plots are on a linear scale, while all other plots are on a logarithmic scale.

It should be pointed out again, that all parameters where fitted onto the uniaxial data only, while only six modes where used. The linear parameters determine the basics of all curves and therefore should be chosen carefully.

As a last remark, it should be noted that the non-linear parameters have a larger influence on elongation than on shear. Therefore, by fitting the other way around, i.e. first on the shear
data, it is not obvious, that good fits will be obtained in elongation.

### 3.4.2 IUPAC A LDPE melt

The transient and steady state uniaxial elongational data for this LDPE melt are taken from Münstedt and Laun (1979). Meissner (1975) has generated the data for transient and steady state shear viscosity, while the transient first normal stress coefficient is taken from Meissner (1972). All data is represented at a temperature of $T = 150 \, ^\circ\text{C}$. The linear relaxation spectrum is given by Laun (1986). The non-linear parameter $q$ and ratio $\frac{\lambda_0}{\lambda_s}$ are fitted to the uniaxial elongational data only. As a guideline, $\alpha$ is chosen as $\frac{1}{q}$, as there is no second normal stress difference or second planar viscosity data available.

The parameters for the model is given in table 3.4. The temperature dependence can be calculated with the WLF-parameters (given in table 3.4) using the following equation [Ferry (1980)]:

\[
\ln \left( \frac{\eta_0(T)T_r \rho_T}{\eta_0(T_r)T \rho_T} \right) = -\frac{C_1 (T - T_r)}{C_2 + T - T_r} = \ln a_T .
\]  

(3.34)
Here, $T_r$ is the reference temperature in Kelvin, $C_1$ and $C_2$ are constants, and $T$ is the temperature where to shift to, also in Kelvin.

The experimental data and the calculated fit for the uniaxial elongation viscosity are given in figure 3.15. The model predicts the experimental data excellent. This could be expected, as the parameters are fitted onto this data.

Without altering the parameters, the shear viscosity and first normal stress difference are calculated and plotted together with the experimental data in figure 3.16. Again, the model gives an excellent agreement with experimental data for the steady state shear viscosity and only show small deviations from experimental data. For the transient curves at larger times, the agreement is less. In cone-plate experiments, the elasticity of the polymer leads to instabilities at the free surface, especially if the first normal stress difference equals or exceeds the shear stress. Normally in the non-linear regime of transient shear experiments in cone-plate rheometers, the shear stress gets to a maximum and then reaches a steady state value.

### Table 3.4: XPP parameters for fitting of the IUPAC A melt at $T = 150 \degree C$, $\nu_i = 2/q_i$. WLF-shift parameters: $T_r = 163 \degree C$, $C_1 = 17.4$, $C_2 = 51.6$ [K].

<table>
<thead>
<tr>
<th>$i$</th>
<th>$G_{0,i}$ [Pa]</th>
<th>$\lambda_{0,i}$ [s]</th>
<th>$q_i$</th>
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</table>

**Figure 3.15**: Transient (a) and steady state (b) uniaxial elongational viscosity $\eta_q$ of the XPP model for IUPAC A melt at $T = 150 \degree C$. $\nu_i = 2/q_i$, $\dot{\varepsilon}_i = 0.001, 0.003, 0.01, 0.03, 0.1, 0.3, 1, 3, 10, 30 \ [s^{-1}].$
Chapter 3

Figure 3.16: Transient (a) and steady state (b) shear viscosity $\eta$, and transient (c) and steady state (d) first normal stress coefficient $\Psi_1$ (bottom) of the XPP model for IUPAC A melt at $T = 150^\circ C$. $\nu_i = 2/\gamma_i, \dot{\gamma} = 0.001, 0.01, 0.1, 0.5, 1, 2, 5, 10, 20 \text{ [s}^{-1}\text{]}$.

However, in these experiments the steady state value is not reached and the experimental data keeps on decreasing. In general, those instabilities get worse, if a larger angle is used. They can be reduced, by using a ring around the cone-plate geometry. For further details, see Pahl et al. (1995).

For the first normal stress coefficient, the model shows a good agreement with the experimental data, particularly in view of the difficulty to obtain reliable experimental results, especially at higher shear rates. In the steady state data, a small overshoot can be seen. For the transient data, the same experimental instabilities occur as for the shear viscosity. Furthermore, the calculated overshoot is rather small.

The calculations for a step-strain experiment for the model are given in figure 3.17. It has, for longer time-scales, for all strains (nearly) the same shape, as experimentally observed [McLeish et al. (1999)]. At small times, the curves do not have the same shape. This is due to the fact that the steps are imposed in a similar way as in experiments, i.e. with a finite time step and shear rate, which is different for all steps. After reaching the maximum, which is the end of the step, a rapid relaxation occurs, followed by a relaxation similar to the linear relaxation modulus, which is for all steps the same. Experimental results are usually shown only after this first rapid relaxation. However, similar shapes have been observed
Figure 3.17: Relaxation moduli of shear stress $G(t, \gamma)$ and 1st normal stress difference $G_N(t, \gamma)$ (a), shifted relaxation moduli (b), and damping functions (c) of the XPP model for IUPAC A melt at $T = 150 \degree C$. $v_i = 2/q_i$. $\gamma = 0.2, 0.6, 1.9, 6.0, 9.5, 15.3, 18.7, 22.4, 30.9$ [\degree C].

for, amongst others, H-polymers [McLeish et al. (1999)] and concentrated solutions [Einaga et al. (1971)]. Further investigation of this feature may be of interest. The relaxation moduli of both the shear stress and first normal stress difference show similar shapes after the step strain, and are almost equal to each other. If the step-strain curves are shifted towards the linear curve, they almost fall on top of each other for intermediate times. However, for the long time range, small deviations can be seen. The bottom plot of figure 3.17 shows the damping functions over the shear strain. The circles represent the shift of the calculations, and the crosses are the experimental data taken from Khan and Larson (1987). The solid line is the double exponential function, as introduced by Laun (1978), which is nearly on top of the experimental data. The dashed line represents the single exponential damping function. The damping functions show, that the model is doing a good job for a wide range of strains. Only, for very high strain, the damping function is somewhat overpredicted compared to the double exponential function.

So, by fitting the non-linear parameters on the uniaxial elongational data set only, good to excellent results for the fits in shear can be obtained.
Table 3.5: XPP parameters for fitting of the Statoil 870H HDPE melt. $T_r = 170$ [°C]. $\nu_l = 2/q_i$.

<table>
<thead>
<tr>
<th>Maxwell parameters</th>
<th>XPP model</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_{0,i}$ [Pa]</td>
<td>$\lambda_{0,i}$ [s]</td>
<td>$q_i$</td>
</tr>
<tr>
<td>1</td>
<td>1.5350 · $10^4$</td>
<td>1.0000 · $10^{-2}$</td>
</tr>
<tr>
<td>2</td>
<td>3.1870 · $10^4$</td>
<td>1.0000 · $10^{-3}$</td>
</tr>
<tr>
<td>3</td>
<td>7.8180 · $10^4$</td>
<td>1.0000 · $10^{-4}$</td>
</tr>
<tr>
<td>4</td>
<td>1.4130 · $10^4$</td>
<td>1.0000 · $10^{-5}$</td>
</tr>
<tr>
<td>5</td>
<td>1.9680 · $10^4$</td>
<td>1.0000 · $10^{-6}$</td>
</tr>
<tr>
<td>6</td>
<td>2.0650 · $10^4$</td>
<td>1.0000 · $10^{-7}$</td>
</tr>
<tr>
<td>7</td>
<td>9.3000 · $10^4$</td>
<td>5.0000 · $10^{-8}$</td>
</tr>
</tbody>
</table>

3.4.3 Statoil 870H HDPE melt

Hachmann (1996) has measured the elongational viscosities for this HDPE melt. The experiments were carried out at a temperature of $T = 150$ [°C]. In shear, the material is characterized by Kraft (1996) at a temperature of $T = 170$ [°C]. The discrete spectrum of 7 relaxation times and moduli is given by Wagner et al. (1998c) at $T = 170$ [°C]. The non-linear parameter $q$ and ratio $\frac{\lambda_{0,i}}{\lambda_{0,i}}$ are manually fitted on the uniaxial elongational data only. The non-linear parameter $\alpha$ is again fitted on the second planar viscosity data. The linear and non-linear parameters for this material at a temperature of $T = 170$ [°C] are given in table 3.5. The shift in temperature can be determined using equation (3.32) and the activation energy given in table 3.5.

To our surprise even for a HDPE melt the model gives a satisfactory agreement with the uniaxial experimental data, as can be seen in figure 3.18. The model shows an upswing which is a bit sooner in time than the experimental data. This might indicate that a change in the stretch evolution equation is necessary for linear polymers. Notice that the highest

![Figure 3.18](image-url)
Differential Constitutive Equations for Polymer Melts: the eXtended Pom-Pom model

Theoretical, for an HDPE melt $q = 1$ is expected for all modes. However, this does not give sufficient elongational thickening behaviour. The physical interpretation of $q$, the amount of arms attached to the backbone, is therefore only partly followed. Maybe a more physical picture can be sketched for parameter $\nu$. It could be regarded as the amount of influence that the polymer material after the branch-point, i.e. the ‘arms’, has on the contribution to the stretch of the considered backbone tube between two branch-points. A long linear polymer chains could be entangled in the surrounding polymer chains, such that it is equally contributing to the stretch as seven branched short polymer chain ‘arms’.

For the first planar elongational viscosity good agreement is obtained, see figure 3.19. For the second planar elongational viscosity data the model underpredicts the data, just as for the Lupolen LDPE melt. However, qualitative agreement, i.e. elongational thinning, is accounted for. The different modes can be seen for the steady state solution, which indicates that not enough modes are used. Improvement might also be obtained by a change in the orientation evolution equation. Good agreement is observed between the experimental and calculated data for the equibiaxial elongational viscosity (figure 3.20).

$q$ for this HDPE material ($q = 7$) is significantly lower than for the LDPE melt ($q = 37$).
This HDPE melt is very elastic and it is difficult to capture the zero-shear viscosity with start-up shear experiments. Therefore it is determined by creep experiments [Kraft (1996)]. This also means that it is difficult to identify a satisfying relaxation spectrum. The shear response is shown in figure 3.21. Although steady state predictions are reasonable, transient predictions are a bit off; the experimental overshoot is overpredicted. The model also overpredicts the end steady state values a bit. For the first normal stress coefficient in shear, the model predicts the right shape, but is mostly overpredicting transient start-up experimental data. For only fitting on the uniaxial data, the predictions in shear are still good.

In general, it can be stated that the Pom-Pom model, although developed for branched molecules, is quite capable of predicting the experimental data of the linear HDPE melt over the full range of different experiments. In elongation the prediction is good, while for shear the model somewhat overpredicts the experimental data. It is mentioned again that the zero-shear viscosity and the linear spectrum for this material are difficult to identify, as it is a highly elastic material. Besides, all parameters where fitted manually where better results may be obtained by an automatic generation of the parameters. Another improvement may be reached by a slight adjustment of the evolution of stretch or orientation equation, in such a way, that it is more in agreement with the molecular topology of an HDPE melt.

3.5 Conclusions

The eXtended Pom-Pom model discussed here can quantitatively describe the behaviour in simple flows for two different commercial LDPE melts. All flow components can be predicted satisfactorily by manually fitting the non-linear parameters on the uniaxial experimental data only. Improvements have been made compared with previous versions of the Pom-Pom model. By eliminating the finite extensibility condition from the original equations, the model predictions are now smooth and more realistic. Moreover, a second normal stress difference is introduced, which was not present in the differential form of McLeish and Larson (1998).
The eXtended Pom-Pom (XPP) model shows a too pronounced thinning for the second planar viscosity. We speculate, that this might be improved by a change in the orientation evolution equation.

For a third material, an HDPE melt, the model predicts the experimental data in a satisfactory way. The elongational experimental data, which is used to fit the non-linear parameters, is described well. For shear, the experimental data is slightly overpredicted. However, it should be pointed out, that the model was mainly developed for polymers with long-chain branches, such as LDPE melts. As HDPE has a different molecular structure, better results may be obtained by adjusting the stretch and orientation equations in such a way that they closer match the molecular topology of HDPE melts. However, it is still quite satisfying to notice, that even for an HDPE melt, the model is doing a good job.

An important aspect for a good description of the experimental data is the linear discrete relaxation spectrum. This spectrum defines how well the linear viscoelastic curve is followed. A good basis for non-linear rheology of commercial polymer melts is the right choice of the discrete linear relaxation spectrum.

Improvements of the fits shown here can be obtained by determining the parameters with a more advanced fit procedure. All non-linear parameters were determined manually by

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**Figure 3.21:** Transient (a) and steady state (b) shear viscosity $\eta$, and transient (c) and steady state (d) first normal stress coefficient $\Psi_1$ of the XPP model for Statoil 870H HDPE melt at $T = 170 \, ^\circ$C. $\nu = 2 / \eta$; $\dot{\gamma} = 0.0001, 0.01, 0.03, 0.1, 0.3, 1.0, 3.0, 10.0 \, [s^{-1}]$. 

The eXtended Pom-Pom (XPP) model shows a too pronounced thinning for the second planar viscosity. We speculate, that this might be improved by a change in the orientation evolution equation.

For a third material, an HDPE melt, the model predicts the experimental data in a satisfactory way. The elongational experimental data, which is used to fit the non-linear parameters, is described well. For shear, the experimental data is slightly overpredicted. However, it should be pointed out, that the model was mainly developed for polymers with long-chain branches, such as LDPE melts. As HDPE has a different molecular structure, better results may be obtained by adjusting the stretch and orientation equations in such a way that they closer match the molecular topology of HDPE melts. However, it is still quite satisfying to notice, that even for an HDPE melt, the model is doing a good job.

An important aspect for a good description of the experimental data is the linear discrete relaxation spectrum. This spectrum defines how well the linear viscoelastic curve is followed. A good basis for non-linear rheology of commercial polymer melts is the right choice of the discrete linear relaxation spectrum.

Improvements of the fits shown here can be obtained by determining the parameters with a more advanced fit procedure. All non-linear parameters were determined manually by
following some basic ground rules as given by McLeish and Larson (1998), Inkson et al. (1999). Only the uniaxial and second planar experimental data was used for fitting. Although it is satisfying that the other data is predicted so well (regarding that it was not used for fitting), better predictions may be expected, if all data is taken in consideration using an automated identification procedure.

In general, it can be noted, that a good basic ground is laid for calculating commercial polymer melts with the multi-mode differential constitutive Pom-Pom model, but there is still room for improvement.
Chapter 4

Viscoelastic Analysis of Complex Polymer Melt Flows using the eXtended Pom-Pom model*

The multi-mode eXtended Pom-Pom model, which is able to quantitatively describe the rheological behaviour of polyethylene melts, is used in combination with the accurate, stable and robust Discrete Elastic Viscous Stress Splitting / Discontinuous Galerkin DEVSS/DG method for a combined numerical/experimental analysis of a low density polyethylene melt flowing through three complex flow geometries. These are the benchmark problems of a contraction flow, confined flow around a cylinder, and flow through a cross-slot device. Numerical results for the eXtended Pom-Pom model are compared to experimental data and the outcome of the conventional Giesekus and PTT models. Particular features as experimentally seen in the complex flows are qualitatively, and to a large extent also quantitatively, described by the eXtended Pom-Pom model, while the Giesekus and PTT models fail in elongational dominated regions. Numerical and experimental difficulties are pointed out for the different complex flows. It is shown that disagreement between experimental and numerical results can be, partly, imputed to experimental uncertainties. The eXtended Pom-Pom model encounters convergence problems in the contraction flow and flow around a cylinder, which are not seen for the Giesekus and PTT models. Furthermore, it is concluded that the cross-slot device is the preferred complex flow to test constitutive models as it is more discriminative and experimentally most convenient in different ways. This particular flow can even function as a rheological apparatus.

4.1 Introduction

Thorough knowledge of the rheological behaviour of polymer melts is crucial in understanding the relation between processing and resulting product properties. Viscoelastic

*This chapter is largely based on: Verbeeten et al. (2001b)
analyses of complex or prototype industrial flows, i.e. simplified characteristic flow geometries which exhibit a combination of shear and elongation, can help to understand these processes. In recent years, substantial progress has been made in both experimental and numerical methods as well as constitutive modelling.

Crucial to the quantitative prediction of the kinematics and stresses in complex flows is the availability of reliable constitutive models. A main problem in constitutive modeling is to obtain a correct description of the nonlinear behaviour in both elongation and shear. Most well-known and widely used models, such as the multi-mode Phan-Thien Tanner (PTT), Giesekus and K-BKZ (Kaye-Bernstein-Kearsley-Zapas) models have been demonstrated to be unable to do so [Baaijens et al. (1997)]. Recently, a new class of constitutive equations has been introduced based on the tube model of Doi and Edwards (1986), which is able to simultaneously describe shear and elongational behaviour of polyethylene melts. Some of them start off in an integral version, e.g. the Pom-Pom model [McLeish and Larson (1998), Inxson et al. (1999), Blackwell et al. (2000)], but an approximation of the differential type is also given for computational convenience in finite element (FE) methods. Others are only available as an integral model, e.g. the MSF model [Rubio et al. (2001)], and no differential approximation exists. Although the newly developed deformation fields method by Peters et al. (2000a) is an attractive way to calculate models of the integral type, FE methods using differential constitutive equations are still more efficient. Furthermore, Verbeeten et al. (2001a) introduced the eXtended Pom-Pom model, a modification of the original differential Pom-Pom model of McLeish and Larson, which is able to describe the behaviour of polyethylene melts over a wide range of rheological data, including reversed flow. This last rheological flow is still rather troublesome for most integral models.

Bishko et al. (1999) already showed results for the original differential Pom-Pom model in a complex 4:1 contraction flow. However, a Lagrangian FE method was applied in their study, which has the disadvantage of a computational mesh that deforms with the fluid. In a strong flow field this means that regular re-meshing is required, which is cumbersome, especially for three-dimensional geometries. To avoid this disadvantage, we choose an Eulerian approach.

Although Bishko et al. (1999) only applied a single-mode version of the Pom-Pom model, good qualitative predictions were obtained for a highly branched configuration. Their results are promising and showed all the specific features that are also encountered in experiments for LDPE melts. However, a full comparison with experimental complex flow data was not possible, since only a multi-mode version can correctly describe the rheology of commercial polymer melts. Furthermore, due to excessive shear-thinning behaviour in fast shearing flows, the shear stress shows a maximum. This causes a numerically unstable flow and a velocity profile with a sharp boundary. A multi-mode version will avoid this, since modes with higher relaxation times would take over after the shear-thinning behaviour sets in for the first mode, resulting in a less shear-thinning behaviour. Moreover, as the shear-thinning behaviour of the eXtended Pom-Pom model is less extreme, this particular model avoids this instability.

Like in Bishko et al. (1999), most studies of polymer melts are conducted on the benchmark contraction or contraction/expansion problem, e.g. Xue et al. (1999), Wapperom and Keunings (2000), and Alves et al. (2000) for purely numerical research, Martyn et al. (2000a, b, c) for a mostly experimental investigation in a three dimensional geometry, and Béraudo et al. (1998) for a combined numerical/experimental study. Less research has been performed on the benchmark flow around a cylinder, e.g. Peters et al. (2000b) and Renardy (2000) for numerical studies, and Schoonen (1998), Baaijens et al. (1997), Hartt
Viscoelastic Analysis of Complex Polymer Melt Flows using the eXtended Pom-Pom model

and Baird (1996) and Baaijens (1994b) for a combined investigation. A viscoelastic analysis of a polymer melt in a cross-slot device has only been published once to our knowledge [Peters et al. (1999)]. This particular complex geometry, however, imposes large strains on the material and is therefore more discriminating towards constitutive models with different elongational properties.

Since different complex flow geometries are investigated in literature and a recent differential model is able to predict rheological data over a full range simultaneously, the objective of this study is twofold. On the one hand, we will investigate the performance of the multi-mode eXtended Pom-Pom model [Verbeeten et al. (2001a)] in the three mentioned complex flow geometries (planar contraction flow, confined flow around a cylinder, cross-slot flow) and compare it with experimental results taken from Schoonen (1998). All geometries were designed to have near two-dimensionality, i.e. a depth-to-height aspect ratio of at least eight in the whole flow domain, such that comparison with two-dimensional calculations is allowed [Schoonen (1998), Schoonen et al. (1998)]. Furthermore, the results will be compared against the performance of the PTT and Giesekus models, to show when and where these well-established conventional models fail. On the other hand, the differences and similarities between the three prototype industrial flows will be examined with respect to local strains, strain rates, stresses and their history in a Lagrangian sense. We will discuss the advantages and drawbacks of these flows when used for testing constitutive models by comparing experimental and numerical results.

For the numerical part of this study, the Discrete Elastic Viscous Stress Splitting technique in combination with the Discontinuous Galerkin method (DEVSS/DG) is used, which is known to be sufficiently stable, robust, accurate and efficient with respect to multi-mode calculations. In section 4.2, the problem definition and the constitutive equations are outlined. The computational method is shortly described in section 4.3 and can be found in more detail in Bogaerds et al. (1999b). The material characterisation and the performance of the three constitutive models in simple rheological flows is given in section 4.4. Results for the three prototype industrial flow geometries are presented in section 4.5, followed by a discussion on the different flows and the conclusions. It is shown that the multi-mode eXtended Pom-Pom model is indeed able to qualitatively, and to a large extent also quantitatively, predict the velocities and stresses in the different complex flow geometries contrary to the PTT and Giesekus models.

4.2 Problem definition

Isothermal and incompressible fluid flows, neglecting inertia, are described by the equations for conservation of momentum (4.1) and mass (4.2):

\[ \nabla \cdot \sigma = 0 , \quad (4.1) \]

\[ \nabla \cdot \vec{u} = 0 , \quad (4.2) \]
where $\nabla$ is the gradient operator, $\sigma$ denotes the Cauchy stress tensor and $\vec{u}$ the velocity field. The Cauchy stress tensor $\sigma$ is defined for polymer melts by:

$$\sigma = -pI + 2\eta_s D + \sum_{i=1}^{M} \tau_i.$$  \hspace{1cm} (4.3)

Here, $p$ is the pressure, $I$ the unit tensor, $\eta_s$ denotes the viscosity of the purely viscous (or solvent) contribution, $D = \frac{1}{2}(L + L^T)$ the rate of deformation tensor, in which $L = (\nabla \vec{u})^T$ is the velocity gradient tensor and $(\cdot)^T$ denotes the transpose of a tensor. The visco-elastic contribution of the $i^{th}$ relaxation mode is denoted by $\tau_i$ and $M$ is the total number of different modes. The multi-mode approach is necessary for most polymeric fluids to give a realistic description of stresses over a broad range of deformation rates. The visco-elastic contribution $\tau_i$ still has to be defined by a constitutive model.

### 4.2.1 Constitutive models

Within the scope of this work, a sufficiently general way to describe the constitutive behaviour of a single mode is obtained by using a differential equation based on the generalized Maxwell-type equation:

$$\nabla \tau_i + f_{GS}(\tau_i, D) + \lambda(\tau_i)^{-1} \cdot \tau_i = 2G_i D,$$  \hspace{1cm} (4.4)

with $G_i$ the plateau modulus of the $i^{th}$ mode obtained from the linear relaxation spectrum determined by dynamic measurements. The upper convected time derivative of the stress $\nabla \tau_i$ is defined as:

$$\nabla \tau_i = \tau_i - L \cdot \tau_i - \tau_i \cdot L^T = \frac{\partial \tau_i}{\partial t} + \vec{u} \cdot \nabla \tau_i - L \cdot \tau_i - \tau_i \cdot L^T,$$  \hspace{1cm} (4.5)

where $t$ denotes time. Both tensorial functions $f_{GS}(\tau_i, D)$ and $\lambda(\tau_i)$ depend upon the chosen constitutive equation. Notice, that by choice of $f_{GS}(\tau_i, D) = 0$ and $\lambda(\tau_i) = \lambda_i$, with $\lambda_i$ the $i^{th}$ linear relaxation time, the Upper Convected Maxwell (UCM) model is retrieved.

For the Giesekus model, the functions are defined as:

$$f_{GS}(\tau_i, D) = 0, \hspace{0.5cm} \lambda(\tau_i)^{-1} = \frac{1}{\lambda_i} \left[ \frac{\alpha_i}{G_i} \tau_i + I \right],$$  \hspace{1cm} (4.6)

with $\alpha_i$ a material parameter to be fitted on the rheological data.

For the exponential PTT model, the functions are defined as:

$$f_{GS}(\tau_i, D) = \xi_i (D \cdot \tau_i + \tau_i \cdot D), \hspace{0.5cm} \lambda(\tau_i)^{-1} = \frac{1}{\lambda_i} \left[ e^{\frac{\tau_i}{\xi_i}} \cdot I \right],$$  \hspace{1cm} (4.7)

with $\xi_i$ the slip parameter from the Gordon-Schowalter derivative and $\xi_i$ a material parameter, both to be fitted on the rheological data.

A new class of constitutive relations based on the tube theory and a simplified topology of branched molecules was recently proposed by McLeish and Larson. The basic idea of the model is that the rheological properties of entangled polymer melts depend on the topological...
structure of the polymer molecules. The simplified topology consists of a backbone with a number of dangling arms at both ends and is called a pom-pom molecule. The backbone is confined by a tube formed by other backbones. A key feature is the separation of relaxation times for the stretch and orientation. For more details we refer to McLeish and Larson (1998), Verbeeten et al. (2001a). Verbeeten et al. (2001a) modified the differential version to the eXtended Pom-Pom model to overcome three problems encountered for the original form: solutions in steady state elongation show discontinuities, the equation for orientation is unbounded for high strain rates, the model does not have a second normal stress difference in shear. A branched molecule can be represented by several equivalent pom-pom modes. The extra stress equation for the eXtended Pom-Pom (XPP) model is defined as:

\[
\tau_i = \sigma - G_i I = 3G_i \Lambda_i^2 S_i - G_i I ,
\]

with \( \Lambda_i \) the backbone tube stretch, defined as the length of the backbone tube divided by the length at equilibrium, and \( S_i \) denoting the orientation tensor. The evolution equations for the orientation and backbone tube stretch are given by:

\[
\nabla S_i + 2[D : S_i] S_i + \frac{1}{\lambda_{b,i} \Lambda_i} \left[ 3 \alpha_i \Lambda_i^4 S_i \cdot S_i + (1 - \alpha_i - 3 \alpha_i \Lambda_i^4 \text{tr}(S_i \cdot S_i)) S_i \right] = \frac{(1 - \alpha_i)}{3} I ,
\]

(4.9)

\[
\dot{\Lambda}_i = \Lambda_i [D : S_i] - \frac{e^{\nu_i (\Lambda_i - 1)}}{\lambda_{s,i}} (\Lambda_i - 1) , \quad \nu_i = \frac{2}{q_i} \quad \lambda_{b,i} = \lambda_i .
\]

Here, \( \lambda_{b,i} \) is the relaxation time of the backbone tube orientation equal to the linear relaxation time \( \lambda_i \), \( \lambda_{s,i} \) is the relaxation time for the stretch, \( \nu_i \) a parameter denoting the influence of the surrounding polymer chains on the backbone tube stretch, and \( q_i \) the amount of arms at the end of a backbone.

Due to its different structure from most differential constitutive equations and non-zero initial conditions, it may be cumbersome to implement the double-equation formulation in FE packages. However, the XPP model can also be written in a fully equivalent single-equation fashion [Verbeeten et al. (2001a)], which has the same structure as the Giesekus and PTT models. In that case the functions from equation (4.4) are defined as:

\[
f_{GS}(\tau_i, D) = 0, \quad \lambda(\tau_i)^{-1} = \frac{1}{\lambda_{b,i}} \left[ \frac{\alpha_i}{G_i} \tau_i + F(\tau_i) I + G_i (F(\tau_i) - 1) \tau_i^{-1} \right] ,
\]

(4.11)

with

\[
F(\tau_i) = 2r_i e^{\nu_i (\Lambda_i - 1)} \left( 1 - \frac{1}{\Lambda_i} \right) + \frac{1}{\lambda_i^2} \left[ 1 - \frac{\alpha_i \text{tr}(\tau_i \cdot \tau_i)}{3G_i^2} \right]
\]

(4.12)

and

\[
\Lambda_i = \sqrt{1 + \frac{\text{tr}(\tau_i)}{3G_i}} , \quad r_i = \frac{\lambda_{b,i}}{\lambda_{s,i}} , \quad \nu_i = \frac{2}{q_i} \quad \lambda_{b,i} = \lambda_i .
\]

(4.13)
Notice, that for this definition of the backbone stretch, we may run into numerical problems if \( \frac{w(\tau_i)}{3\lambda_i} \) gets smaller than \(-1\), by which the square root in equation (4.13) becomes imaginary. Physically, \( \text{tr}(\tau_i) \) can not become smaller than 0. However, numerically we have encountered these unrealistic values near the re-entrant corner in a contraction flow and at the front and back stagnation points in a flow around a cylinder for high enough flow rates. Unphysical negative backbone stretch values in the double-equation XPP model were also encountered at the exact same locations. This is a numerical artifact, similar to the negative values for the trace of the extra stress, \( \text{tr}(\tau_i) \), encountered in the Giesekus and PTT models. The cross-slot flow, on the other hand, is a smooth flow in that respect and no unphysical stretch is predicted, both for the single-equation as well as the double-equation XPP model. We would like to remark, that these unrealistic negative backbone stretch values do not occur during calculations of the rheological flows, i.e. without the convective term, either. We will elaborate more on this problem in sections 4.5 and 4.6.

A disadvantage for a two-dimensional numerical implementation, concerning both versions, is the non-zero third stress component \( \tau_{zz} \), contrary to the Giesekus and PTT models. Compared to the single-equation form, the double-equation formulation has an extra equation for the stretch, resulting in a larger system matrix in FE codes. However, as we eliminate the extra stresses, or, equivalently, the orientation tensor and the stretch, at element level (see section 4.3), the computational cost of these two extra equations is relatively low. Despite the disadvantages, the double-equation XPP model is preferred over the single-equation formulation, as it still proceeds if negative backbone stretch values are calculated, while in the single-equation version calculations stop if \( \frac{w(\tau_i)}{3\lambda_i} \) gets smaller than \(-1\).

### 4.3 Computational method

The DEVSS/DG method, Baaijens et al. (1997), which is a combination of the Discrete Elastic Viscous Stress Splitting (DEVSS) technique of Guénette and Fortin (1995) and the Discontinuous Galerkin (DG) method, developed by Lesaint and Raviart (1974), is used. Application to the double-equation XPP model is discussed in this section. The weak formulation and solution strategy for the Giesekus and PTT models is similar and can be found in more detail in Bogaers et al. (1999b) and Baaijens et al. (1997).

#### 4.3.1 DEVSS/DG method

Consider the problem described by the equations (4.1), (4.2), and (4.9) and (4.10). Following common FE techniques, these equations are converted into a mixed weak formulation:

**Problem DEVSS/DG:** Find \((\vec{u}, p, \bar{D}, S, \Lambda_i)\) for any time \(t\) such that for all admissible test functions \((\vec{v}, q, E, s_i, l_i)\),

\[
(D_v, 2\eta_qD + 2\eta(D - \bar{D}) + \sum_{i=1}^{M} \Gamma_i(3\lambda_i^2 S_i - I) - \nabla \cdot \vec{v}, p) = 0 ,
\]  

(4.14)
\[ (q, \nabla \cdot \vec{u}) = 0, \quad (4.15) \]

\[ \left( E, \vec{D} - \bar{D} \right) = 0, \quad (4.16) \]

\[ \begin{align*}
\left( s_i, S_i \right) + 2[D : S_i] S_i &+ \frac{1}{\lambda_{s,i} \Lambda_i^4} \left[ 3\alpha_i \Lambda_i^4 S_i \cdot S_i \\
&\quad + (1 - \alpha_i - 3\alpha_i \text{tr}(S_i \cdot S_i)) S_i - \frac{(1 - \alpha_i)}{3} I \right] \\
&- \sum_{e=1}^{K} \int_{\Gamma_{\text{in}}} s_i : \vec{u} \cdot \vec{n} (S_i - S_{\text{ext}}^i) \, d\Gamma = 0 \quad \forall \, i \in \{1, 2, \ldots, M\},
\end{align*} \]

\[ \left( l_i, \Lambda_i - \Lambda_i [D : S_i] \right) + \frac{e^{\eta_i}(\Lambda_i - 1)}{\lambda_{s,i}} (\Lambda_i - 1) \\
- \sum_{e=1}^{K} \int_{\Gamma_{\text{in}}} l_i \vec{u} \cdot \vec{n} (\Lambda_i - \Lambda_i^\text{ext}) \, d\Gamma = 0 \quad \forall \, i \in \{1, 2, \ldots, M\}. \quad (4.18) \]

Here, \( (\cdot, \cdot) \) denotes the \( L^2 \)-inner product on the domain \( \Omega \), \( D_v = \frac{1}{2} (\nabla \vec{u} + (\nabla \vec{u})^T) \), \( \bar{\eta} \) an auxiliary viscosity, \( \Gamma_{\text{in}}^e \) is the inflow boundary of element \( \Omega^e \), \( \vec{n} \) the unit vector pointing outward normal on the boundary of the element \( \Omega^e \) and \( S_{\text{ext}}^i \) and \( \Lambda_{\text{ext}}^i \) denote the orientation tensor and backbone stretch of the neighboring, upwinding element.

A stabilization term \( 2\bar{\eta}(D - \bar{D}) \) has been added to the momentum equation (4.14), where the discrete approximation \( \bar{D} \) is obtained from an \( L^2 \) projection of the rate of deformation tensor (equation (4.16)). The auxiliary viscosity \( \bar{\eta} = \sum_{i=1}^{M} G_i \lambda_i \) is found to give satisfactory results.

Upwinding is performed on the element boundaries by adding integrals on the inflow boundary of each element. Time discretisation of the constitutive equation is attained using an implicit Euler scheme, with the exception of the external components \( S_{\text{ext}}^i \) and \( \Lambda_{\text{ext}}^i \) which are taken explicitly (i.e. \( S_{\text{ext}}^i = S_{\text{ext}}^i(t_n) \) and \( \Lambda_{\text{ext}}^i = \Lambda_{\text{ext}}^i(t_n) \)). Hence, the terms \( \int_{s_i : \vec{u} \cdot \vec{n}} (S_i - S_{\text{ext}}^i) \, d\Gamma \) and \( \int_{l_i \vec{u} \cdot \vec{n}} (\Lambda_i - \Lambda_{\text{ext}}^i) \, d\Gamma \) have no contributions to the Jacobian which allows for local elimination of the orientation tensor and backbone stretch.

### 4.3.2 Solution strategy

In order to obtain an approximation of Problem DEVS/DG, a 2D domain is divided into quadrilateral elements. A bi-quadratic interpolation for the velocity \( \vec{u} \), bi-linear for the pressure \( p \) and discrete rate of deformation \( \bar{D} \), and a discontinuous bi-linear interpolations for the orientation tensor \( S_i \) and stretch \( \Lambda_i \) are known to give stable results (see Bogaers et al. (1999b) and Baaijens et al. (1997)). Integration of equation (4.14) to (4.18) over an element is performed using a \( 3 \times 3 \)-Gauss quadrature rule common in FE analysis.
To obtain the solution of the nonlinear equations, a one step Newton-Raphson iteration process is carried out. Consider the iterative change of the nodal degrees of freedom \((\delta_u, \delta_p, \delta_D, \delta_S, \delta_\Lambda)\) as variables of the algebraic set of linearized equations. This linearized set is given by:

\[
\begin{pmatrix}
Q_{uu} & Q_{up} & Q_{uD} & Q_{uS} & Q_{uA} \\
Q_{pu} & 0 & 0 & 0 & 0 \\
Q_{Du} & 0 & Q_{DD} & 0 & 0 \\
Q_{Su} & 0 & 0 & Q_{SS} & Q_{SA} \\
Q_{La} & 0 & 0 & Q_{AS} & Q_{LA}
\end{pmatrix}
\begin{pmatrix}
\delta_u \\
\delta_p \\
\delta_D \\
\delta_S \\
\delta_\Lambda
\end{pmatrix} =
\begin{pmatrix}
f_u \\
f_p \\
f_D \\
f_S \\
f_\Lambda
\end{pmatrix},
\tag{4.19}
\]

where \(f_\alpha, (\alpha = \bar{u}, p, \bar{D}, \bar{S}, \bar{\Lambda})\) correspond to the residuals of equations (4.14) to (4.18), while \(Q_{\alpha\beta}\) follow from linearisation of these equations. Due to the fact that \(\bar{S}_{\alpha}^{\text{st}}\) and \(\bar{\Lambda}_{\alpha}^{\text{st}}\) have been taken explicitly in equations (4.17) and (4.18), matrices \(Q_{SS}, Q_{SA}, Q_{AS},\) and \(Q_{LA}\) form a block diagonal structure which allows for calculation of \(Q_{SS}^{-1}\) on element level. Consequently, this enables the reduction of the global DOF's by static condensation of the orientation tensor and backbone stretch block. A further reduction of the size of the Jacobian is obtained by a decoupling approach. First, the ‘Stokes’ problem is solved \((\bar{u}, p)\) after which the updated solution is used to find a new approximation for \(\bar{D}\). The following problems now emerge:

**Problem DEVSS/DG\(^a\):** Given \((\bar{u}, p, \bar{D}, \bar{S}, \bar{\Lambda})\) at \(t = t_n\), find a solution at \(t = t_{n+1}\) of the algebraic set:

\[
\begin{pmatrix}
Q_{uu} - (Q_{uS} Q_{uA}) & (Q_{SS} Q_{SA})^{-1} (Q_{Su}) \\
(Q_{PU}) & (Q_{LA})^{-1} (Q_{up})
\end{pmatrix}
\begin{pmatrix}
\delta_u \\
\delta_p
\end{pmatrix} =
\begin{pmatrix}
f_u - (Q_{uS} Q_{uA}) & (Q_{SS} Q_{SA})^{-1} (f_S) \\
(f_p)
\end{pmatrix},
\tag{4.20}
\]

and **Problem DEVSS/DG\(^b\):** Given \(\bar{D}\) at \(t = t_n\) and \(\bar{u}\) at \(t = t_{n+1}\), find \(\delta_D\) from:

\[
(Q_{DD}) (\delta_D) = - (f_D).\tag{4.21}
\]

Notice that \(f_D\) is now taken with respect to the new velocity approximation, i.e. \(f_D(\bar{u}^{n+1}, \bar{D}^n)\). The nodal increments of the orientation tensor and backbone stretch are retrieved element by element following:

\[
\begin{pmatrix}
\delta_S \\
\delta_\Lambda
\end{pmatrix} =
\begin{pmatrix}
(Q_{SS} Q_{SA})^{-1} (f_S) \\
(f_\Lambda)
\end{pmatrix},
\tag{4.22}
\]

with \(f_S\) and \(f_\Lambda\) also taken with respect to the new velocity approximation \((f_S(\bar{S}_v^n, \bar{u}^{n+1}), f_\Lambda(\bar{\Lambda}_v^n, \bar{u}^{n+1}))\).

To solve the non-symmetrical system of problem DEVSS/DG\(^a\) an iterative solver is used based on the Bi-CGSTAB method of Van der Vorst (1992). The symmetrical set of algebraic
equations of problem DEVSS/DG is solved using a Conjugate-Gradient solver. Incomplete LU preconditioning is applied to both solvers. In order to enhance the computational efficiency of the Bi-CGSTAB solver, static condensation of the center-node velocity variables results in filling of the zero block diagonal matrix in problem DEVSS/DG and, in addition, achieves a further reduction of global degrees of freedom. The above decoupling procedure enables the use of iterative solvers. The use of Bi-CGSTAB on the full problem was unsuccessful.

Finally, to solve the above sets of algebraic equations, both essential and natural boundary conditions must be imposed on the boundaries of the flow channels. At the entrance and the exit of the flow channels the velocity profiles are prescribed. At the entrance, the values of the orientation tensor and backbone stretch of a few elements downstream the inflow boundary, imposing a periodic boundary condition for these stress variables.

### 4.4 Material Characterisation

The polymer melt that is investigated in this work is a commercial grade low density polyethylene (DSM, Stamylan LD 2008 XC43), further referred to as LDPE. This long-chain branched material has been extensively characterised by Schoonen (1998) and is also given in Peters et al. (1999).

The parameters for a four mode Maxwell model are obtained from dynamic measurements at a temperature of $T = 170 \, ^\circ\text{C}$. The non-linear parameters $q$ and the ratio \( \frac{\lambda_s}{\lambda_b} \) for the XPP model are determined using the transient uniaxial elongational data [Zoetelief and Palmen (2000)] only. Since second planar elongational or second normal stress difference data is not available for this material, the anisotropy parameter $\alpha$ in this model is chosen as $\alpha = 0.3$. Anisotropy is decreasing from the free ends inwards, and by choosing $\alpha$ as an inverse function of the number of arms $q$, this is indeed accomplished (see Verbeeten et al. (2001a)). Both the Giesekus and PTT models are incapable of satisfactorily predicting the elongational data for this material. Therefore, their non-linear parameters ($\alpha$, and $\varepsilon, \xi$) are fitted on the

| Table 4.1: Linear and non-linear parameters for fitting of the DSM Stamylan LD 2008 XC43 LDPE melt. $T_r = 170 \, ^\circ\text{C}$. $v_i = 2/q_i$. Activation energy: $E_0 = 48.2$ [kJ/mol]. WLF-shift parameters: $C_1 = 14.3$, $C_2 = 480.8$ [K]. |
|---------------------------------|----------|-----------------|---------|--------|--------|--------|--------|
| $i$ | $G_i$ [Pa] | $\lambda_1$ [s] | $q_i$ | $\frac{\lambda_s}{\lambda_b}$ | $\alpha_i$ | $\varepsilon_i$ | $\xi_i$ |
| 1   | $7.2006 \cdot 10^4$ | $3.8946 \cdot 10^{-3}$ | 1    | 7.0    | 0.30   | 0.30   | 0.15   | 0.08   |
| 2   | $1.5770 \cdot 10^4$ | $5.1390 \cdot 10^{-2}$ | 1    | 5.0    | 0.30   | 0.30   | 0.14   | 0.07   |
| 3   | $3.3340 \cdot 10^3$ | $5.0349 \cdot 10^{-1}$ | 2    | 3.0    | 0.15   | 0.25   | 0.12   | 0.06   |
| 4   | $3.0080 \cdot 10^2$ | $4.5911 \cdot 10^0$ | 10   | 1.1    | 0.03   | 0.15   | 0.10   | 0.05   |
steady shear data. Because the non-linear parameters are more sensitive in elongation than in shear, it is tried to prescribe as good as possible the uniaxial elongational data. All parameters are given in table 4.1.
Figure 4.1 shows the rheological behaviour of the three constitutive models and measured data in uniaxial and simple shear behaviour. The ‘steady state’ data points in the uniaxial elongational viscosity plot are the end points of the transient curves. Since the samples break at the end of the transient measurements, it is hard to say if steady state has truly been reached. However, sometimes it is claimed that steady state coincides with break-up of the samples [McKinley and Hassager (1999)].

The XPP model is the only model that can satisfactorily predict the uniaxial behaviour both in a transient and quasi-steady state sense. The Giesekus and PTT models are unable to predict the strong strain hardening effect of this material without showing large discrepancies in simple shear. Moreover, the Giesekus model even predicts the wrong shape of the steady state curve, as it ends in a plateau for high strain rates. This conclusion is more difficult to draw from figure 4.1(b) shown here, but from measurements of other low density polyethylene melts (see Münstedt and Laun (1979), Hachmann (1996)), it is known that, at high strain rates, these long-chain branched materials show an elongational thinning behaviour in a steady state sense. In the steady state curve of the PTT model, the different modes can be recognized due to excessive elongational thinning behaviour at high strain rates.

For simple shear, all models show a rather good agreement with the measured data (figure 4.1(c)). The Giesekus and PTT model are somewhat overpredicting the measurements. However, at higher shear rates, these models are in better agreement with the data than the XPP model, which is underpredicting the measurements. At shear rates over \(10^2 \text{ s}^{-1}\), the curves for all models drop rapidly (see figure 4.1(d)), as it is the end of the last mode. Since these high rates do not occur in the complex flows, this does not cause any problems in the further analysis.

In the start-up of the first normal stress difference, the different modes for the XPP model can be detected (see figure 4.1(e)). This could be avoided by choosing more Maxwell modes. That would also result in a smoother curve for the steady state uniaxial viscosity predicted by the PTT model. However, as computational time increases significantly with every mode added, four Maxwell modes is considered as a satisfying optimum between a good description of the rheological behaviour and computational cost.

In general, the XPP model shows the best overall agreement with experimental rheological data. Therefore, this model is also expected to perform best in the prototype industrial flow geometries.

### 4.5 Complex Flows

A comparison is made between numerical and experimental results for three complex flows: planar contraction flow, flow around a cylinder between two parallel plates and flow through a cross-slot device. These benchmark flow geometries are known to have a simple shear region, a pure elongational region, and a combined shear/elongational region, which defines them as complex flow geometries. Velocities were measured using Particle Tracking Velocimetry, while stresses are obtained by the field wise Flow Induced Birefringence method recording isochromatic fringe patterns. For reasons of not being too extensive, we will present results for one flow rate only. For more details on the experimental aspects and more experimental results, we refer to Schoonen (1998).
All geometries are designed to have a depth-to-height ratio of almost 8:1 throughout the whole flow domain. Schoonen (1998) demonstrated that with an aspect ratio of 8:1 the influence of the confining front and back walls is about 6% maximum on the isochromatic stress patterns within the flow rate range used in this investigation. This was confirmed in numerical studies by Schoonen et al. (1998) and Bogaers et al. (1999b). This is a sufficiently small deviation to be nominally two-dimensional and compare experimental results to two-dimensional calculations. The general rule for deviations due to three-dimensional effects is that the integrated effect of experimental stresses (which represents the birefringence patterns) is lower near walls and higher over centerlines in comparison to two-dimensional calculations. The contraction region of the planar contraction flow is an exception regarding the 6% deviation. Besides the increasing elongation rate, also the shear gradients at the front and back wall increase in that region due to an increasing velocity. Consequently, these higher shear gradients contribute to a higher stress. Therefore, it is even more important to have a sufficiently high depth to height aspect ratio over the whole flow domain in contraction flows, if comparing experiments to two-dimensional calculations.

To characterise the strength of the different flows, the dimensionless Weissenberg number indicates the amount of elasticity in the flow:

\[ W_i = \frac{\bar{\lambda} \bar{u}_{2D}}{h}, \]  

(4.23)

Here, \( \bar{\lambda} \) denotes the viscosity averaged relaxation time for the material (\( \bar{\lambda} = (\sum \lambda_i^2 G_i)/(\sum \lambda_i G_i) \)), \( \bar{u}_{2D} \) is the two-dimensional mean velocity and \( h \) a characteristic length of the flow geometry.

To link the calculated stresses to the measured isochromatic fringe patterns, the semi-empirical stress optical rule is used. It states that the deviatoric part of the refractive index tensor is proportional to the deviatoric part of the stress tensor:

\[ n^d = C\sigma^d, \]  

(4.24)

in which \( C \) is the stress optical coefficient, identified to equal (see Peters et al. (1999)):

\[ C = 1.47 \cdot 10^{-9} \text{ [Pa}^{-1}] \].  

(4.25)

The stress optical coefficient is slightly dependent on temperature [Lodge (1994)]. Furthermore, it is generally agreed that the rule fails if polymer orientation and stretching saturates, i.e. in strong extensional regions.

For two-dimensional flows, the stress optical rule can be simplified to:

\[ \tau_{FRG} = \sqrt{4\tau_{xy}^2 + N_1^2} = \frac{k\lambda}{dC}, \]  

(4.26)

with \( \tau_{FRG} \) defined as the isochromatic fringe stress, \( \tau_{xy} \) the shear stress in the \( xy \)-plane, \( N_1 = \tau_{xx} - \tau_{yy} \) the first normal stress difference, \( \lambda \) the wave length of the light used in the measurements, \( d \) the light path length in the birefringent medium, which in these cases are the depths of the flow cells, and \( k \) the fringe order of the observed dark fringe bands where extinction of the light occurs.
4.5.1 Contraction Flow

A schematic of half the flow geometry is shown in figure 4.2(a). Experiments were performed at a temperature of 170 °C, resulting in a viscosity averaged relaxation time for the material of $\lambda = 1.7415$ [s]. The upstream and downstream half heights of the geometry are $h = 0.775$ [mm] and $H = 2.55$ [mm], respectively, giving an actual contraction ratio of 3.29. The depth of the flow cell equals $d = 40$ [mm] to create a nominally two-dimensional flow, resulting in a depth-to-height ratio of 7.84 upstream and 25.81 downstream. The extracted two-dimensional mean upstream velocity, i.e. in the centerplane, is equal to $\bar{U}_{2D} = 2.27$ [mm/s], and consequently in the downstream channel $\bar{u}_{2D} = 7.47$ [mm/s]. By taking half the downstream channel height and the downstream two-dimensional mean velocity as characteristic values, the flow averaged Weissenberg number is:

$$ Wi = 16.8. \quad (4.27) $$

Notice, that the averaged Weissenberg number of the longest relaxation time used in the calculations is $Wi = 44.3$, and may even be much higher locally.

Part of the FE mesh used for the calculations of all three models is given in figure 4.2(b). Only half of the geometry is meshed due to symmetry. The contraction is placed at $x/h = 0$, while the inlet is at $x/h = -20$ and the outlet at $x/h = 30$. The periodic boundary for the inlet stresses is situated at $x/h = -10$. At the entrance and exit, a fully developed velocity profile is prescribed. No slip boundary conditions are imposed on the top confining wall, and the velocity in y-direction is suppressed for the symmetry line $y/h = 0$.

The time step $\Delta t$ for the XPP, Giesekus, and PTT models were 0.001 [s], 0.1 [s], and 0.1 [s], respectively. Preferable, the time step is taken as high as possible, while still having the calculations converge to the steady state. Unfortunately, with this mesh and this best choice for the time step, the solution for the XPP model was diverging after $t = 2.8$ [s]. This time frame is sufficiently long for the first three modes to completely develop, but is only around half the time of the longest relaxation time ($\lambda_4 = 4.5911$ [s]). Thus, the steady state solution for the XPP model was not reached yet. For the shear stress, the contribution of the longest relaxation time may even be neglected due to a significantly lower modulus. However, for the normal stresses, both in shear and elongation, the contribution can not be neglected.

![Figure 4.2: Schematic (a) and detail FE mesh (b) of half the planar contraction flow.](image)

The origin of the coordinate system is at the center of the contraction plane. $T = 170$ [°C], $\lambda = 1.7415$ [s], $\bar{U}_{2D} = 2.27$ [mm/s], $h = 0.775$ [mm], $H = 2.55$ [mm], $d = 40$ [mm], #elements=1000, #nodes=4161, #DOF($\bar{u}, \rho$)=7403, #DOF($\bar{D}$)=3243, #DOF($S, \Lambda$)=4×#elements×20=80000.
We suspect that the significantly more strain hardening behaviour than the other two models, resulting in a thinner downstream stress layer as is also appearing for a UCM model (see Hagen and Renardy (1997)), and the not sufficiently fine mesh to resolve this stress layer, are some of the reasons for divergence. As an indication for the XPP model, the velocities and stresses at time step \( t = 2.8 \) [s] will be shown anyway. A steady state solution for the other two models was reached without convergence problems.

Results of calculated and measured velocity profiles over four different cross-sections \((x/h = -6, -4, -1, 1)\) and the centerline \((y/h = 0)\) are shown in figure 4.3. The velocities for the cross-sections are made dimensionless with the two-dimensional mean upstream velocity \( \bar{U}_{2D} = 2.27 \) [mm/s]. In general, the predicted velocities are in good agreement with the measured data points for all three models. It should be noted, that the velocity profiles for the XPP model might still change as steady state has not been reached, however it is unlikely, since the influence of the stresses on the kinematics is relatively low. The PTT model is somewhat overpredicting the velocity profile for the third cross-section \((x/h = -1)\). Furthermore, the downstream velocity over the centerline \((y/h = 0)\) is overpredicted by all three models, which can be ascribed to the higher aspect ratio in the downstream channel. This is an experimental three dimensional effect, which is not accounted for in the calculations. Given a certain flow-rate in a duct, the mean velocity in the plane of symmetry \((z = 0)\) will become relatively lower for increasing aspect ratio, since the velocity profile is flattened. The velocity increase and the location of the overshoot for the centerline velocity is in excellent agreement with the measurements. The XPP model shows the best agreement.

The full field isochromatic fringe patterns are shown in figure 4.4. The top parts of every subfigure are the experimental results, while the bottom parts are the calculated ones. Qualitatively, all models predict a good representation of the isochromatic fringe patterns over the whole flow field. A ‘butterfly’ shaped region is seen just before the contraction, and the recirculation region has about the same shape and size as in the experiments. However, some mismatches, different for every model, between experiments and calculations can still be detected. The experimental size of the ‘butterfly’ is larger than seen in the calculations.

![Dimensionless velocities](image1)

(a) Cross-section velocities

![Velocities over centerline](image2)

(b) Centerline velocity

**Figure 4.3:** Calculated and measured velocity profiles in the planar contraction flow over four cross-sections (a) \((x/h = -6, -4, -1, 1)\), and over the centerline (b) \((y/h = 0)\) for \( Wi = 16.8, T = 170 ^\circ C \).
Also, over the centerline, all models predict one fringe less just before the contraction in comparison to the experiments. For the Giesekus and PTT models, the isochromatic fringes around the re-entrant corner have a more or less rounded shape. The XPP model shows a more flattened and oval shape of the fringes and the ‘butterfly’ is pushed to the top wall, similar to the experimental pattern.

A more quantitative comparison between experiments and predictions of the three models can be found in figure 4.5. For stresses along the centerline (figure 4.5(a)), excellent agreement is found up to \( x/h = -1 \) for the PTT model, after which the model underpredicts the experimental stresses. The Giesekus model is a bit behind the PTT model, but also has a slightly higher maximum stress. Besides a poor elongational description for these two models, end-effects of the front and back walls influence the deviation from downstream experimental results. On the one hand, small layers at the front and the back wall do not experience the elongational flow and, therefore, show a lower measured stress level. On the other hand, shear layers near the viewing windows introduce higher stress levels, which is maximum along the centerline. These shear layers become more pronounced because of the increase in velocity in the contraction region. The XPP model shows the worst agreement with experiments, but this is mainly due to not having reached steady state yet.

The line \( y/h = 1 \) intersects the butterfly patterns. Further away from the contraction, the experimental values are predicted excellently by the PTT and Giesekus models. However, closer to the contraction \( ( -1 \leq x/h \leq 0 ) \) the stresses are lower than the experiments. Here,
Chapter 4

Figure 4.5: Calculated and measured stresses in the planar contraction flow over the cross-sections \((y/h = 0)\) (a), \((y/h = 1)\) (b), \((x/h = 0)\) (c), and \((x/h = 4.8)\) (d) for the XPP, Giesekus, and PTT models at \(Wi = 16.8\), \(T = 170 \, ^\circ C\).

the XPP model follows best the experimental values. Since the deformation rates are higher near the walls, steady state values are also reached earlier in time. Therefore, the XPP model might have reached its steady state in that region. Just before the re-entrant corner, oscillations are present for all three models. On the one hand, this is a numerical aspect, as a geometrical singularity is approached, and could be avoided by a finer mesh, consequently increasing the CPU-time. On the other hand, this is a material aspect, initiated by higher elasticities as a consequence of the strain hardening effect.

Very close to the re-entrant corner, stresses are difficult to measure due to bright light intensities. The same problem occurs at the upper wall right after the contraction, as a thin stress layer is present here. In this area, no experimental stresses could be extracted, as can be noted close to \(x/h = 0\) in figure 4.5(b), close to \(y/h = -1\), 1 in figure 4.5(c), and close to \(y/h = -1\), 1 in figure 4.5(d).

For the stresses along the lines \(x/h = 0\) (figure 4.5(c)) and \(x/h = 4.8\) (figure 4.5(d)), similar agreement can be found as for \(y/h = 1\). Near the centerline, the Giesekus and PTT models are in better agreement with experiments than near the upper wall. While the XPP
model is doing better closer to the wall. Notice that the PTT model is predicting far lower stresses away from the centerline at \( x/h = 0 \) than the other two models. Furthermore, all models show a steep increase in stresses when approaching the corner. Obviously, further away from the contraction line at \( x/h = 4.8 \), in a region with less elongational deformation, agreement is better. The general three-dimensional deviation rules are followed for this prototype industrial flow: stresses are overpredicted near confining walls and underpredicted near the centerline.

If a material particle is followed along the centerline, the strain rate that it experiences in a Lagrangian sense is shown in figure 4.6(a). Notice that the particle experiences elongation only for a very short time, with a maximum of around \( \dot{\varepsilon} = 4.7 \, \text{s}^{-1} \), almost independently of the model. This means that the strain is rather small. The stresses that it can build up in that time interval are given in figure 4.6(b). The three bottom lines (which are nearly on top of each other) are equal to the lines shown in figure 4.5(a), but now as a function of Lagrangian time instead of position. For comparison, the three top lines are the stresses that would have been build up, if the maximum strain rate \( \dot{\varepsilon} = 4.7 \, \text{s}^{-1} \) is constantly experienced by the material. Here, the difference in elongational behaviour between the three models is shown very clearly again. Since the material flowing over the centerline only is extended for a very short time, and is not pre-oriented by shear, stresses can hardly build up. This region only experiences a minor excursion into the non-linear extensional regime. This makes the contraction flow a rather weak flow to test constitutive models.

The highest stresses, however, do not appear on the centerline, but near the re-entrant corner (which is experimentally not very well accessible). Material in that region has first been oriented by shear, followed by extension. The re-entrant corner is also the region where the highest effective strain rate occurs. This effective strain rate is defined as:

\[
\dot{\varepsilon}_{\text{eff}} = \frac{1}{2} \sqrt{2D : D},
\]

which equals \( \dot{\varepsilon} \) in pure elongational regions and \( \frac{1}{2} \dot{\gamma} \) in pure shear regions. In figure 4.7.
Table 4.2: Maximum values of the effective strain rate, Weissenberg number, fringe stress, and backbone stretch in the contraction flow geometry for the XPP, Giesekus and PTT models at \( Wi = 16.8, T = 170 \, ^\circ C \).

<table>
<thead>
<tr>
<th></th>
<th>XPP</th>
<th>Giesekus</th>
<th>exp. PTT</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Maximum</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>effective</td>
<td>( x/h = 0.018 )</td>
<td>( x/h = 0.018 )</td>
<td>( x/h = 0.018 )</td>
</tr>
<tr>
<td>strain rate</td>
<td>( y/h = 1 )</td>
<td>( y/h = 1 )</td>
<td>( y/h = 1 )</td>
</tr>
<tr>
<td>eqn. (4.28)</td>
<td>( \dot{\varepsilon}_{\text{eff,max}} = 48.33 , \text{s}^{-1} )</td>
<td>( \dot{\varepsilon}_{\text{eff,max}} = 38.84 , \text{s}^{-1} )</td>
<td>( \dot{\varepsilon}_{\text{eff,max}} = 36.62 , \text{s}^{-1} )</td>
</tr>
<tr>
<td><strong>Fringe stress</strong></td>
<td>( Wi = 221.89 )</td>
<td>( Wi = 178.33 )</td>
<td>( Wi = 168.14 )</td>
</tr>
<tr>
<td>eqn. (4.26)</td>
<td>( \tau_{\text{FRG,max}} = 4.53 \times 10^5 , \text{Pa} )</td>
<td>( \tau_{\text{FRG}} = 2.68 \times 10^5 , \text{Pa} )</td>
<td>( \tau_{\text{FRG}} = 1.86 \times 10^5 , \text{Pa} )</td>
</tr>
<tr>
<td><strong>Backbone</strong></td>
<td></td>
<td></td>
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<td>( \tau_{\text{FRG,max}} = 5.95 \times 10^5 , \text{Pa} )</td>
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<td>( \tau_{\text{FRG,max}} = 1.91 \times 10^5 , \text{Pa} )</td>
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<td>( \dot{\varepsilon}_{\text{eff}} = 29.73 , \text{s}^{-1} )</td>
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<td>eqn. (4.13)</td>
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<td>( \Lambda_{\text{max}} = 1.35 )</td>
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<td>( \dot{\varepsilon}_{\text{eff}} = 29.73 , \text{s}^{-1} )</td>
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<tr>
<td></td>
<td>( Wi = 221.89 )</td>
<td>( Wi = 151.76 )</td>
<td>( Wi = 136.51 )</td>
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<tr>
<td></td>
<td>( \tau_{\text{FRG,max}} = 4.53 \times 10^5 , \text{Pa} )</td>
<td>( \tau_{\text{FRG}} = 2.57 \times 10^5 , \text{Pa} )</td>
<td>( \tau_{\text{FRG}} = 1.91 \times 10^5 , \text{Pa} )</td>
</tr>
</tbody>
</table>
somewhat higher than for the other two models. This might be an indication why solutions for this model diverge after $t = 2.8 \text{s}$. Furthermore, notice that the highest stresses do not always coincide in location with the highest effective strain rate. The residence time of fluid elements and the type of deformation (extension or shear) are the key issues for stress to build up. This will become even more clear in the other two complex flow geometries.

### 4.5.2 Flow around a Cylinder

A schematic of the planar flow geometry is shown in figure 4.8(a). Experiments were performed at a temperature of $170 \degree \text{C}$, resulting in a viscosity averaged relaxation time for the material of $\bar{\lambda} = 1.7415 \text{s}$. The radius of the cylinder is $R = 1.1875 \text{mm}$, the channel height equals $H = 4.95 \text{mm}$, and the depth of the flow cell $d = 40 \text{mm}$. The depth-to-height ratio results in 8.08, creating a nominally two-dimensional flow. The height-to-diameter ratio equals 2.08. The characteristic mean two-dimensional velocity at the inflow is $\bar{u} = 1.975 \text{mm/s}$. As a characteristic length, the radius of the cylinder $R$ is chosen, giving the flow averaged Weissenberg number:

$$Wi = 2.9.$$  \hspace{1cm} (4.29)

The averaged Weissenberg number of the longest relaxation time is $Wi = 7.6$.

A detail of the FE mesh used for the calculations of all three models is given in figure 4.8(b). Only half of the geometry is meshed due to symmetry. The center of the cylinder is placed at $x/R = 0, y/R = 0$, while the inlet is at $x/R = -8$ and the outlet at $x/R = 15$. The periodic boundary for the inlet stresses is situated at $x/R = -5$. At the entrance and exit, a fully developed velocity profile is prescribed. No slip boundary conditions are imposed on the top confining wall and the cylinder, and the velocity in $y$-direction is suppressed for the symmetry line $y/R = 0$. The time step $\Delta t$ for the XPP, Giesekus, and PTT models were 0.001 [s], 0.002 [s], and 0.002 [s], respectively.

Figure 4.9 shows the normalized velocities profiles over five different cross-sections ($x/R = -4, -2.5, -1.5, 1.5, 2.5$) and the velocities over the centerline ($y/R = 0$). The measured data points show a slight asymmetry at cross-sections closest to the cylinder, indicating a minor displacement of the cylinder. In general, the predicted velocities are in excellent agreement with the measured data points for all three models. Over the centerline,
the XPP model underpredicts the measured velocity profile downstream of the cylinder, although the centerline exit velocity is predicted correctly. We suspect that viscous heating is of importance here, resulting in higher velocities due to a lower viscosity (see figure 8 in Peters and Baaijens (1997)). This is analyzed in more detail further on in this section. The PTT model shows the highest overshoot right after the cylinder, although this is difficult to see.

The measured and calculated isochromatic stress patterns for all three models are shown in figure 4.10. The XPP model shows an amazing resemblance, and all details are predicted correctly in this qualitative picture. Both the Giesekus and PTT models show a good agreement, except for the thin stress layer around the cylinder and in the wake of the cylinder. At this downstream centerline, the Giesekus and PTT models relax too fast and thus fringes do not extend far enough. The thin stress layer around the cylinder is a difficult region, both numerically and experimentally. On the numerical side, it causes divergence of the calculations for high Weissenberg numbers. In fact, for higher mean velocities, solutions of the XPP model, which is the most strain hardening, diverged and a finer mesh was necessary. The Giesekus and PTT models, on the other hand, could still reach a steady state solution with the same mesh. Experimentally, it is most difficult to count the fringes very close to the cylinder due to a small misalignment of the optical set-up (as was already indicated by the velocity profiles) or to beam deflections (see figures 7.76 to 7.78 in Schoonen (1998)). By using a laser in the optical set-up, fringe transitions are observable within 0.02 [mm] of the cylinder, which was not possible using a conventional mercury lamp as a light source.

Figure 4.11 shows a more quantitative comparison for the stresses over the centerline $y/R = 0$ and along the line $x/R = 0$. Notice, that it was impossible to count fringes up to the downstream stagnation point. Here, the fringes show vague transitions, probably accounted for by, again, temperature gradients due to viscous heating [Peters and Baaijens (1997), Schoonen (1998)]. Figure 4.11(a) indicates clearly, that the Giesekus and PTT models underpredict the stress upswing in this elongational area with at least 50%, both on the upstream and downstream centerline. The XPP model predicts accurately the fringes over the upstream centerline, but overpredicts the stresses downstream of the cylinder. The stress
Viscoelastic Analysis of Complex Polymer Melt Flows using the eXtended Pom-Pom model

Figure 4.10: Calculated and measured isochromatic fringe patterns of the planar flow around a cylinder for the XPP model (a), the Giesekus model (b) and the PTT model (c) at $Wi = 2.9$. $T = 170 \, ^\circ C$. 

(a) eXtended Pom-Pom model

(b) Giesekus model

(c) exponential PTT model
Figure 4.11: Calculated and measured stresses in the planar flow around a cylinder over the centerline \((y/R = 0)\) \((a)\) and over the cross-section \((x/R = 0)\) \((b)\) for the XPP, Giesekus, and PTT models at \(Wi = 2.9\). \(T = 170 \, ^{\circ}\)C.

relaxation a few diameters away from the rear stagnation point is correctly predicted again, contrary to the other two models. Again, this rises the suspicion of viscous heating.

Peters and Baaijens (1997) have investigated numerically the influence of viscous heating in a flow around a cylinder for a one-mode PTT model with typical polystyrene melt parameters. They found an increase in temperature at the back of the cylinder and in its wake. Due to this rise in temperature the viscosity decreased and thus higher velocities and lower stresses were predicted. Already at \(Wi = 4\) a reduction of the stress up to 40% and differences in downstream peak velocities of \(~8\%\) was found in their calculations. The temperature dependency of the viscosity of a polystyrene melt, however, is higher than for a long-chain branched melt. Therefore, the influence of viscous heating on the viscosity, velocity profile and stresses decreases for an LDPE melt. The Nahme-Griffith number \(Na\) is a dimensionless number to a priori estimate viscous heating. It is defined as:

\[
Na = \frac{U^2|\frac{\partial \eta}{\partial T}|}{k},
\]

with \(U\) a characteristic velocity, here the centerline exit velocity is chosen, \(|\frac{\partial \eta}{\partial T}|\) a characteristic temperature rise necessary to change the viscosity substantially (\(|\frac{\partial \eta}{\partial T}| = 0.025\eta\) for the LDPE melt, and \(|\frac{\partial \eta}{\partial T}| = 0.05\eta\) for the PS melt), and \(k\) the thermal conductivity \((k = 0.223 \, \text{W/m} \cdot \text{K} \) for the LDPE melt, and \(k = 0.167 \, \text{W/m} \cdot \text{K} \) for the PS melt). For the calculations in Peters and Baaijens (1997) the Nahme-Griffith number was estimated at \(Na = 3.8\), while for the conditions and material in this article it is \(Na = 0.07\). The large difference is mostly due to the difference in velocities, which is a factor 10 higher for the PS melt. These estimations contradict the idea of possible viscous heating.

However, the presence of temperature effects was experimentally clearly shown by Schoonen (1998). Another approximation for the error due to viscous heating may be given by estimating the temperature increase of a fluid particle flowing very close to the cylinder,
Viscoelastic Analysis of Complex Polymer Melt Flows using the eXtended Pom-Pom model

Figure 4.12: Calculated strain rates (a) and first normal stress differences (three bottom lines, b) in the planar flow around a cylinder over the downstream centerline ($y/R = 0, x/R \geq 1.01$) as a function of Lagrangian time for the XPP, Giesekus, and PTT models at $Wi = 2.9, T = 170 \, ^{\circ}$C.

by using (see e.g. Bird et al. (1987)):

$$\Delta T = \frac{2 \eta_0 (2u_{cl})}{k}, \quad (4.31)$$

with $u_{cl}$ the upstream centerline velocity. The factor 2 in the velocity term arises from the ratio $u \sim \frac{H}{2R}$, since we are interested in the temperature effects alongside the cylinder. This results in an estimated increase of the temperature for our flow of $\Delta T = 0.6 \, [K]$. Since the viscosity change is about 2.5%/K, a temperature increase of $\Delta T = 0.6 \, [K]$ would result in an approximated error of 1.5%.

Besides viscous heating and assuming that the stress optical rule still holds, also beam deflections and refractions in the experiments cause deviations between the calculations and experimental data. Especially in the wake of the cylinder, beam deflections are considerable (see section 7.9.2 in Schoonen (1998)). To come to strong conclusions about the experimental deviation from the ideal situation, more investigation on this part is needed. A full analysis of the light path through a polymer melt with refractive index gradients in an axisymmetric flow cell has been performed by Harrison et al. (2001). To our knowledge, this is the first example where all effects are taken into account.

Over the cross-section $x/R = 0$ (see figure 4.11(b)), a mainly shear dominated region, all three models are in good agreement with the experimental data, except for the XPP model near the wall of the cylinder ($y/R = 1$). The XPP model shows a peak which is due to a distorted fringe pattern at that exact spot (see figure 4.10(a)). The other two models do show such a distorted fringe pattern also, however not at position $x/R = 0$. Due to misalignment of the cylinder, it is impossible to detect if such a distorted patterns is also present in the experiments.

To see if fluid elements in this particular complex flow can reach their elongational planar steady state, a particle is followed along the downstream centerline starting just downstream the rear stagnation point at $x/R = 1.01$. Its strain rate as a function of the Lagrangian time for all three models is plotted in figure 4.12(a). The difference in time to travel over
Maximum values of the effective strain rate, Weissenberg number, fringe stress, and PTT (c) models at \( Wi = 2.9 \), \( T = 170 \) [°C].

The centerline is surprisingly large. Furthermore, the maximum strain rate imposed on the material differs somewhat. The consequences for these differences on the stresses are shown in figure 4.12(b). The bottom line for each model, showing a typical peak value, is the same as plotted in figure 4.11(a), however now as a function of time instead of position. The top line for the different models is the build-up in stress if a constant strain rate equal to the maximum strain rate from figure 4.12(a) is imposed on the material, thus being able to reach its steady state value. For all three models, the planar elongational steady state stress is just not reached. However, a far higher build-up in stress occurs over the centerline in comparison to the contraction flow. Since the residence time over the centerline for the PTT model is larger and the steady state values are lower, this model gets closer to its steady state.

**Table 4.3:** Maximum values of the effective strain rate, Weissenberg number, fringe stress, and backbone stretch in the planar flow around a cylinder for the XPP, Giesekus and PTT models at \( Wi = 2.9 \), \( T = 170 \) [°C], \( \lambda = 1.7415 \) [s].

<table>
<thead>
<tr>
<th></th>
<th>XPP</th>
<th>Giesekus</th>
<th>exp. PTT</th>
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<tr>
<td><strong>Maximum effective</strong></td>
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<tr>
<td>strain rate</td>
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<tr>
<td>( \dot{\varepsilon}_{\text{eff}} )</td>
<td>( x/R = 0.008 ) [s]</td>
<td>( x/R = 0.008 ) [s]</td>
<td>( x/R = 0.008 ) [s]</td>
</tr>
<tr>
<td>( W_{\text{i}} )</td>
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<td>( 67.06 ) [-]</td>
<td>( 67.34 ) [-]</td>
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<tr>
<td>( \lambda )</td>
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<td>( 1.13 ) [-]</td>
<td>( 1.13 ) [-]</td>
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<tr>
<td><strong>Maximum fringe</strong></td>
<td></td>
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<tr>
<td>stress</td>
<td>eqn. (4.26)</td>
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<tr>
<td>( \dot{\varepsilon}_{\text{frg}} )</td>
<td>( x/R = 1.54 ) [s]</td>
<td>( x/R = 0.008 ) [s]</td>
<td>( x/R = 0.008 ) [s]</td>
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<tr>
<td>( W_{\text{i}} )</td>
<td>( 8.59 ) [-]</td>
<td>( 67.06 ) [-]</td>
<td>( 67.34 ) [-]</td>
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<tr>
<td>( \lambda )</td>
<td>( 1.20 ) [-]</td>
<td>( 1.13 ) [-]</td>
<td>( 1.13 ) [-]</td>
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<tr>
<td><strong>Maximum backbone</strong></td>
<td></td>
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<td>stretch</td>
<td>eqn. (4.13)</td>
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<tr>
<td>( \dot{\varepsilon}_{\text{frg}} )</td>
<td>( x/R = 1.54 ) [s]</td>
<td>( x/R = 0.008 ) [s]</td>
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<td>( W_{\text{i}} )</td>
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<td>( \lambda_{\text{max}} )</td>
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A detail of the mesh and the locations where the highest effective strain rate, fringe stress and backbone stretch occur, are given in figure 4.13 and table 4.3. Again, the location of the highest effective strain rate (equation (4.28)), denoted with a star, is not necessarily the location of the highest fringe stress (equation (4.26)), indicated by a circle, or highest backbone stretch (equation (4.13)), denoted with a cross. For the high strain hardening XPP model, the highest stress is located at the downstream centerline, a purely elongational region, while the Giesekus and PTT model have their highest stress on the wall of the cylinder in a shear dominated region. Notice also, that the highest Weissenberg number for this particular complex flow is around $Wi = 70$, significantly higher than the flow averaged Weissenberg number.

We conclude, that the flow around a cylinder is also not very suitable to test constitutive models by comparing calculations with experiments. Mostly because the interesting area of non-linear planar elongation, i.e. the wake of the cylinder, is an experimentally difficult region with a lot of side effects. The rest of the inhomogeneous flow regions are still of great interest, because geometrical singularities are not present in this flow cell.

### 4.5.3 Cross-Slot Flow

The planar cross-slot flow is a complex flow geometry with an experimentally easily accessible stagnation point. Material flows in from two opposite sides, and flows out perpendicular to the inflow again at two opposite sides (figure 4.14(a)). Experiments were performed at a temperature of $T = 150 \, ^\circ C$. Using the given activation energy from table 4.1 and the temperature dependent Arrhenius function, linear parameters can be transformed to this temperature. This results in a viscosity averaged relaxation time for the material of $\bar{\lambda} = 3.4294 \, [s]$. Half the height of the channels is $h = 2.5 \, [mm]$ and the

![Figure 4.14](image-url)
depth is \( d = 40 \text{ [mm]} \), giving a depth-to-height ratio of 8. The corners are rounded with a radius of \( h/2 = 1.25 \text{ [mm]} \). The mean two-dimensional in- and outflow velocities are \( \bar{u} = 4.50 \text{ [mm/s]} \). If half the channel height is chosen as a characteristic length, the flow averaged Weissenberg number results:

\[
Wi = 6.2,
\]

while the averaged Weissenberg number for the longest relaxation time equals \( Wi = 16.3 \).

A detail of the FE mesh used for the calculations of all three models is given in figure 4.14(b). Only a quarter of the geometry is meshed due to symmetry. The stagnation point is the origin of the coordinate system. The inlet is placed at \( y/h = 10 \) and the outlet at \( x/h = 20 \). The periodic boundary for the inlet stresses is situated at \( y/h = 6 \). At the entrance and exit, a fully developed velocity profile is prescribed. No slip boundary conditions are imposed on the top confining wall, and the velocity in x- and y-direction is suppressed for the symmetry lines \( x/h = 0 \) and \( y/h = 0 \), respectively. The time step \( \Delta t \) is 0.002 [s] for the XPP, Giesekus, and PTT models.

Figure 4.15: Calculated and measured velocity profiles in the planar cross-slot flow over five cross-sections in y-direction (a) \( y/h = 3.2, 2.5, 2.0, 1.5, 0.5 \), over six cross-sections in x-direction (b) \( x/h = 0.6, 1.0, 1.4, 1.8, 2.4, 3.2 \), and over the symmetry lines (c) \( y/h = 0, x/h = 0 \) at \( Wi = 6.2, T = 150 \text{ [°C]} \).
Figure 4.15(a) shows the measured and calculated velocity profiles over several cross-sections of the inflow channel ($y/h = 3.2, 2.5, 2.0, 1.5, 0.5$). All three models show a perfect match with the measurements, with only a slight difference between the models at the cross-section closest to the stagnation point ($y/h = 0.5$). In the outflow channel, velocities at different cross-section ($x/h = 0.6, 1.0, 1.4, 1.8, 2.4, 3.2$) are measured also and compared to the calculations, as given in figure 4.15(b). Here, differences between the models are larger. Especially the PTT model overpredicts the velocity near the symmetry line, and underpredicts it near the confining wall, giving a worse agreement closer to the stagnation point. The XPP model is performing best, and the Giesekus model shows a good agreement also. The centerline velocities, in figure 4.15(c), show the same tendency: a large overprediction for the PTT model; a small overprediction for the Giesekus model; an excellent agreement for the XPP model. However, the maximum outflow velocity is predicted correctly by all three models.

The isochromatic light intensities for the experiments and three models are shown in figure 4.16. Again, the XPP model shows an excellent agreement with the experiments, except for the fully developed in- and outflow regions. Here, all models overpredict the stresses by almost one fringe. This is most probably due to shifting the linear parameters to a different temperature, resulting in an overprediction in shear, although the exact origin of the error could not be determined. In the outflow region over the centerline, both the Giesekus and PTT models underpredict the stress relaxation.

The centerline stress build-up and relaxation is quantitatively shown in figure 4.17. From this figure, it is more clear that all three models correctly describe the first part of the stress build-up. The maximum is underpredicted by the PTT and Giesekus models, and overpredicted by the XPP model. The stress relaxation of the Giesekus and PTT models is much too fast. The XPP model is excellently following the experimental data a little away from the stagnation point. The small and high peak as shown by the XPP model in the stagnation point, could not be observed experimentally due to the high stress gradient, which made it impossible to distinguish all individual fringes very close to the stagnation point. Furthermore, due to the high extension, possibly the stress optical rule fails in this region. If the overprediction of stresses in the fully developed in- and outflow ducts is corrected for, meaning a reduction of the stresses by approximately 20%, the fringe stress over the centerline is correctly predicted by the XPP model.

To see if planar extensional steady state is reached, a particle is tracked over the centerline, starting at $x/h = 1 \cdot 10^{-6}, y/h = 5$ and passing very closely the stagnation point at $x/h \approx 1 \cdot 10^{-3}, y/h \approx 1 \cdot 10^{-3}$. Figure 4.18(a) shows the velocity gradient of this fluid particle as a function of the Lagrangian time for all three models. The plateau in the curves corresponds to the stagnation region, where velocities are low, subsequently, residence time is long and an almost constant elongation rate is experienced by the material. Notice, that residence time in the stagnation region is lower with higher elongation rate. The PTT model predicts the highest elongation rate and the XPP model the lowest. The stresses that are build up during flow over the centerline as a function of time are plotted in figure 4.18(b). Again, the curves furthest to the right, correspond to the fluid elements flowing over the centerline and are equal to the curves in figure 4.17. The curves most left correspond to the stresses that are build up if the maximum strain rates of figure 4.18(a) are constantly imposed on the material. It is obvious from the figure, that in the stagnation region, stresses do reach their planar elongational steady state values. The XPP and Giesekus models even predict a higher peak stress, meaning that
Figure 4.16: Calculated and measured isochromatic fringe patterns of the planar cross-slot flow for the XPP model (a), the Giesekus model (b) and the PTT model (c) at \( Wi = 6.2 \).

\( T = 150 \, [\degree C] \).
the location of the highest strain rate does not necessarily have to be the location of the highest stress. From the last graph, we can conclude, that the cross-slot device can be used as a rheological tool and the planar elongational steady state values can be extracted from this complex flow. It is, however, more cumbersome to determine experimentally the strain rate that the particle experiences in the stagnation region. The strain rate could be determined by performing calculations, but it depends on the model that is used. From figure 4.15(c), an experimental strain rate can be estimated: \( \dot{\varepsilon}_{\text{exp}} = 2.0 \sim 2.1 \text{[s}^{-1}] \). The XPP, Giesekus and PTT models predict \( \dot{\varepsilon}_{\text{XPP}} = 2.2 \text{[s}^{-1}] \), \( \dot{\varepsilon}_{\text{Gsk}} = 2.3 \text{[s}^{-1}] \), and \( \dot{\varepsilon}_{\text{PTT}} = 2.7 \text{[s}^{-1}] \).

Figure 4.19 shows the locations of the highest effective strain rate (a star), the highest fringe stress (a circle), and the highest backbone stretch (a cross). The corresponding values are given in table 4.4. The differences between the models are rather large, especially for the kinematics, which was surprising. For example, the highest local Weissenberg number, is for the XPP model \( Wi = 71.25 \), while for the other two models it is around 60. Unexpectedly, the highest backbone stretch for the PTT model does not coincide with the location of the
highest fringe stress. As expected, the highest backbone stretch occurs in the stagnation point, the location of an infinite elongation strain and a purely extensional region. However, the highest stress for the PTT model is situated at the top confining wall in a shear dominated region. This means that the stresses that this PTT model can build up in shear are larger than for elongation, which is not in agreement with this high strain hardening LDPE material, but might be the case for a less strain hardening, for example HDPE, material.

Table 4.4: Maximum values of the effective strain rate, Weissenberg number, fringe stress, and backbone stretch in the planar cross-slot flow for the XPP, Giesekus and PTT models at $Wi = 6.2$, $T = 150^\circ$C, $\lambda = 3.4294$ [s].

<table>
<thead>
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<th>XPP</th>
<th>Giesekus</th>
<th>exp. PTT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum effective strain rate $\dot{\varepsilon}_{\text{eff, max}}$</td>
<td>$x/h = 1.37$ [s$^{-1}$]</td>
<td>$x/h = 1.37$ [s$^{-1}$]</td>
<td>$x/h = 1.40$ [s$^{-1}$]</td>
</tr>
<tr>
<td>$Wi$</td>
<td>$71.25$ [-]</td>
<td>$61.98$ [-]</td>
<td>$57.78$ [-]</td>
</tr>
<tr>
<td>$\tau_{\text{FRG,max}} = 1.00 \times 10^5$ [Pa]</td>
<td>$\tau_{\text{FRG,max}} = 1.52 \times 10^5$ [Pa]</td>
<td>$\tau_{\text{FRG,max}} = 8.44 \times 10^4$ [Pa]</td>
<td></td>
</tr>
<tr>
<td>$\Lambda$</td>
<td>$1.12$ [-]</td>
<td>$1.12$ [-]</td>
<td>$1.12$ [-]</td>
</tr>
<tr>
<td>Maximum fringe stress $\dot{\varepsilon}_{\text{frg, max}}$</td>
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<td>$x/h = 0$ [-]</td>
<td>$x/h = 1.40$ [-]</td>
</tr>
<tr>
<td>$Wi$</td>
<td>$19.95$ [-]</td>
<td>$20.90$ [-]</td>
<td>$57.78$ [-]</td>
</tr>
<tr>
<td>$\tau_{\text{FRG,max}} = 2.69 \times 10^5$ [Pa]</td>
<td>$\tau_{\text{FRG,max}} = 1.52 \times 10^5$ [Pa]</td>
<td>$\tau_{\text{FRG,max}} = 8.44 \times 10^4$ [Pa]</td>
<td></td>
</tr>
<tr>
<td>$\Lambda$</td>
<td>$1.39$ [-]</td>
<td>$1.23$ [-]</td>
<td>$1.12$ [-]</td>
</tr>
<tr>
<td>Maximum backbone stretch $\dot{\varepsilon}_{\text{frg, max}}$</td>
<td>$x/h = 0$ [-]</td>
<td>$x/h = 0$ [-]</td>
<td>$x/h = 0$ [-]</td>
</tr>
<tr>
<td>$Wi$</td>
<td>$19.95$ [-]</td>
<td>$20.90$ [-]</td>
<td>$24.49$ [-]</td>
</tr>
<tr>
<td>$\tau_{\text{FRG,max}} = 2.69 \times 10^5$ [Pa]</td>
<td>$\tau_{\text{FRG,max}} = 1.52 \times 10^5$ [Pa]</td>
<td>$\tau_{\text{FRG,max}} = 8.36 \times 10^4$ [Pa]</td>
<td></td>
</tr>
</tbody>
</table>
4.6 Discussion

The contraction flow can be identified as a flow with a minimum excursion into the non-linear elongational regime over the centerline. Therefore, all models investigated here show more or less the same behaviour in this flow and differences are rather minimal. The region with the highest backbone stretch and combination of shear and elongation, denoted by the effective strain rate, are close to the geometrical singular re-entrant corner. As a consequence, experimental stresses are difficult to determine due to high light intensities, and accuracy of the calculated solutions are lowest in that region because of oscillations. Although this particular prototype industrial flow is closely connected to real industrial applications, it is not very discriminating in identifying the differences between constitutive models. On the other hand, since it has some particular features, such as a thin stress layer at the lateral wall after the contraction and a recirculation zone just before the contraction, which differs with changing material behaviour, it is still a rather interesting geometry to investigate. Especially the re-entrant corner and resulting thin stress layer are responsible for numerical problems, such as divergence of the solution. These problems get worse with more strain hardening models and materials, as there are the UCM model (see Hagen and Renardy (1997)) and long-chain branched materials. Mesh refinement at the re-entrant corner and along the lateral wall after the contraction is necessary to reach a steady state solution at high Weissenberg numbers at, consequently, higher computational costs.

Differences between constitutive models are more easily seen in the flow around a cylinder and in the cross-slot device. Even for the kinematics, especially in extension dominated regions, rather large distinctions could be detected. Most previous studies concluded that the kinematic variables, such as velocities and strain or shear rates, are hardly influenced by the constitutive models. However, these quantities are the basis for build up in stresses: a small difference in strain rate may result in a large difference in stresses, mostly for significantly strain hardening materials. Vice versa, stresses will influence the velocities and velocity gradients within the flow, be it moderately, resulting again in differences for the stresses. It was surprising to see how the models differed in residence time and strain rate over the centerline for the flow around a cylinder. Together with their different rheological behaviour in elongation, that resulted in almost reaching the steady state values for the PTT model or being still quite far off for the XPP model. Therefore, one should take care in using the kinematic variables of a certain model to compute the stresses for another model, as is done in decoupled methods and streamline integration. Results may be very different from computations of a coupled method.

The flow around a cylinder encounters more severe experimental and numerical problems, however, than the cross-slot device. Around the cylinder thin stress layers with high stress gradients are present, causing a number of difficulties. Experimentally, it is hard to detect all fringes very close to the cylinder, since a small optical misalignment causes reflection of the light and distortion of the fringe pattern. Moreover, in the wake of the cylinder, heat transport is rather low and therefore this region is susceptible for viscous heating causing the fluid to be less viscous and resulting in higher velocities, lower stresses and optical distortions, which is not accounted for in the calculations. On the numerical side, thin stress layers with high stress gradients cause divergence of the numerical scheme and reach steady state solutions can not be reached. During calculations for a higher Weissenberg number as shown in this article, divergence for the XPP model occurred and a finer mesh was necessary to proceed in
time, but still a steady state solution could not be reached.

The cross-slot device is a rather friendly complex flow geometry. No severe experimental and numerical problems were encountered whatsoever. The three-dimensional effects on the measurements are small if a sufficiently large depth-to-height ratio is taken. These effects are more or less the same for the whole flow geometry, contrary to the contraction flow, where three-dimensional effects increase just before the contraction plane. All regions of the flow geometry are easily accessible for measurements, and no alignment problems or serious viscous heating are present. Only very close to the stagnation point, individual fringes can no longer be detected. Numerically, it is friendly also, as the thin stress layer in the stagnation point region does not cause divergence of the solution at the calculated flow rates. Another advantage of the cross-slot device, is that differences between elongational behaviour of constitutive models are detected immediately and a steady state elongational stress is easily reached in the stagnation point. Therefore, this complex flow geometry is rather useful to test the behaviour of constitutive models. In fact, it could be used as extra information to determine the non-linear material parameters along with other rheological measurements. Being a confined flow is a big advantage, since non strain hardening melts can also be tested. The latter being a huge problem in most standard elongational devices.

Although the XPP model is able to quantitatively describe the rheological behaviour of the LDPE melt, an exact quantitative description within the complex flows has not been fully accomplished. However, most particular features are better predicted by the XPP model than the Giesekus or PTT model. A number of reasons are responsible for the mismatches. First of all, the numerical model is fitted on the uniaxial rheological data only. These measurements are difficult to perform and accuracy can be rather low. Any mismatch would automatically occur in the complex flow calculations. The error is estimated at approximately 10%. Also, since only a four mode fit is used, the gaps in between the different modes are relatively large. Furthermore, the rheological data is plotted on logarithmic scales, while all complex flow data has been plotted on linear scales, enlarging mismatches. Second, shifting the linear parameters from one temperature to another gives an additional error to the computations. Third, measurements in the complex flow geometries contain errors due to, e.g. beam deflections (∼ 10%), misalignment (∼ 0 – 3%), and viscous heating (∼ 0 – 10%), resulting in a change of the stress optical rule because of its temperature dependence, still assuming it to hold. Also, three-dimensional effects (∼ 6%) are present in the experiments, but not accounted for in the two-dimensional calculations. These effects are reduced as much as possible by taking large enough depth to height ratios, however a complete elimination of these effects is impossible. The three-dimensional effects causes experimental results to be lower near the walls and higher in the middle of the flow over the centerline in comparison to two-dimensional calculations (see for example Schoonen et al. (1998), Bogaerds et al. (1999b)). And last, discretisation within FE methods gives a certain accuracy to the solutions, which decreases near singularities and high stress gradients, although these are suspected to be negligible with respect to the experimental accuracy.
4.7 Conclusions

The combination of the robust, stable and accurate DEVSS/DG method and the molecular based *eXtended Pom-Pom* model is presented for calculations in three different complex flow geometries and compared to experimental results and the numerical outcomes of the more conventional Giesekus and PTT models. The particular features that are experimentally seen in these complex flows, such as the shape of the 'butterfly' pattern, length of the stress tail after cylinder and stagnation point, due to the slow relaxation of the fringes in the downstream region, are qualitatively, and to a large extent quantitatively, predicted by the *eXtended Pom-Pom* model. A full quantitative prediction on all the details has still not been achieved and will be problematic due to the numerous numerical and experimental errors that are hard to quantify precisely.

The cumbersome experiments to measure uniaxial elongational viscosities are relatively inaccurate, while this rheological data on a logarithmic scale is the only data used for fitting the non-linear parameters. Furthermore, only four modes are used to fit the rheological curves and gaps between the modes will contribute to further inaccuracies. Both the contraction flow and flow around a cylinder have thin stress layers where experimental data is difficult to extract and is the main cause for divergence of numerical solutions. Other experimental problems are present, such as viscous heating, beam deflection, alignment of the geometry, a possible breakdown of the stress optical rule, etc. Although the geometries are designed to have near two-dimensionality, still three-dimensional effects are present in the experiments, and are significant over the centerline just before the contraction plane. Here, elongational stresses at the front and back wall diminish, but 'parasitic' shear stresses due to a higher velocity increase and consequently results in higher fringe stresses.

Although the contraction flow geometry is closely linked to industrial applications, for testing constitutive models, it is less interesting. Almost no excursion into the non-linear extensional regime is provoked over the centerline by this particular flow. On the other hand, the flow around a cylinder confined by two parallel plates and the cross-slot flow do impose high strains on the material and larger differences between the models can easily be detected, mostly in elongational dominated regions. Moreover, even for the kinematic quantities, *i.e.* velocities and velocity gradients, differences are relatively large. It is important to realize that decoupled computations, which use the kinematic field for one model to calculate the stresses for another model, may give completely different results compared to fully coupled calculations.

For the flow around a cylinder, it has been shown that elongational steady state values are just not reached. Furthermore, the more pronounced elongational region, in the wake of the cylinder, is not easily accessible for experimental data due to possible misalignment of the cylinder and susceptibility to viscous heating. Such experimentally difficult accessible regions are not present in the cross-slot device. Moreover, planar elongational steady state values are reached, which makes this flow device equipped for being a rheological apparatus, if the stress optical rule indeed applies. Values extracted from the stagnation region could be used together with rheological uniaxial elongational viscosities to determine the non-linear parameters more accurately.

Since the *eXtended Pom-Pom* model is molecular based, extra valuable information could be extracted from the computation of complex flow geometries that is not accessible experimentally. Amongst others, the theoretical macroscopic stretch and orientation of fluid
elements can be monitored both in time as well as position. This may give an extra insight and understanding of the behaviour of these polyethylene melts in industrial applications. It should be noted, however, that one should take some reservation in interpreting results from this, still largely phenomenological, constitutive model.
Chapter 5

Numerical analysis of the planar contraction flow for a polyethylene melt

The Discrete Elastic Viscous Stress Splitting technique in combination with the Discontinuous Galerkin (DEVSS/DG) method encounters divergence problems for a transient contraction flow problem depending on the constitutive model and its rheological behaviour, the mesh, and time step. Both the single-equation as well as the double-equation formulation of the eXtended Pom-Pom model (XPP) are investigated. The XPP model gives a quantitative description of a wide range of rheological experiments for polyethylene melts. Although fully equivalent, the two versions of the XPP model show different numerical behaviour. After a small change in the structure, as proposed by Van Meerveld [Submitted J. Non-Newtonian Fluid Mech. (2001)], the single-equation XPP version demonstrates improved convergence properties, not observed for the double-equation XPP implementation. With a specific mesh and time step, the high strain hardening modified single-equation XPP model can reach steady state results. For comparison, the Giesekus and PTT models are also investigated. For large time steps, calculations with both these models are converging. For smaller time steps, the Giesekus model shows divergence problems. The PTT model does not encounter any divergence, regardless of its high or low strain hardening behaviour or the chosen time step.

5.1 Introduction

In recent years, the performance of numerical methods for viscoelastic flow analysis has improved significantly. A review on mixed finite element methods for viscoelastic flow analysis is given in Baaijens (1998b). Furthermore, constitutive models have become available that are able to describe the behaviour of polyethylene melts over a wide range of rheological data, e.g. the MSF model by Rubio et al. (2001) and the Pom-Pom model [McLeish and Larson (1998), Inkson et al. (1999), Blackwell et al. (2000), Verbeeten et al. (2001a)]. Both a robust numerical method and a reliable constitutive model are crucial in predictive modelling of viscoelastic materials.

The robustness and efficiency of the Discrete Elastic Viscous Stress Splitting technique
A drawback of the method is that it is not unconditionally stable in transient calculations at high Weissenberg numbers, as shown by Bogaers et al. (1999a). They found a temporal instability in a simple couette flow for a single-mode Upper Convected Maxwell (UCM) model depending on the amount of elasticity. However, the DEVSS/DG method has proven to be very robust and accurate in non-smooth problems [Baaijens (1998a)]. This contrary to numerical techniques that apply the SUPG method for handling the convective terms in the constitutive equation.

As a constitutive model, the multi-mode eXtended Pom-Pom (XPP) model is capable of quantitatively describing the rheological behaviour of polyethylene melts over a full range of well-defined rheometric experiments [Verbeeten et al. (2001a)]. Good agreement is found for transient and steady state shear, including reversed flow, and different elongational flows with this model. More conventional models, such as the Giesekus and Phan-Thien Tanner (PTT) models, are unable to correctly describe the non-linear behaviour in both shear and elongational simultaneously.

In a recent study, Verbeeten et al. (2001b) performed calculations for a commercial grade low density polyethylene melt flowing through three benchmark complex flow geometries using the XPP model and the DEVSS/DG method. They encountered convergence difficulties for the contraction flow and the confined flow around a cylinder. Unphysical negative backbone stretch values occurred near the re-entrant corner of the contraction, i.e. a geometrical singularity, and at the front and back stagnation points in the flow around a cylinder. Both complex flow problems are known to have a thin shear stress boundary layer, situated around the cylinder and along the top wall after the re-entrant corner, respectively. Thus, as suggested, the mesh used in their study may not have been sufficiently fine to capture the steep stress gradients in these thin stress layers.

Motivated by the results of Verbeeten et al. (2001b), we will investigate the divergence problem for the contraction flow. It is, however, difficult to demonstrate if a temporal or physical instability is the cause of divergence, since no analytical solution is at hand. First, the divergence problem will be tackled by using standard solutions: mesh refinement, time step reduction, addition of solvent viscosity, and rounding off the re-entrant corner to eliminate the geometrical singularity. The conventional Giesekus and PTT model and both the single-equation formulation as well as the double-equation version of the eXtended Pom-Pom model will be investigated. Although fully equivalent, the two XPP versions show different numerical behaviour.

The structure of the XPP model will be examined and compared to the Giesekus and PTT models. Van Meerveld (2001) looked at the integral Pom-Pom model from a GENERIC point of view. He proposed a small change in the evolution equation for the backbone stretch. This alternative formulation is adapted also in this study to see if a better performance can be achieved.

In section 5.2, the problem definition and the constitutive equations are outlined. The computational method is shortly described in section 5.3 and can be found in more detail in Bogaers et al. (1999b). The material characterisation and the performance of the three constitutive models in simple rheological flows is given in section 5.4. Section 5.5 describes the numerical investigation, the parameter influence and the change in the structure towards the divergence problem. The conclusion and a discussion on this matter is given in section 5.6.
Depending on the used model, its structure, and its strain hardening behaviour, calculations with the DEVSS/DG method can reach the steady state solution. The newly proposed adaptation [Van Meerveld (2001)] results in better convergence for the single-equation XPP model, while no improvement is seen for the double-equation formulation.

### 5.2 Problem definition

Isothermal and incompressible fluid flows, neglecting inertia, are described by the equations for conservation of momentum (5.1) and mass (5.2):

$$\nabla \cdot \sigma = 0, \quad (5.1)$$

$$\nabla \cdot \vec{u} = 0, \quad (5.2)$$

with $\nabla$ the gradient operator, $\sigma$ the Cauchy stress tensor and $\vec{u}$ the velocity field. The Cauchy stress tensor $\sigma$ is defined for polymer melts by:

$$\sigma = -pI + 2\eta_s D + \sum_{i=1}^{M} \tau_i. \quad (5.3)$$

Here, $p$ is the pressure, $I$ the unit tensor, $\eta_s$ denotes the viscosity of the purely viscous (or solvent) contribution, $D = \frac{1}{2}(L + LT)$ the rate of deformation tensor, in which $L = (\nabla \vec{u})^T$ is the velocity gradient tensor and $(\cdot)^T$ denotes the transpose of a tensor. The visco-elastic contribution of the $i^{th}$ relaxation mode is denoted by $\tau_i$ and $M$ is the total number of different modes. The multi-mode approach is necessary for most polymeric fluids to give a realistic description of stresses over a broad range of deformation rates. The visco-elastic contribution $\tau_i$ still has to be defined by a constitutive model.

#### 5.2.1 Constitutive models

Within the scope of this work, a sufficiently general expression for the extra stress tensor of the $i^{th}$ relaxation mode is given by:

$$\nabla \tau_i + B_i \cdot \tau_i + \tau_i \cdot B_i^T + G_i(B_i + B_i^T) = 2G_i(1 - \xi_i)D, \quad (5.4)$$

with $B_i$ the averaged, macroscopic slip tensor, $G_i$ the plateau modulus, and $\xi_i$ a slip parameter that, if non-zero, accounts for the Gordon-Schowalter derivative. The upper convected time derivative of the extra stress $\tau_i$ is defined as:

$$\nabla \tau_i = \frac{\partial \tau_i}{\partial t} + \vec{u} \cdot \nabla \tau_i - L \cdot \tau_i - \tau_i \cdot L^T, \quad (5.5)$$

with $t$ denoting time. The slip tensor $B_i$ depends upon the chosen constitutive equation. For the Giesekus model, $\xi_i = 0$ and the tensor $B_i$ is defined as:

$$B_i = \frac{\alpha_i}{2G_i \lambda_i} \sigma_i + \frac{(1 - 2\alpha_i)}{2\lambda_i} I - \frac{G_i(1 - \alpha_i)}{2\lambda_i} \sigma_i^{-1}. \quad (5.6)$$
with \( \alpha_i \) an adjustable parameter, \( \lambda_i \) the \( i \)th linear relaxation time, and \( \sigma_i \) is defined as \( \sigma_i = \tau_i + G_iI \). Both the plateau modulus \( G_i \) and the relaxation time \( \lambda_i \) are obtained from the linear relaxation spectrum determined by dynamic measurements, while \( \alpha_i \) controls the anisotropic drag. Notice that for \( \alpha_i = 0 \), the Upper Convected Maxwell (UCM) model is retrieved.

For the exponential PTT model, \( \mathbf{B}_i \) is defined as:

\[
\mathbf{B}_i = -\xi e^{\frac{\epsilon_i(\tau_i)}{\lambda_i}} \mathbf{D} + \frac{\partial e^{\epsilon_i(\tau_i)}}{2\lambda_i} \mathbf{I} - G_i \frac{\partial e^{\epsilon_i(\tau_i)}}{2\lambda_i} \sigma_i^{-1} .
\]

(5.7)

with \( \xi \) an adjustable parameter, controlling the amount of strain softening.

The eXtended Pom-Pom (XPP) model [Verbeeten et al. (2001a)] is a modification of the differential version of the original Pom-Pom model by McLeish and Larson (1998) incorporating branch-point withdrawal as introduced by Blackwell et al. (2000). The basic idea of this model is that the rheological properties of entangled polymer melts depend on the topological structure of the polymer molecules. The simplified topology consists of a backbone tube with a number of dangling arms at both ends and is called a pom-pom molecule. A key feature is the separation of relaxation times for the stretch and orientation. For the Pom-Pom model, the extra stress tensor is expressed as:

\[
\mathbf{\tau}_i = \sigma_i - G_i \mathbf{I} = 3G_i \lambda_i^2 \mathbf{S}_i - G_i \mathbf{I} ,
\]

(5.8)

with \( \lambda_i \) the backbone tube stretch, defined as the length of the backbone tube divided by the length at equilibrium, and \( \mathbf{S}_i \) denoting the orientation tensor. The evolution equations for the orientation tensor \( \mathbf{S}_i \) and backbone tube stretch \( \lambda_i \) are given by:

\[
\nabla^\tau \mathbf{S}_i + 2[(1 - \xi_i)D : \mathbf{S}_i]\mathbf{S}_i + \mathbf{B}_i : \mathbf{S}_i + \mathbf{S}_i \cdot \mathbf{B}_i^T - 2[\mathbf{B}_i : \mathbf{S}_i]\mathbf{S}_i = 0 ,
\]

(5.9)

\[
\dot{\mathbf{\lambda}}_i = \Lambda_i[(1 - \xi_i)D : \mathbf{S}_i] - \Lambda_i[\mathbf{B}_i : \mathbf{S}_i] .
\]

(5.10)

In case of the XPP model, the slip parameter \( \xi_i = 0 \), and the slip tensor \( \mathbf{B}_i \) is given by:

\[
\mathbf{B}_i = \frac{\alpha_i}{2G_i \lambda_{bi}} \sigma_i + \left[ \frac{1 - \alpha_i - 3\alpha_i \lambda_i^4 \text{tr}(\mathbf{S}_i \cdot \mathbf{S}_i)}{2\lambda_{bi} \lambda_i^4} \right] + \frac{r_i e^{\nu_i(1 - 1)}}{\lambda_{bi}^2} \left( \frac{1}{\lambda_i} \right) \mathbf{I} - \frac{G_i(1 - \alpha_i)}{2\lambda_{bi}} \sigma_i^{-1} .
\]

(5.11)

Here, \( \lambda_{bi} \) is the relaxation time of the backbone tube orientation equal to the linear relaxation time \( \lambda_i \), while \( r_i = \frac{\lambda_{bi}}{\lambda_{bi}^2} \) is the ratio between the orientation relaxation time and the stretch relaxation time \( \lambda_{bi} \), and \( \nu_i = \frac{2}{\lambda_i} \) is a parameter denoting the influence of the surrounding polymer chains on the backbone tube stretch with \( q_i \) the amount of arms at the end of a backbone.

Due to its different structure from most differential constitutive equations and non-zero initial conditions, it may be cumbersome to implement the above double-equation formulation in FE packages. However, the XPP model can also be written in a fully equivalent single-equation fashion by substituting the slip tensor of equation (5.11) into equation (5.5).
Values for the backbone stretch are then calculated from equation (5.8):

\[ \Lambda_i = \sqrt{1 + \frac{\text{tr}(\tau_i)}{3G_i}} \]  

(5.12)

Notice, that for this definition of the backbone stretch, we may run into numerical problems if \( \frac{\text{tr}(\tau_i)}{3G_i} < -1 \), by which the square root in equation (5.12) becomes imaginary. Physically, \( \text{tr}(\tau_i) \) is always 0 or positive. However, numerically we have encountered these unrealistic values near the re-entrant corner in a contraction flow and at the front and back stagnation points in a flow around a cylinder for high enough flow rates, both for the XPP model as well as the Giesekus and PTT models.

Similar to the XPP model, both the Giesekus and PTT models can be split up in an orientation and stretch equation. Substitution of equation (5.6) (for the Giesekus model) or equation (5.7) (for the PTT model) into the equations (5.9) and (5.10) result in the evolution equations for the backbone orientation and backbone stretch.

### 5.3 Computational method

Due to its efficient handling of multiple relaxation modes and robustness near geometrical singularities, the DEVSS/DG method, Baaijens et al. (1997), is applied. It is a combination of the Discrete Elastic Viscous Stress Splitting (DEVSS) technique of Guénée and Fortin (1995) and the Discontinuous Galerkin (DG) method, developed by Lesaint and Raviart (1974). Application to the double-equation XPP model is discussed in this section. The weak formulation and solution strategy for the Giesekus and PTT models is similar and can be found in more detail in Bogaerds et al. (1999b) and Baaijens et al. (1997).

#### 5.3.1 DEVSS/DG method

Consider the problem described by the equations (5.1), (5.2), and (5.9), (5.10) and (5.11). Following common FE techniques, these equations are converted into a mixed weak formulation:

**Problem DEVSS/DG:** Find \((\vec{u}, p, \bar{D}, S_i, \Lambda_i)\) for any time \(t\) such that for all admissible test functions \((\vec{v}, q, E, s_i, l_i)\),

\[
\left( D_v, 2\eta_s D + 2\eta\left(D - \bar{D}\right) + \sum_{i=1}^{M} G_i (3\Lambda_i^2 S_i - I) \right) - \left( \nabla \cdot \vec{v}, p \right) = 0, 
\]

(5.13)

\[
(\vec{q}, \nabla \cdot \vec{u}) = 0, 
\]

(5.14)

\[
\left( E, D - \bar{D} \right) = 0, 
\]

(5.15)
\[
(\mathbf{S}_i, \mathbf{S}_i + 2[D : \mathbf{S}_i] \mathbf{S}_i + \frac{1}{\lambda_{b,i} \Lambda_i^4} \left[3 \alpha_i \Lambda_i^4 \mathbf{S}_i \cdot \mathbf{S}_i + (1 - \alpha_i - 3 \alpha_i \Lambda_i^4 \text{tr}(\mathbf{S}_i \cdot \mathbf{S}_i) \mathbf{S}_i - \frac{(1 - \alpha_i)}{3} \mathbf{I}\right] - \sum_{e=1}^{K} \int_{\Gamma^e_{in}} s_i : \bar{\mathbf{n}} \cdot \mathbf{n} (\mathbf{S}_i - \mathbf{S}_i^{\text{ext}}) \, d\Gamma = 0 \quad \forall i \in \{1, 2, \ldots, M\}. \tag{5.16}
\]

\[
(l_i, \Lambda_i - \bar{\Lambda}_i [D : \mathbf{S}_i] + \frac{r_{e} e^{\nu(\Lambda_i - 1)}}{\lambda_{b,i}} (\Lambda_i - 1)) - \sum_{e=1}^{K} \int_{\Gamma^e_{in}} l_i \bar{\mathbf{n}} \cdot \mathbf{n} (\Lambda_i - \Lambda_i^{\text{ext}}) \, d\Gamma = 0 \quad \forall i \in \{1, 2, \ldots, M\}. \tag{5.17}
\]

Here, \((\cdot, \cdot)\) denotes the \(L_2\)-inner product on the domain \(\Omega\), \(D = \frac{1}{2} (\nabla \bar{v} + (\nabla \bar{v})^T)\), \(\bar{n}\) an auxiliary viscosity, \(\Gamma^e_{in}\) is the inflow boundary of element \(\Omega^e\), \(\bar{n}\) the unit vector pointing outward normal on the boundary of the element \((\Omega^e)\) and \(\mathbf{S}_i^{\text{ext}}\) and \(\Lambda_i^{\text{ext}}\) denote the orientation tensor and backbone stretch of the neighboring, upwinding element.

Time discretisation of the constitutive equation is attained using an implicit Euler scheme, with the exception of the external components \(\mathbf{S}_i^{\text{ext}}\) and \(\Lambda_i^{\text{ext}}\) which are taken explicitly (i.e. \(\mathbf{S}_i^{\text{ext}} = \mathbf{S}_i^{\text{ext}}(t_n)\) and \(\Lambda_i^{\text{ext}} = \Lambda_i^{\text{ext}}(t_n)\)).

### 5.3.2 Solution strategy

A two-dimensional flow domain is divided into quadrilateral elements as a spatial discretisation. The interpolation of the velocity field \(\bar{\mathbf{u}}\) is bi-quadratic, the pressure \(p\) and discrete rate of deformation fields \(D\) are interpolated bi-linearly, while the orientation tensor \(\mathbf{S}_i\) and backbone stretch \(\Lambda_i\) fields have a discontinuous bi-linear interpolation. The equations (5.13) to (5.17) are integrated over elements using a \(3 \times 3\)-Gauss quadrature rule.

The non-linear equations are solved using a one step Newton-Raphson iteration. Within the linearized set of equations, the extra stress related variables \(\mathbf{S}_i\) and \(\Lambda_i\) form a block diagonal structure due to the fact that the components in the upwinding elements are taken explicitly. This enables elimination of the extra stress variables at element level. A further reduction of the system matrix is obtained by a decoupling approach. First, the ‘Stokes’ problem \((\bar{\mathbf{u}}, p)\) is solved, after which the updated solution is used to find a new approximation for \(\mathbf{D}\). Notice, that this introduces an small extra inconsistency for the stabilization term \(2\eta(D - \mathbf{D})\) in the momentum equation (5.13), since \(\mathbf{D}\) is taken at time \(t_{n+1}\), while \(\mathbf{D}\) is taken at time \(t_n\). Finally, the nodal increments of the orientation tensor and backbone stretch are retrieved element by element.

To solve the non-symmetrical system of the ‘Stokes’ problem \((\bar{\mathbf{u}}, p)\) an iterative solver is used based on the Bi-CGSTAB method of Van der Vorst (1992). The symmetrical set of algebraic equations of problem \((\mathbf{D})\) is solved using a Conjugate-Gradient solver. Incomplete LU preconditioning is applied to both solvers. In order to enhance the computational efficiency of the Bi-CGSTAB solver, static condensation of the center-node velocity variables results in filling of the zero block diagonal matrix in the ‘Stokes’ problem and, in addition,
achieves a further reduction of global degrees of freedom. The above decoupling procedure enables the use of iterative solvers. The use of the Bi-CGSTAB solver in combination with the incomplete LU preconditioning on the problem \((\vec{u}, p, D)\) was unsuccessful.

To solve the above sets of algebraic equations, both essential and natural boundary conditions must be imposed on the boundaries of the flow channels. At the entrance of the flow channels the velocity profiles are prescribed. At the exit, either the velocity profile is prescribed together with a pressure point that is set to zero, or the velocities perpendicular to the outflow directions are suppressed. At the entrance, the values of the orientation tensor and backbone stretch of a few elements downstream the inflow channel are prescribed along the inflow boundary, imposing a periodic boundary condition for these stress variables.

### 5.4 Material Characterisation

Since a multi-mode approach is necessary for a realistic description of polymer melts, we want to investigate convergence difficulties for multi-mode calculations. Parameters are identified for a commercial grade polymer melt, a low density polyethylene (DSM, Stamylan LD 2008 XC43), further referred to as LDPE. This long-chain branched material has been extensively characterised by Schoonen (1998) and is also given in Peters et al. (1999).

The parameters for a four mode Maxwell model are obtained from dynamic measurements at a temperature of \(T = 170 \, ^\circ\text{C}\). The non-linear parameters \(q_i\) and the ratio \(\frac{\lambda_i}{\nu_i}\) for the XPP model are determined using the transient uniaxial elongational data [Zoetelief and Palmen (2000)] only. Since second planar elongational or second normal stress difference data is not available for this material, the anisotropy parameter \(\alpha_i\) in this model is chosen as \(\frac{\lambda_b,i}{\lambda_s,i}\), similar to Verbeeten et al. (2001b). Both the Giesekus and PTT models are incapable of predicting the shear and elongational data simultaneously. Therefore, their non-linear parameters \((\alpha_i, \epsilon_i, \xi_i)\) are fitted on the steady shear data. Because the non-linear parameters are more sensitive in elongation than in shear, it is tried to prescribe as good as possible the uniaxial elongational data. All parameters are given in table 5.1.

Figure 5.1 shows the rheological behaviour of the three constitutive models and measured

| Table 5.1: Linear and non-linear parameters for fitting of the DSM Stamylan LD 2008 XC43 LDPE melt. \(T = 170 \, ^\circ\text{C}\), \(\nu_i = 2/q_i\). Activation energy: \(E_0 = 48.2 \, \text{kJ/mol}\). WLF-shift parameters: \(C_1 = 14.3, C_2 = 480.8 \, \text{K}\). |
| --- | --- | --- | --- | --- |
| \(i\) | \(G_i \, [\text{Pa}]\) | \(\lambda_i \, [\text{s}]\) | \(q_i\) | \(\frac{\lambda_i}{\nu_i}\) | \(\alpha_i\) | \(\epsilon_i\) | \(\xi_i\) |
| 1 | 7.2006-10^4 | 3.8946-10^{-3} | 1 | 7.0 | 0.30 | 0.30 | 0.15 | 0.08 |
| 2 | 1.5770-10^4 | 5.1390-10^{-2} | 1 | 5.0 | 0.30 | 0.30 | 0.14 | 0.07 |
| 3 | 3.3340-10^3 | 5.0349-10^{-1} | 2 | 3.0 | 0.15 | 0.25 | 0.12 | 0.06 |
| 4 | 3.0080-10^2 | 4.5911-10^0 | 10 | 1.1 | 0.03 | 0.15 | 0.10 | 0.05 |
Figure 5.1: Transient (a) and quasi-steady state (b) uniaxial viscosity $\eta_u$, transient (c) and steady state (d) shear viscosity $\eta_s$, and transient (e) and steady state (f) first normal stress coefficient $\Psi_1$ at $T = 170 \, ^\circ\text{C}$ of the XPP, Giesekus and PTT models for DSM Stamylan LD2008 XC43 LDPE melt.

Data in uniaxial and simple shear behaviour. The 'steady state' data points in the uniaxial elongational viscosity plot are the end points of the transient curves. Since the samples break at the end of the transient measurements, it is hard to say if steady state has truly been reached. However, sometimes it is claimed that steady state coincides with break-up of the samples.
Numerical analysis of the planar contraction flow for a polyethylene melt

The XPP model is the only model that can satisfactorily predict the uniaxial behaviour both in a transient and quasi-steady state sense. The Giesekus and PTT models are unable to predict the strong strain hardening effect of this material without showing large discrepancies in simple shear. As expected, the Giesekus model predicts the wrong shape of the steady state curve, as it ends in a plateau for high strain rates. Low density polyethylene melts are in general elongational thinning in a steady state sense at high strain rates (see for example data from Münstedt and Laun (1979), Hachmann (1996)). In the steady state curve of the PTT model, the different modes can be recognized due to the excessive elongational thinning behaviour of the model at high strain rates.

For simple shear, all models show a rather good agreement with the measured data (figure 5.1(c)). For intermediate shear rates, the Giesekus and PTT model are somewhat overpredicting the measurements. However, at higher shear rates, these models are in better agreement with the data than the XPP model, which is underpredicting the measurements. At shear rates over $10^2 \text{s}^{-1}$, the curves for all models drop rapidly (see figure 5.1(d)), as it is outside the range of the relaxation spectrum. For the contraction flow problem, maximum shear and strain rates of $\dot{\gamma}_{\text{max}} \approx 50 \text{s}^{-1}$ and $\dot{\varepsilon}_{\text{max}} \approx 40 \text{s}^{-1}$ were observed around the re-entrant corner. Thus, calculations all fall within the range of the chosen relaxation spectrum.

The start-up of the first normal stress difference reflects the different modes for the XPP model (see figure 5.1(e)). This can be avoided by choosing more relaxation times. That would also result in a smoother curve for the steady state uniaxial viscosity predicted by the PTT model. However, for this model it would not improve the prediction of the elongational data. Furthermore, as computational time increases significantly with every mode added, four Maxwell modes is considered as a satisfying optimum between a good description of the rheological behaviour and computational cost.

In general, the XPP model shows the best overall agreement with experimental rheological data.

### 5.5 Convergence characteristics

The convergence (or divergence) characteristics of the DEVSS/DG method in combination with the XPP model are investigated. Motivated by the divergence problems encountered by Verbeeten et al. (2001b), the flow through a planar contraction flow is examined. For a particular mesh and time step, they observed divergence of the calculations when using the XPP model. As a result, no steady state values could be reached, while this was not a problem for the Giesekus and PTT models. Both numerical and constitutive modelling issues are examined.

A schematic of the flow and its characteristics are given in figure 5.2. To characterize the shear strength of the flow, a dimensionless Weissenberg number is defined:

$$Wi = \frac{\bar{\lambda}u_{\text{2D}}}{h} = 16.8.$$ (5.18)

Here, $\bar{\lambda}$ denotes the viscosity averaged relaxation time for the material ($\bar{\lambda} = (\sum_{i=1}^{M} \lambda_{i} G_{i})/(\sum_{i=1}^{M} \lambda_{i})$), $u_{\text{2D}}$ is the mean downstream velocity and $h$ half the downstream channel height. The Weissenberg number is calculated using the characteristic
values given in figure 5.2. The maximum averaged Weissenberg number of the flow, using the longest relaxation time, is:

\[ W_i_{\text{max}} = \frac{\lambda_{\text{max}}}{\bar{u}_2D} = 44.3, \] (5.19)

and may even be higher locally.

5.5.1 Numerical solutions

To see if the divergence of the calculations could be avoided, standard procedures are followed such as mesh refinement, time step reduction, addition of solvent viscosity and rounding off the corner.

First, meshes with a sharp corner are investigated such that a singularity is present. Three meshes as depicted in figure 5.3 are used having mesh characteristics given in table 5.2. The contraction is placed at \(x/h = 0\), while the inlet is at \(x/h = -20\) and the outlet at \(x/h = 30\). The periodic boundary for the inlet stresses is situated at \(x/h = -10\). At the entrance and exit, a fully developed velocity profile is prescribed. No slip boundary conditions are imposed on the top confining wall, and the velocity in y-direction is suppressed for the symmetry line \(y/h = 0\).

Mesh M1 is the same mesh as used in Verbeeten et al. (2001b). Calculations with the Giesekus and PTT models using this mesh and a time step of \(\Delta t = 0.1\) s produced convergent results. Since only a single Newton-Raphson iteration is performed for every time step, the calculations are not really transient. However, for comparison with experiments, we were

| Table 5.2: Mesh characteristics of the planar contraction flow. |
|----------------------|----------------|----------------|
| #elements            | Mesh M1 | Mesh M2 | Mesh M3 |
| #nodes               | 4161    | 5189    | 8041    |
| #DOF(\(\vec{u}, p\)) | 7403    | 9235    | 14253   |
| #DOF(D)              | 3243    | 4047    | 6213    |
| #DOF(S, \(\Lambda\))=4\times#elements\times20 | 80000  | 99680   | 156000  |
mostly interested in the steady state solutions.

For the single-equation eXtended Pom-Pom formulation (sXPP), calculations using $\Delta t = 0.1 \text{s}$ diverged almost immediately. For a time step of $\Delta t = 0.002 \text{s}$, imaginary backbone stretch values occurred ($\frac{\text{d} \Lambda_i}{\text{d} t} < -1$) at the re-entrant corner for $t = 0.368 \text{s}$, resulting in a complex system matrix and the calculations to stop. The FE code was adjusted for the sXPP version, forcing the backbone stretch values to be positive ($\Lambda_i \geq 0$) at critical points. However, since this is possibly inconsistent with neighbouring nodes, the double-equation formulation of the eXtended Pom-Pom model (dXPP) was implemented. The latter formulation computes the backbone stretch values directly from the stretch evolution equation (5.10), allowing negative values and still being consistent. Both the orientation tensor $O(1)$ and the backbone stretch values $O(10)$ remain the same order in magnitude independent of the chosen parameters. This in contrast to the sXPP version and the Giesekus and PTT models.

These adjustments only delayed the onset of divergence. The best result was obtained using the dXPP version, which started diverging after $t = 2.8 \text{s}$. No steady state was reached, as the longest relaxation time $\lambda_{\text{max}} = 4.5911 \text{s}$ is almost twice as large. In case of the dXPP version, negative backbone stretch values were only encountered just before the onset of divergence. For both the sXPP version as well as the Giesekus and PTT models, $\frac{\text{d} \Lambda_i}{\text{d} t} < -1$ occurred when calculations were still converging. Furthermore, we would like to remark that whenever the backbone stretch values become negative or $\frac{\text{d} \Lambda_i}{\text{d} t} < -1$, the material is no longer incompressible at that exact location ($\text{tr}(D) \neq 0$), which is usually at the re-entrant corner.

Figure 5.3: Detail of FE meshes of half the planar contraction flow.
Table 5.3: Characteristics of calculations for the planar contraction flow.

<table>
<thead>
<tr>
<th>Model</th>
<th>Mesh</th>
<th>$\Delta t$</th>
<th>Convergence</th>
<th>$t_{\text{end}}$</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Giesekus</td>
<td>M1</td>
<td>0.1 s</td>
<td>+</td>
<td>30.8 s</td>
<td></td>
</tr>
<tr>
<td>Giesekus</td>
<td>M1</td>
<td>0.002 s</td>
<td>-</td>
<td>2.742 s</td>
<td></td>
</tr>
<tr>
<td>Giesekus</td>
<td>M1</td>
<td>0.001 s</td>
<td>-</td>
<td>2.675 s</td>
<td></td>
</tr>
<tr>
<td>PTT</td>
<td>M1</td>
<td>0.1 s</td>
<td>+</td>
<td>10.8 s</td>
<td></td>
</tr>
<tr>
<td>PTT</td>
<td>M1</td>
<td>0.002 s</td>
<td>+</td>
<td>8.800 s</td>
<td></td>
</tr>
<tr>
<td>sXPP</td>
<td>M1</td>
<td>0.002 s</td>
<td>-</td>
<td>0.368 s</td>
<td></td>
</tr>
<tr>
<td>sXPP</td>
<td>M1</td>
<td>0.002 s</td>
<td>-</td>
<td>1.718 s</td>
<td>$\Lambda_i &gt; 0$</td>
</tr>
<tr>
<td>dXPP</td>
<td>M1</td>
<td>0.002 s</td>
<td>-</td>
<td>1.758 s</td>
<td></td>
</tr>
<tr>
<td>dXPP</td>
<td>M1</td>
<td>0.001 s</td>
<td>-</td>
<td>2.813 s</td>
<td></td>
</tr>
<tr>
<td>dXPP</td>
<td>M2</td>
<td>0.001 s</td>
<td>-</td>
<td>2.821 s</td>
<td></td>
</tr>
<tr>
<td>dXPP</td>
<td>M3</td>
<td>0.002 s</td>
<td>-</td>
<td>1.446 s</td>
<td></td>
</tr>
<tr>
<td>dXPP</td>
<td>M3</td>
<td>0.001 s</td>
<td>-</td>
<td>2.792 s</td>
<td></td>
</tr>
<tr>
<td>dXPP</td>
<td>M3</td>
<td>0.0005 s</td>
<td>-</td>
<td>2.757 s</td>
<td></td>
</tr>
<tr>
<td>dXPP</td>
<td>M1</td>
<td>0.002 s</td>
<td>-</td>
<td>1.778 s</td>
<td>$\eta_s = 0.0002\eta_0$</td>
</tr>
<tr>
<td>dXPP</td>
<td>M1</td>
<td>0.002 s</td>
<td>-</td>
<td>0.622 s</td>
<td>$\eta_s = 0.01\eta_0$</td>
</tr>
<tr>
<td>dXPP</td>
<td>M1</td>
<td>0.002 s</td>
<td>-</td>
<td>0.648 s</td>
<td>$\eta_s = 0.05\eta_0$</td>
</tr>
<tr>
<td>dXPP</td>
<td>M1</td>
<td>0.002 s</td>
<td>-</td>
<td>1.748 s</td>
<td>Free outflow boundary</td>
</tr>
<tr>
<td>dXPP</td>
<td>M1</td>
<td>0.01 s</td>
<td>-</td>
<td>0.250 s</td>
<td>Convergence per $\Delta t$</td>
</tr>
</tbody>
</table>

Table 5.3 gives all characteristics of the calculations for the sharp corner contraction flow. Mesh M1 seems sufficiently fine to resolve the problem, as further mesh refinement could not delay divergence. Furthermore, it appears that the DEVSS/DG encounters a temporal instability with decreasing time step. This assumption is supported by calculations using the Giesekus model, which unexpectedly diverged with decreasing time step. Also, the dXPP formulation in mesh M3 and $\Delta t = 0.0005$ s encountered divergence sooner in time than the calculation with mesh M2 and $\Delta t = 0.001$ s. Baaijens (2001) observed a similar time step dependent instability for this method. However, calculations with the PTT model converged without any problems, contradicting the temporal stability assumption. It is speculated, that the strain hardening behaviour of the latter model is sufficiently low, consequently predicting lower stresses and elasticity, to avoid the temporal instabilities. This is in accordance with Bogaerds et al. (1999a), who found an instability depending on the amount of elasticity in the flow for the DEVSS/DG method. Besides, the PTT model may have a structure which is
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Figure 5.4: Development of stresses near corner singularity using mesh M1.

numerically more friendly, maybe related to the lack of anisotropy.

Since we are only interested in steady state results, \( \Delta t \) was increased and more iterations within a time step were performed until convergence was reached. Although this avoids the temporal instability, eventually no convergence of the Newton iteration process was achieved.

Adding a little solvent viscosity did not enhance convergence either. In fact, adding 1% of the zero shear rate viscosity or more solvent viscosity, calculations diverged sooner in time. Also, changing the outflow boundary conditions by suppressing the velocities in y-direction and deleting the prescription of a pressure point did not help to reach convergence.

Figure 5.4 shows the development in time of the stresses near the corner singularity. Stress gradients are high and a thin stress layer is present at the upper wall after the re-entrant corner. This is also the location where the instability is initiated. Therefore, the influence of a rounded corner is investigated to see if this diminishes the instabilities.

The four meshes used to investigate the influence of a rounded corner are shown in figure 5.5, and their characteristics in table 5.4. The corner has a radius of \( R = 0.1 \) mm, similar to the experimental set-up which is used for comparing experimental and numerical results in Verbeeten et al. (2001b). As can be concluded from table 5.5, which demonstrates the characteristics of the calculations with the rounded corner, divergence occurs even sooner in time when the corner is rounded. The development in time of the stresses around the rounded corner are depicted in figure 5.6. From this figure, it seems that stresses are convected more easily around a rounded corner in comparison to a sharp corner. Therefore, stresses and stress gradients are higher and that may influence convergence in a negative sense. Also

Table 5.4: Mesh characteristics of the planar contraction flow with a rounded corner (\( R = 0.1 \) mm).

<table>
<thead>
<tr>
<th></th>
<th>Mesh R1</th>
<th>Mesh R2</th>
<th>Mesh R3</th>
<th>Mesh R4</th>
</tr>
</thead>
<tbody>
<tr>
<td>#elements</td>
<td>1095</td>
<td>1773</td>
<td>1956</td>
<td>2034</td>
</tr>
<tr>
<td>#nodes</td>
<td>4557</td>
<td>7345</td>
<td>8045</td>
<td>8391</td>
</tr>
<tr>
<td>#DOF(( \vec{u}, p ))</td>
<td>8108</td>
<td>13044</td>
<td>14245</td>
<td>14876</td>
</tr>
<tr>
<td>#DOF(D)</td>
<td>3552</td>
<td>5700</td>
<td>6201</td>
<td>6486</td>
</tr>
<tr>
<td>#DOF(S, ( \Lambda )) = 4 \times #elements \times 20</td>
<td>87600</td>
<td>141840</td>
<td>156480</td>
<td>162720</td>
</tr>
</tbody>
</table>
Figure 5.5: Detail of FE meshes of half the planar contraction flow with a rounded corner ($R = 0.1\,\text{mm}$).

Table 5.5: Characteristics of calculations for the planar contraction flow with a rounded corner ($R = 0.1\,\text{mm}$).

<table>
<thead>
<tr>
<th>Model</th>
<th>Mesh</th>
<th>$\Delta t$</th>
<th>Convergence</th>
<th>$t_{end}$</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>dXPP</td>
<td>R1</td>
<td>0.001 s</td>
<td></td>
<td>1.281 s</td>
<td></td>
</tr>
<tr>
<td>dXPP</td>
<td>R1</td>
<td>0.0005 s</td>
<td></td>
<td>1.260 s</td>
<td></td>
</tr>
<tr>
<td>dXPP</td>
<td>R2</td>
<td>0.002 s</td>
<td></td>
<td>1.320 s</td>
<td></td>
</tr>
<tr>
<td>dXPP</td>
<td>R3</td>
<td>0.002 s</td>
<td></td>
<td>2.120 s</td>
<td></td>
</tr>
<tr>
<td>dXPP</td>
<td>R3</td>
<td>0.0005 s</td>
<td></td>
<td>2.084 s</td>
<td></td>
</tr>
<tr>
<td>dXPP</td>
<td>R4</td>
<td>0.0005 s</td>
<td></td>
<td>1.662 s</td>
<td></td>
</tr>
<tr>
<td>sXPP</td>
<td>R4</td>
<td>0.002 s</td>
<td></td>
<td>1.392 s</td>
<td>$\Lambda_i &gt; 0$</td>
</tr>
<tr>
<td>Giesekus</td>
<td>R1</td>
<td>0.1 s</td>
<td></td>
<td>5.8 s</td>
<td></td>
</tr>
<tr>
<td>Giesekus</td>
<td>R1</td>
<td>0.002 s</td>
<td></td>
<td>1.578 s</td>
<td></td>
</tr>
</tbody>
</table>
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for the Giesekus model, divergence is observed, even for $\Delta t = 0.1 \text{ s}$ which resulted in convergence for the sharp corner. However, the mesh R1 used in that case shows a rather bad transition of elements right after the corner.

None of the proposed numerical solutions seem to aid to overcome the divergence problem. Surprisingly, rounding off the re-entrant corner and thus eliminating the geometrical singularity has only worsened the problem. Although difficult to conclude with confidence from these calculations, problems may be accounted for by a temporal instability of the DEVSS/DG method as found in simple couette flows for a single-mode UCM model by Bogaers et al. (1999a). Moreover, it could be due to the highly strain hardening behaviour of the eXtended Pom-Pom model with the chosen set of parameters. This is supported by calculations with the PTT model that show no convergence problems at all. With the parameters given in table 5.1, the PTT model shows the lowest strain hardening effect. Furthermore, we will investigate the structure of the XPP model and compare it to the Giesekus and PTT models and examine if the proposed change by Van Meerveld (2001) has a positive effect.

5.5.2 Constitutive solutions

Due to its increased strain hardening behaviour, the XPP model builds up higher stresses than the Giesekus and PTT models. As a consequence, the thin stress layer at the upper wall right after the re-entrant corner has a longer wake and takes more time to develop. Figure 5.7 shows the development of the stresses in time for the XPP model and the steady state stresses for the Giesekus and PTT models.

Initially, the XPP model develops a long thin stress boundary layer with steep stress gradients near the upper wall right after the re-entrant corner. A small oscillation with a long wavelength develops within this stress boundary layer. In time, the thin stress boundary layer seems to move along the upper wall in downstream direction. However, the oscillation grows to an instability at the re-entrant corner and along the downstream channel wall. For the Giesekus model, such a stress boundary layer is significantly shorter, has less steep gradients and develops faster in time, while for the PTT model it is hardly detected at all.

As a next step, the influence of strain hardening on the convergence problems was investigated. The XPP parameters were changed such that the behaviour is less strain hardening (LSH) with similar elongational behaviour as the PTT model. Also, new parameters for the PTT model were chosen, invoking high strain hardening (HSH) behaviour.
such that a better description of the uniaxial elongational data is accomplished. The parameters are given in Table 5.6 and the model predictions for steady state shear viscosity and uniaxial elongational viscosity are shown in Figure 5.8. Obviously, the PTT HSH model overpredicts the steady state shear viscosity significantly at intermediate shear rates, if a better prediction in elongation is accomplished.

As can be seen in Table 5.7, divergence still occurred for the dXPP formulation. By choosing $\alpha = 0$, which means no anisotropy, calculations diverged even a little sooner. This rejects the idea that anisotropy has a negative effect on the numerical stability. Also,
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calculation for both the sXPP version with LSH parameters as well as for the PTT model with HSH parameters did converge. This intensifies the idea that the parameters in the dXPP formulation have less influence on its numerical behaviour than for the sXPP version. Namely, the backbone stretch $\Lambda_i$ and the orientation tensor $S_i$ in the dXPP formulation are computed separately and stay about the same order of magnitude, while they are joined together in the extra stress tensor $\tau_i$ for the sXPP version magnifying it even more due to $\Lambda_i^2$. Furthermore, the structure of the XPP model is examined and compared to the Giesekus and PTT models, as the latter was able to handle high strain hardening parameters.

Considering the possibility of negative backbone stretch values in numerical calculations, the (irreversible) stretch dynamics of the model is of importance. Substituting the slip tensor $B_i$ (equation (5.11)) into the evolution equation for the backbone tube stretch (5.10) results in:

$$\dot{\Lambda}_i = \Lambda_i [D : S_i] - \frac{r_i \nu_i (\Lambda_i - 1)}{\lambda_{b,i}} (\Lambda_i - 1).$$

(5.20)

| Table 5.6: Linear and non-linear parameters for fitting of the DSM Stamylan LD 2008 XC43 LDPE melt. $T_i = 170 [°C]$. $\nu_i = 2/\dot{g}_i$. Activation energy: $E_0 = 48.2 [kJ/mol]$. WLF-shift parameters: $C_1 = 14.3$, $C_2 = 480.8 [K]$. LSH = Low Strain Hardening; HSH = High Strain Hardening. |
|---|---|---|---|---|---|---|
| | Maxwell parameters | XPP\textsubscript{LSH} | exp. PTT\textsubscript{HSH} |
| | $G_i$ [Pa] | $\lambda_i$ [s] | $q_i$ | $\alpha_i$ | $\varepsilon_i$ | $\xi_i$ |
| 1 | $7.2006 \cdot 10^4$ | $3.8946 \cdot 10^{-3}$ | 1 | 1.0 | 0.30 | 0.30 | 0.30 |
| 2 | $1.5770 \cdot 10^4$ | $5.1390 \cdot 10^{-2}$ | 1 | 1.0 | 0.30 | 0.20 | 0.20 |
| 3 | $3.3400 \cdot 10^3$ | $5.0349 \cdot 10^{-1}$ | 1 | 1.0 | 0.30 | 0.02 | 0.01 |
| 4 | $3.0080 \cdot 10^2$ | $4.5911 \cdot 10^0$ | 3 | 1.0 | 0.10 | 0.02 | 0.01 |

Figure 5.8: Quasi-steady state uniaxial viscosity $\eta_u (a)$, and steady state shear viscosity $\eta_s (b)$ at $T = 170 [°C]$ of the XPP and PTT models for DSM Stamylan LD2008 XC43 LDPE melt.
Table 5.7: Characteristics of calculations for the planar contraction flow with adjustments to the constitutive equations. LSH = Low Strain Hardening; HSH = High Strain Hardening.

<table>
<thead>
<tr>
<th>Model</th>
<th>Mesh</th>
<th>$\Delta t$</th>
<th>Convergence</th>
<th>$t_{end}$</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>dXPP</td>
<td>M1</td>
<td>0.002 s</td>
<td>—</td>
<td>2.224 s</td>
<td>LSH (see table 5.1)</td>
</tr>
<tr>
<td>dXPP</td>
<td>M1</td>
<td>0.001 s</td>
<td>—</td>
<td>2.146 s</td>
<td>LSH</td>
</tr>
<tr>
<td>dXPP</td>
<td>M1</td>
<td>0.001 s</td>
<td>—</td>
<td>2.004 s</td>
<td>LSH + $\alpha = 0$</td>
</tr>
<tr>
<td>dXPP</td>
<td>M1</td>
<td>0.002 s</td>
<td>—</td>
<td>1.710 s</td>
<td>$\lambda_0 = \frac{\lambda_0}{r} e^{-\nu} ([\Lambda - 1])$</td>
</tr>
<tr>
<td>dXPP</td>
<td>M1</td>
<td>0.001 s</td>
<td>—</td>
<td>1.861 s</td>
<td>$\lambda_0 = \frac{\lambda_0}{r} e^{-\nu} ([\Lambda - 1])$</td>
</tr>
<tr>
<td>dXPP</td>
<td>M1</td>
<td>0.001 s</td>
<td>—</td>
<td>2.838 s</td>
<td>$\frac{r \nu}{\lambda_0} e^{\nu} ([\Lambda - 1]) (1 - \frac{1}{\lambda_0^2})$</td>
</tr>
<tr>
<td>dXPP</td>
<td>M1</td>
<td>0.0005 s</td>
<td>—</td>
<td>1.831 s</td>
<td>$\frac{r \nu}{\lambda_0} e^{\nu} ([\Lambda - 1]) (1 - \frac{1}{\lambda_0^2})$, LSH</td>
</tr>
<tr>
<td>dXPP</td>
<td>M1</td>
<td>0.001 s</td>
<td>—</td>
<td>2.079 s</td>
<td>$\frac{r \nu}{\lambda_0} e^{\nu} ([\Lambda - 1]) (1 - \frac{1}{\lambda_0^2})$, LSH</td>
</tr>
<tr>
<td>dXPP</td>
<td>R4</td>
<td>0.002 s</td>
<td>—</td>
<td>1.802 s</td>
<td>$\frac{r \nu}{\lambda_0} e^{\nu} ([\Lambda - 1]) (1 - \frac{1}{\lambda_0^2})$, LSH</td>
</tr>
<tr>
<td>dXPP</td>
<td>R4</td>
<td>0.0005 s</td>
<td>—</td>
<td>1.792 s</td>
<td>$\frac{r \nu}{\lambda_0} e^{\nu} ([\Lambda - 1]) (1 - \frac{1}{\lambda_0^2})$, LSH</td>
</tr>
<tr>
<td>sXPP</td>
<td>M1</td>
<td>0.002 s</td>
<td>+</td>
<td>11.020 s</td>
<td>$\Lambda_i &gt; 0$, LSH</td>
</tr>
<tr>
<td>sXPP</td>
<td>M1</td>
<td>0.001 s</td>
<td>—</td>
<td>3.740 s</td>
<td>$\frac{r \nu}{\lambda_0} e^{\nu} ([\Lambda - 1]) (1 - \frac{1}{\lambda_0^2})$</td>
</tr>
<tr>
<td>sXPP</td>
<td>M1</td>
<td>0.001 s</td>
<td>—</td>
<td>2.171 s</td>
<td>$\frac{r \nu}{\lambda_0} e^{\nu} ([\Lambda - 1]) (1 - \frac{1}{\lambda_0^2})$</td>
</tr>
<tr>
<td>sXPP</td>
<td>M1</td>
<td>0.0005 s</td>
<td>+</td>
<td>15.000 s</td>
<td>$\frac{r \nu}{\lambda_0} e^{\nu} ([\Lambda - 1]) (1 - \frac{1}{\lambda_0^2})$, LSH</td>
</tr>
<tr>
<td>sXPP</td>
<td>M1</td>
<td>0.001 s</td>
<td>+</td>
<td>10.411 s</td>
<td>$\frac{r \nu}{\lambda_0} e^{\nu} ([\Lambda - 1]) (1 - \frac{1}{\lambda_0^2})$, LSH</td>
</tr>
<tr>
<td>sXPP</td>
<td>M1</td>
<td>0.02 s</td>
<td>—</td>
<td>0.34 s</td>
<td>$\frac{r \nu}{\lambda_0} e^{\nu} ([\Lambda - 1]) (1 - \frac{1}{\lambda_0^2})$</td>
</tr>
<tr>
<td>sXPP</td>
<td>R4</td>
<td>0.002 s</td>
<td>+</td>
<td>12.000 s</td>
<td>$\frac{r \nu}{\lambda_0} e^{\nu} ([\Lambda - 1]) (1 - \frac{1}{\lambda_0^2})$, LSH + $\alpha_i = 0$</td>
</tr>
<tr>
<td>sXPP</td>
<td>R4</td>
<td>0.002 s</td>
<td>—</td>
<td>2.518 s</td>
<td>$\frac{r \nu}{\lambda_0} e^{\nu} ([\Lambda - 1]) (1 - \frac{1}{\lambda_0^2})$</td>
</tr>
<tr>
<td>sXPP</td>
<td>R4</td>
<td>0.0005 s</td>
<td>—</td>
<td>4.801 s</td>
<td>$\frac{r \nu}{\lambda_0} e^{\nu} ([\Lambda - 1]) (1 - \frac{1}{\lambda_0^2})$</td>
</tr>
<tr>
<td>PTT</td>
<td>M1</td>
<td>0.001 s</td>
<td>+</td>
<td>12.000 s</td>
<td>HSH</td>
</tr>
</tbody>
</table>

Negative backbone stretch values would lead to a negative affine motion ($\Lambda_i [D : S_i] < 0$) and a decrease of the exponential term $e^{\nu} ([\Lambda - 1])$, meaning an increase of the stretch relaxation time. Hence, the irreversible stretch dynamics become relatively smaller, and the reversible part $\Lambda_i [D : S_i]$, which is negative, can dominate. Consequently, the backbone stretch values become even more negative. This could all be initiated, if $[D : S_i]$ in the affine motion...
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is negative, as was detected by Wapperom and Keunings (2001) in a contraction/expansion flow. From a physical point of view, the stretch relaxation time should drop if the backbone tube is out of equilibrium. A simple solution which avoids an increase in relaxation time is taking the absolute value of the term \((\Lambda_i - 1)\) in the exponential part: \(e^{\nu_i(|\Lambda_i - 1|)}\). However, this proved not to be very effective, see table 5.7.

If the evolution equation for the backbone stretch of the Giesekus and PTT models is compared to the XPP model, a difference in structure can be noted. Substituting the equations (5.6) and (5.7) into equation (5.10) will give the backbone stretch equations for the Giesekus model:

\[
\dot{\Lambda}_i = \Lambda_i [D : S_i] - \frac{1}{2\lambda_{b,i}} \left( 3\Lambda_i^2 \alpha_i \text{tr}(S_i \cdot S_i) + (1 - 2\alpha_i)\Lambda_i - \frac{(1 - \alpha_i)}{\Lambda_i} \right),
\]

and for the PTT model:

\[
\dot{\Lambda}_i = \Lambda_i [(1 - \xi_i) D : S_i] - \frac{e^{\nu_i[(\Lambda_i^2 - 1)]}}{2\lambda_{b,i}} \left( \Lambda_i - \frac{1}{\Lambda_i} \right).
\]

If equation (5.12) is used, the expression for the PTT model can also be written as:

\[
\dot{\Lambda}_i = \Lambda_i [(1 - \xi_i) D : S_i] - \frac{\nu_i^* (\Lambda_i^2 - 1)}{2\lambda_{b,i}} \left( \Lambda_i - \frac{1}{\Lambda_i} \right), \quad \nu_i^* = 3\epsilon_i.
\]

Notice that the stretch relaxation for the Giesekus and PTT models are proportional to \(\Lambda_i - \frac{1}{\Lambda_i}\), which introduces a singularity for \(\Lambda_i = 0\) and guarantees \(\Lambda_i > 0\). A similar structure for the XPP model would also be preferable, as Van Meerveld (2001) suggested. The slip tensor \(B_i\) for the XPP model then becomes:

\[
B_i = \alpha_i \frac{\sigma_i}{2G_i\lambda_{b,i}} + \left[ \frac{1 - \alpha_i - 3\alpha_i\Lambda_i^4 \text{tr}(S_i \cdot S_i)}{2\lambda_{b,i}\Lambda_i^2} + \frac{r_i e^{\nu_i[(\Lambda_i^2 - 1)]}}{\lambda_{b,i}} \left( 1 - \frac{1}{\Lambda_i^2} \right) \right] I - \frac{G_i (1 - \alpha_i)}{2\lambda_{b,i}} \sigma_i^{-1}.
\]

The steady state behaviour of the modified eXtended Pom-Pom model (mXPP) together with the original XPP model is given in figure 5.9. Both models show very similar curves. The mXPP version has a later and steeper upswing in elongation and as a consequence the curve for the first normal stress difference lies also under the original version.

In case of the single-equation formulation, the implementation can be numerically consistent by choosing

\[
\Lambda_i^2 = 1 + \frac{\text{tr}(\tau_i)}{3G_i},
\]

and

\[
\Lambda_i = \sqrt{1 + \frac{[\text{tr}(\tau_i)]}{3G_i}} \geq 1.
\]
which is only present in the exponential term and secures its minimum at $\Lambda_i = 1$. Although negative values for $\operatorname{tr}(\tau_i)$ were still encountered around the re-entrant corner, calculations were able to proceed. Steady state values were reached using mesh M1 and $\Delta t = 0.0005$ s, demonstrating the improvement of the single-formulation model. As convergence is reached with the smallest time step chosen in this study, this undermines the hypothesis of a possible temporal instability. It is even difficult to detect a trend regarding the time step, as divergence sets in sooner for calculations using $\Delta t = 0.001$ s instead of $\Delta t = 0.002$ s. Also for a rounded corner, the single-equation modified XPP model performs better. Calculations with mesh R4 and time step $\Delta t = 0.002$ s can get up to almost double the time.

On the other hand, the dXPP formulation does not show any improvement using this alternative backbone stretch evolution equation, if the performed calculations are regarded. However, tables 5.3 and 5.7 still contain gaps to pose very strong conclusions. More calculations have to be performed to see if an ideal combination of mesh, time step and structure of the model can be found which may lead to convergence and steady state results.

For the converged calculations of the modified single-equation XPP and high strain hardening PTT models, the velocities and stresses are compared to experimental data in figures 5.10, 5.11 and 5.12. In the quantitative comparison, also results for the Giesekus model are shown.

Figure 5.9: Quasi-steady state uniaxial viscosity $\eta_u$ (a), steady state shear viscosity $\eta_s$ (b), and first normal stress coefficient $\Psi_1$ (c) at $T = 170^\circ C$ of the XPP, and mXPP models for DSM Stamylan LD2008 XC43 LDPE melt.
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Figure 5.10: Calculated and measured velocity profiles in the planar contraction flow over four cross-sections (a) \((x/h = -6, -4, -1, 1)\), and over the centerline (b) \((y/h = 0)\) for the modified XPP, Giesekus, and high strain hardening PTT models at \(Wi = 16.8\).

The calculated velocity profiles are in good agreement with the experimental data and hardly differ from the results shown in Verbeeten et al. (2001b). The largest difference is shown for the PTT\(_{\text{HSH}}\) model in comparison with the low strain hardening PTT model. The high strain hardening parameter set shows a better quantitative agreement in the contraction plane itself. However, the overshoot is more pronounced.

In the full field isochromatic fringe patterns (figure 5.11), the top parts are the experimental results, while the bottom halves are the computational solutions. The steady state results for the modified sXPP and PTT\(_{\text{HSH}}\) models differ significantly more. Obviously, the PTT\(_{\text{HSH}}\) model overpredicts the stresses in the upstream channel and the size of the ‘butterfly’, due to an overprediction of the shear components. The modified sXPP calculations show a better agreement in the upstream channel, however the ‘butterfly’ size is still underpredicted.

A more quantitative comparison of the stresses is given in figure 5.12. For the stresses along the centerline (figure 5.12(a)), the PTT\(_{\text{HSH}}\) model shows the best agreement. Although
the modified sXPP model shows the best description for the steady uniaxial elongational data, it shows the least accurate prediction over the centerline. Possibly, its transient startup elongational behaviour lacks behind in time. Also, the parameters of the model are determined on a logarithmic scale, while the stresses over the centerline are plotted on a linear scale. Furthermore, the three-dimensional effects are most pronounced in this region as velocities increase. To draw more confident conclusions regarding these effects, full three-dimensional calculations would provide more insight.

For the other three intersection lines, the modified eXtended Pom-Pom model shows a good agreement between calculations and experiments. Since these intersections involve more shear stresses, the PTTₜₜₜ model largely overpredicts the experimental stresses.

### 5.6 Conclusions and discussion

The divergence problems for the combination of the DEVSS/DG method with the XPP model in a transient contraction flow problem are investigated in this study. It is difficult to point
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out the exact cause of the onset of divergence. It may be due to the locally very high stress gradients which the mesh is unable to resolve, given a certain time step. On the other hand, the temporal instability of the DG method as was found by Bogaerds et al. (1999a) may influence divergence of the problem. Recently, Bogaerds et al. (2001) showed that instabilities are also dependent on the shape of the elements in the mesh; long shaped elements in the flow direction increase stability.

Both the single-equation (sXPP) as well as the double-equation (dXPP) formulation of the eXtended Pom-Pom model were investigated. Although fully equivalent, they show different numerical responses. For the dXPP version, negative backbone stretch values are only encountered just before onset of divergence. Since the backbone stretch values in the single-equation version are derived from \( \tau_i \) instead of calculated directly, negative values are encountered already earlier in the calculations. This leads to complex backbone stretch values and numerical inconsistencies.

No numerical remedy was encountered to overcome divergence of the calculations. Mesh refinement, decreasing the time step, or changing the boundary conditions at best delayed divergence. By increasing \( \Delta t \) and having more iterations per time step, or adding solvent viscosity divergence was encountered even sooner. Rounding off the re-entrant corner to remove the geometrical singularity also caused more difficulties in resolving the problem. Loss of convergence was probably encountered sooner because of an enhanced convection into the downstream flow channel of high stresses imposed by the re-entrant corner.

For transient calculations, the DEVSS/DG method becomes more unstable at higher elasticities (see Bogaerds et al. (1999a)), i.e. higher flow rates in the flow geometry or higher stresses as a consequence of higher strain hardening behaviour. This is consistent with the observation that calculations with the single-equation formulation converge if a parameter set is chosen that describes a lower strain hardening behaviour of the material, and a steady state solution is reached. This holds both for a geometry with a corner singularity as well as a rounded re-entrant corner. However, calculations using the PTT model always converged, no matter whether low or high strain hardening parameters were chosen. Furthermore, to our surprise, steady state solutions for the dXPP formulation were never reached, no matter if a low or high strain hardening parameter set was chosen. Most probably, the extra stress variables \( \Lambda_i \) and \( S_i \) stay about the same order in magnitude, hardly changing by a change of material parameters. The sXPP version calculates the extra stress \( \tau_i \) directly, which is magnified by the modulus and the square of the backbone stretch values.

An adaptation of the stretch relaxation term was proposed by Van Meerveld (2001), which is proportional to \( \Lambda - 1/\Lambda \) and similar to the structure of the Giesekus and PTT models. As a consequence, the single-equation formulation of this modified eXtended Pom-Pom model is numerically more consistent and stable. For mesh M1 and time step \( \Delta t = 0.0005 \) s, the calculations converged and a steady state solution was found. For the double-equation formulation, however, this adaptation did not resolve the convergence problems. The calculations performed in this study do not cover the full range of possible parameter settings. More numerical experiments should be carried out to find the ideal combination of mesh, time step and structure to reach steady state solutions in case of the double-equation formulation of the eXtended Pom-Pom model.

The steady state results for the modified sXPP version are in good agreement with the experimental data. Although the model shows a good agreement with uniaxial viscosity data, experimental stresses over the centerline are surprisingly underpredicted. This discrepancy
is expected to arise from three-dimensional effects. More investigation is needed to confirm that assumption.

In the presented solution method, the ‘Stokes’ problem \(( \vec{u}, p )\) and the discrete rate of deformation problem \(( \mathcal{D} )\) are decoupled. As a result, the stabilization term \(2\eta( \mathcal{D} - \mathcal{D} )\) in the momentum equation (5.13) is inconsistent: \( \mathcal{D} \) is taken at time \( t_{n+1} \), while \( \mathcal{D} \) is taken at time \( t_n \). This decoupling may also provoke an early onset of divergence. By choosing a different preconditioner, the coupled problem \(( \vec{u}, p, \mathcal{D} )\) can be solved while still using iterative solvers.

The DEVSS/DG method shows divergence problems, depending on the constitutive model, the mesh, the time step, and the material behaviour. More stable methods may improve convergence when solving complex flows. The recently proposed DEVSS-G/SUPG-\( \theta \) method by Bogaerds et al. (2001) does not show the temporal instability problems in plane couette flows which are encountered for the DEVSS/DG method. Moreover, it uses a different preconditioner which is able to solve the coupled problem \(( \vec{u}, p, \mathcal{D} )\). However, since it is a SUPG-based method, it is less robust for non-smooth flow geometries.
Chapter 6

Conclusions and recommendations

In this thesis, a combined numerical/experimental analysis for the evaluation of differential constitutive models is performed. In chapter 2, three-dimensional experimental results of a polymer solution flowing through a cross-slot device are compared to fully three-dimensional computations using the Giesekus, Phan-Thien Tanner (PTT), and Feta models. A modification of the original differential Pom-Pom model by McLeish and Larson (1998) is introduced in chapter 3. Its performance in a wide range of rheological experiments for both low density as well as high density polyethylene melts is shown. This eXtended Pom-Pom model is tested in three Prototype Industrial Flows (PIF): a planar contraction flow, a planar flow around a confined cylinder, and a cross-slot flow. Numerical solutions are also compared to the Giesekus and PTT models, and to velocities extracted with Particle Imaging Velocimetry and integrated stresses using Flow Induced Birefringence techniques. An additional analysis of the planar contraction flow is carried out in chapter 5, resulting in a small modification of the eXtended Pom-Pom model. As a numerical method for all prototype industrial flow computations, the Discrete Elastic Viscous Stress Splitting technique in combination with the Discontinuous Galerkin method, as proposed by Baaijens et al. (1997), was used.

6.1 Conclusions

The extension of the DEVSS/DG method to the third dimension resulted in an accurate numerical tool for viscoelastic flow simulations that efficiently handles multiple relaxation times. It is robust in the sense that it is able to cope with geometrical singularities. The DEVSS/DG method may encounter instabilities in transient calculations for flows with pronounced elasticity. Convergence problems are encountered for this method depending on (the structure of) the constitutive model, its rheological behaviour invoked by the parameter choice, the mesh, and the time step. However, temporally stable numerical techniques, such as the DEVSS-G/SUPG method, have in general more trouble solving non-smooth flows.

Enhanced flexibility in independently controlling the shear and elongational properties of the rheological behaviour has been accomplished in the Feta model. This model, however, lacks a sound physical background. Some disadvantages are the overprediction of the first normal stress difference in shear and the absence of an overshoot in start-up shear flows. Moreover, it does not predict an equibiaxial viscosity. The concept of the Feta model may
be a good starting point for a single-mode model. Such a model would imply an enormous reduction in computational time and resources.

The Pom-Pom model by McLeish and Larson (1998) is a breakthrough in the field of viscoelastic constitutive equations. Starting from a physical concept, it is able to correctly describe the non-linear behaviour in shear and elongation. The original differential version, improved with local branch-point withdrawal, is modified to overcome three drawbacks: steady state elongational viscosities show discontinuities, the equation for orientation is unbounded for high strain rates, and the model does not have a second normal stress difference in shear. A good to excellent quantitative agreement with experimental data is accomplished for both low density and high density polyethylene melts over a wide range of rheological experiments using the eXtended Pom-Pom model, which is exceptional. A major advantage is that the non-linear parameters can be determined by using the uniaxial viscosity data only.

Within three Prototype Industrial Flows, the eXtended Pom-Pom (XPP) model shows a good quantitative agreement with experimental velocity and stress data at different flow rates. Its overall performance supersedes the behaviour of the more conventional PTT and Giesekus models in these inhomogeneous complex flows. For the planar contraction flow, the XPP model encountered convergence problems at first instance. However, after a small modification, as proposed by Van Meerveld (2001), improved numerical performance is achieved while still having a correct rheological description.

6.2 Recommendations

The numerical method still encounters convergence problems for the double-equation version of the eXtended Pom-Pom model. Furthermore, steady state results for the contraction geometry with a rounded corner could not be obtained. Currently, the DEVSS/DG method solves the linear set of equations by decoupling the system matrix into a ’Stokes’ problem \((\vec{u}, p)\) and a discrete rate of deformation problem \((\bar{D})\). A possible improvement may be accomplished by solving the coupled problem \((\vec{u}, p, \bar{D})\) at once. It avoids the temporal inconsistency due to the decoupling that is present in the stabilization term \(2\eta(\bar{D} - \bar{D})\) of the momentum equation. The DEVSS-G/SUPG-\(\theta\) implementation, recently proposed by Bogaerds et al. (2001), uses a different preconditioner that can solve the coupled problem. It shows a more stable behaviour, possibly accounted for by the SUPG method applied to handle the convective terms in the constitutive equations.

Several reasons may account for the presence of discrepancies between the experimental data and the computations in the Prototype Industrial Flows for the eXtended Pom-Pom model. First of all, only the uniaxial elongational viscosity data is used to determine the parameters. To obtain accurate experimental data for that particular flow is troublesome. Frequently, the imposed strain rate does not agree with the strain rate in the experiments. This is believed to be caused by internal slip of the material. As a result, the measured elongational viscosity is often too high [Schulze et al. (1999)]. An improved parameter set may be obtained if the full range of rheological data is used in an automated fitting procedure. Furthermore, rheological data is always presented on a logarithmic scale. The parameter fitting procedure is also performed on a logarithmic scale, making it less accurate. Since the numerical results
Conclusions and recommendations

and experimental data for PIF’s are mostly compared on a linear scale, differences between computations and experiments seem usually larger for Prototype Industrial Flow data.

For the planar contraction flow, the largest discrepancies are found in the contraction plane around $x/h = 0$. They are assumed to arise from three-dimensional effects. A full three-dimensional analysis of the flow would be worthy to investigate these assumptions.

In chapter 4, it is mentioned that the XPP model overpredicts the stresses in the wake of the cylinder because of viscous heating, amongst others. A non-isothermal investigation of this particular PIF would provide an insight in the amount of temperature dependency. Most probably, the temperature effects are larger in a flow around a cylinder compared to the flow in a cross-slot device. In the former flow, material elements undergo compression approaching the front stagnation point, shearing along the cylinder wall, and elongation in the rear stagnation region. The thin shear stress boundary layers account for the temperature increase and the deformation history changes the rheological behaviour significantly more than in a cross-slot flow. In the latter flow, no pre-shearing is present for material elements approaching the stagnation point. Therefore, it is assumed that the effects of viscous heating are more pronounced in the flow around a confined cylinder.

Differential models have a better reputation in predicting reversed flows than integral models. The eXtended Pom-Pom model shows a good agreement with reversed flow experiments (see chapter 3). Therefore, it would be interesting to investigate the performance of the XPP model in extrudate swell problems or contraction/expansion geometries. The numerical technique applied in this thesis can easily be extended for free surface flows, still using the Eulerian approach. Van Rens (1999) applied a similar numerical technique for the simulation of aluminium extrusion processes.

An often heard criticism on the Pom-Pom models is the large amount of non-linear parameters. For every pom-pom mode, the eXtended Pom-Pom model has three non-linear parameters. However, since they follow a certain trend, determination of the parameters is fairly simple. Therefore, it is believed that the number of non-linear parameters can be reduced. First, one of the key features for the Pom-Pom model is the separation of relaxation times for stretch and orientation. The eXtended Pom-Pom model intrinsically has a difference between the relaxation times for the stretch and orientation. If the backbone tube is stretched, the relaxation time for the stretch is reduced by the exponential term: $\lambda_s = \lambda_0 e^{-\nu(\Lambda - 1)}$. Simultaneously, the relaxation time for the orientation increases due to the multiplication of the linear relaxation time and the backbone tube stretch squared: $\lambda_b = \lambda_0 \Lambda^2$. Therefore, the ratio between the linear stretch and orientation relaxation times can equal 1, $r = \lambda_{0,b}/\lambda_{0,s} = 1$, provided that a good discrete relaxation spectrum is chosen. Second, thorough investigation may provide a function to connect the non-linear parameters $q$, or equivalently $\nu$, of the different modes. Third, a connection between the anisotropy parameter $\alpha$ and the number of arms $q$ may be present. If these functions can be found, this would reduce the amount of non-linear parameters in the eXtended Pom-Pom model to a single one.

Öttinger (2000) investigated the thermodynamic admissibility of the differential Pom-Pom model. It was concluded that the Pom-Pom model falls within the non-equilibrium thermo-dynamical framework GENERIC [Grmela and Öttinger (1997), Öttinger and Grmela (1997)]. However, some modifications were suggested in the evolution equation for the orientation tensor, very similar to that of the eXtended Pom-Pom model (see appendix B). A small drawback from his suggested formulation is that it has a bifurcation: the solution is non-
unique due to the quadratic dependence on the orientation tensor. If the steady state is solved directly, solutions are different from solutions derived in a transient sense. Nevertheless, the physical solution is always found if transient calculations are performed. This is a similar problem as seen for the Giesekus model. Therefore, it is also of interest to implement the Ottinger version of the Pom-Pom model into the Finite Element code, improved with the local branch-point displacement of Blackwell et al. (2000) and the suggestion of Van Meerveld (2001), and to investigate its convergence characteristics. Furthermore, a GENERIC check of the eXtended Pom-Pom model still needs to be performed, although it is expected to be thermodynamically correct.

A last remark on constitutive models is related to the Phan-Thien Tanner model. In chapter 5 it is shown that the PTT model has good convergence characteristics. Unfortunately, the model is too strong strain thinning, which can be detected by the individual modes in steady state elongational viscosity plots. A simple modification of the present relaxation time of the model, \( \lambda_{\text{PTT}} = \lambda_0 e^{-\varepsilon \frac{\Lambda^2}{\eta_0}} = \lambda_0 e^{-\nu^* (\Lambda^2 - 1)} \), could provide significant improvement. Following the ideas of Blackwell et al. (2000), the relaxation time should decrease as an exponential function of the backbone tube stretch \( \Lambda \) instead of \( \Lambda^2 \): \( \lambda_{\text{new}} = \lambda_0 e^{-\nu^* (\Lambda - 1)} \approx \lambda_0 e^{-\varepsilon \frac{\Lambda}{\eta_0^{2/3}}} \). The convergence characteristics of this suggested modification still has to be investigated.

Apart from this change in the relaxation time, an open question is the implementation of a second normal stress difference in shear and the second planar viscosity in the PTT model. Currently, this is accounted for by the Gordon-Schowalter derivative, which is not very physical. Both \( N_2 \) and \( \eta_2 \) disappear instantly if the flow is stopped, since they are related to the rate of deformation \( D \) instead of to the extra stress \( \tau \). The Pom-Pom model is one step ahead of the PTT model with regard to this characteristic.
Appendix A

Rewrite procedure for the orientation equation

As a starting point, the equation for the auxiliary tensor $A$ is taken:

$$
\nabla A + \frac{1}{\lambda_{0b}} \left[ A - \frac{1}{3} I \right] = 0 \iff \dot{A} = L \cdot A + A \cdot L^T - \frac{1}{\lambda_{0b}} \left[ A - \frac{1}{3} I \right]. \quad (A.1)
$$

To get to the backbone orientation tensor $S$, the auxiliary tensor $A$ is divided by its trace:

$$
S = \frac{A}{I_A} \iff A = I_A \cdot S. \quad (A.2)
$$

Now, the time derivative of equation (A.2) is taken:

$$\dot{A} = \dot{I}_A \cdot S + I_A \cdot \dot{S}. \quad (A.3)
$$

As $\dot{I}_A = I_A$ holds, for the time derivative of the trace of auxiliary tensor $A$, the trace of equation (A.1) is taken:

$$I_A = 2 \left[ D : A \right] - \frac{1}{\lambda_{0b}} \left[ I_A - 1 \right]. \quad (A.4)
$$

If the equations (A.2), (A.3) and (A.4) are substituted into equation (A.1), the following relation occurs:

$$I_A \cdot S + I_A \cdot \dot{S} = L \cdot A + A \cdot L^T - \frac{1}{\lambda_{0b}} \left[ A - \frac{1}{3} I \right], \quad (A.5)
$$

which can also be written as:

$$2 \left[ D : I_A \cdot S \right] S - \frac{1}{\lambda_{0b}} \left[ I_A \cdot S - S \right]
+ I_A \cdot \dot{S} = I_A \cdot L \cdot S + I_A \cdot S \cdot L^T - \frac{1}{\lambda_{0b}} \left[ I_A \cdot S - \frac{1}{3} I \right]. \quad (A.6)
$$

By dividing this last equation with the trace of the auxiliary tensor $A$, it reduces to:

$$\nabla S + 2 \left[ D : S \right] S + \frac{1}{\lambda_{0b} I_A} \left[ S - \frac{1}{3} I \right] = 0. \quad (A.7)$$
Appendix B

Enhanced Pom-Pom models according to Öttinger (2000)

The Green-Kubo type expression for the orientation equation as proposed by Öttinger reads:

\[ \nabla A + \frac{1}{\lambda_b} I_A \left[ (3S + \alpha_1 I + \alpha_2 S^{-1}) \cdot \left( S - \frac{1}{3} I \right) 
+ \left( \alpha_3 I + \alpha_4 S \right) \text{tr} \left( I - \frac{1}{3} S^{-1} \right) \right] = 0, \quad S = \frac{A}{I_A}, \]  

(B.1)

where \( \alpha_1, \alpha_2, \alpha_3 \geq 0 \) and \( \alpha_4 \) is arbitrary. Öttinger suggested that, for numerical purposes, it may be convenient to suppress all occurrences of \( S^{-1} \) by choosing \( \alpha_2 = \alpha_3 = \alpha_4 = 0 \). Equation (B.1) then reduces to:

\[ \nabla A + \frac{1}{\lambda_b} I_A \left[ 3S \cdot S + (\alpha_1 - 1)S - \frac{1}{3} \alpha_1 I \right] = 0, \quad S = \frac{A}{I_A}. \]  

(B.2)

Although he did not mention this, in this case, to correctly describe linear visco-elasticity, the relaxation time for the backbone tube orientation must be chosen as \( \lambda_b = \lambda_{0b} (1 + \alpha_1) \), where \( \lambda_{0b} \) is obtained from dynamic measurements. The attention is drawn to the fact that for zero \( \alpha_1 \), still a second normal stress difference \( \Psi_2 \) is present. By increasing \( \alpha_1 \), \( \Psi_2 \) is decreased, which is opposite to the XPP model.

The set of equations (3.3), (3.4) and (B.2) can also be written as a single equation:

\[ \nabla \tau + \lambda_1(\tau)^{-1} \cdot \tau = 2 G_0 D, \]  

(B.3)

with

\[ \lambda_1(\tau)^{-1} = \frac{1}{\lambda_b} \left[ \frac{1}{G_0 A^2} \tau + f_1(\tau)^{-1} I + G_0 \left( f_1(\tau)^{-1} - \frac{1 + \alpha_1 A^4}{A^2} \right) \tau^{-1} \right], \]  

(B.4)

\[ \frac{1}{\lambda_b} f_1(\tau)^{-1} = \frac{2}{\lambda_s} \left( 1 - \frac{1}{A} \right) + \frac{1}{\lambda_b} \left[ \frac{1}{A^4} + \alpha_1 - \frac{I_{x,x}}{3 G_0 A^4} \right], \]  

(B.5)

and

\[ \Lambda = \sqrt{1 + \frac{I_{x,x}}{3 G_0}}, \quad \lambda_s = \lambda_{0s} e^{-\nu (\Lambda^{-1})}, \quad \nu = \frac{2}{q}. \]  

(B.6)
Again, the different parts for stretch and orientation can be detected. The extra stress equation (B.3) is referred to as the single-equation Improved Pom-Pom (SIPP) model. The combined set of the orientation equation (B.2), the stretch equation (3.3) and the extra stress equation (3.4) is referred to as the double-equation Improved Pom-Pom (DIPP) model. The addition Improved is used to point out that local branch-point displacement is incorporated in the model [Blackwell et al. (2000)]. The finite extensibility condition ($\Lambda \leq q$) has been taken out for reasons mentioned earlier. For the DIPP model, it is pointed out, that within a coupled Finite Element method, extra boundary conditions are needed for $\Lambda$ and $S$. For convenience, an overview is given of the equations for the two models in tables B.1 to B.2.

It should be mentioned, that these two models show numerical problems (they are suspected to have a bifurcation), and for the rest they give similar results as the XPP model.

**Table B.1: DIPP equation set.**

**Double-equation Improved Pom-Pom (DIPP) model**

<table>
<thead>
<tr>
<th>Viscoelastic stress: $\tau = G_0 \left( 3 \Lambda^2 S - I \right)$.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evolution of orientation: $\dot{A} + \frac{1}{\lambda_b} I_3 \left[ 3S \cdot S + (\alpha_1 - 1)S - \frac{1}{3} \alpha_1 I \right] = 0$, $S = \frac{A}{I_3}$, $\lambda_b = \lambda_{0b} (1 + \alpha_1)$.</td>
</tr>
<tr>
<td>Evolution of the backbone stretch: $\dot{\Lambda} = \Lambda \left[ D : S \right] - \frac{1}{\lambda_s} (\Lambda - 1)$, $\lambda_s = \lambda_{0s} e^{-\nu (\Lambda - 1)}$, $\nu = \frac{2}{q}$.</td>
</tr>
</tbody>
</table>

**Table B.2: SIPP equation set.**

**Single-equation Improved Pom-Pom (SIPP) model**

<table>
<thead>
<tr>
<th>Viscoelastic stress: $\nabla \tau + \lambda_1(\tau)^{-1} \cdot \tau = 2 G_0 D$.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relaxation time tensor: $\lambda_1(\tau)^{-1} = \frac{1}{\lambda_b} \left[ \frac{1}{G_0 \Lambda^2} \tau + f_1(\tau)^{-1} I + G_0 \left( f_2(\tau)^{-1} - \frac{1 + \alpha_1 \Lambda^4}{\Lambda^2} \right) \tau^{-1} \right]$.</td>
</tr>
<tr>
<td>Extra function: $\frac{1}{\lambda_b} f_1(\tau)^{-1} = \frac{2}{\lambda_s} \left( 1 - \frac{1}{\Lambda} \right) + \frac{1}{\lambda_b} \left[ \frac{1}{\Lambda^4} + \alpha_1 - \frac{I_r \tau}{3 G_0 \Lambda^4} \right]$.</td>
</tr>
<tr>
<td>Backbone stretch and relaxation times: $\Lambda = \sqrt{1 + \frac{I_r}{3 G_0}}$, $\lambda_b = \lambda_{0b} (1 + \alpha_1)$, $\lambda_s = \lambda_{0s} e^{-\nu (\Lambda - 1)}$, $\nu = \frac{2}{q}$.</td>
</tr>
</tbody>
</table>
Appendix C

The rheological behaviour of the PTT and original Pom-Pom models

To illustrate that the PTT model is only capable of satisfactory describing the rheological behaviour of low density polyethylene melts up to a certain point, this model is presented for the well-characterized Lupolen 1810H LDPE melt [Hachmann (1996), Kraft (1996)]. Furthermore, the original differential Pom-Pom (OPP) model [McLeish and Larson (1998)] and the version with incorporation of local branch-point withdrawal (PP) [Blackwell et al. (2000)] are compared to the eXtended Pom-Pom (XPP) model [Verbeeten et al. (2001a)] for the same material.

C.1 PTT model

Three sets of parameters for the PTT model are given in table C.1. Since it is believed that the Gordon-Schowalter derivative is physically incorrect for incorporation of a second normal stress difference in shear, for set 1 the slip-parameter $\xi$ is taken zero for all modes. As can be clearly seen in figure C.1, this set correctly predicts the uniaxial elongation. Notice, that for $10^{-4} \leq \dot{\varepsilon} \leq 10^{-1}$ the different modes can be detected in the steady state uniaxial viscosity plot. This is due to the too enhanced strain thinning behaviour of the PTT model at high strain rates. On the contrary, the shear response is rather largely overpredicted. The slip parameter

| Table C.1: PTT parameter sets for fitting of the Lupolen 1810H melt at $T = 150$ °C. |
|-----------------|-----------------|-----------------|-----------------|
| $t$             | $G_0, i$, Pa     | $\lambda_0, i$, s | $\varepsilon_i$ | $\xi_i$ | $\varepsilon_i$ | $\xi_i$ | $\varepsilon_i$ | $\xi_i$ |
| 0               | 1.0000 \cdot 10^{-2} | 1.0000 \cdot 10^{-4} | 0.150 | 0 | 0.150 | 0.10 | 0.150 | 0.060 |
| 1               | 2.1662 \cdot 10^{0} | 1.0000 \cdot 10^{-1} | 0.080 | 0 | 0.080 | 0.10 | 0.080 | 0.030 |
| 2               | 3.7775 \cdot 10^{0} | 3.9811 \cdot 10^{0} | 0.040 | 0 | 0.040 | 0.10 | 0.040 | 0.020 |
| 3               | 6.955 \cdot 10^{1} | 2.5119 \cdot 10^{1} | 0.025 | 0 | 0.025 | 0.10 | 0.025 | 0.015 |
| 4               | 1.183 \cdot 10^{2} | 1.5849 \cdot 10^{2} | 0.007 | 0 | 0.007 | 0.10 | 0.007 | 0.005 |
| 5               | 4.1614 \cdot 10^{2} | 1.0000 \cdot 10^{3} | 0.015 | 0 | 0.015 | 0.10 | 0.015 | 0.010 |
\( \xi \) is needed to correct for the overprediction in shear.

Set 2 is chosen, such that the uniaxial elongation is predicted correctly again. The results are shown in figure C.2. The steady state shear viscosity and first normal stress coefficients are also predicted correctly. Since the slip parameter \( \xi \) is larger than the elongation parameter \( \varepsilon \), oscillations occur in the start-up shear responses. These oscillations are not seen in the experiments.

For set 3, the \( \xi \) parameter is reduced, such that oscillations in start-up shear responses disappear. The uniaxial elongation is predicted correctly (see figure C.3). Unfortunately, shear responses are overpredicted again.

For such a strain hardening melt, the PTT model is unable to predict all features correctly. If elongation is predicted correctly, shear is overpredicted, or oscillations occur in the start-up shear behaviour. If shear is predicted correctly, elongation is underpredicted.

### C.2 Original differential Pom-Pom model

In table C.2, the parameters for the OPP and PP models are given. The comparison of these version with the XPP model and the rheological data of the Lupolen 1810H LPDE melt is shown in figure C.4. To reduce the number of curves, the OPP model is only shown in a steady state sense.

For the steady state uniaxial elongational viscosity, the OPP model shows significant peaks. These are smoothed out by the incorporation of the local branch-point withdrawal. The PP version, however, still shows discontinuities due to the maximum stretch condition \( (\Lambda_i \leq q_i) \). The XPP model has a smooth behaviour without any discontinuities. In the transient uniaxial viscosity plots, all three versions of the Pom-Pom model perform well for the shown strain rates.

The largest difference can be noted in shear. Both the OPP and PP versions show a more pronounced shear thinning and transient overshoot compared to the XPP version. This is related to the different evolution equations for the orientation tensor. The former two versions are too shear thinning if compared to the experimental data. In first normal stress coefficient, the XPP model shows an overprediction, while the OPP and PP versions are underpredicting the data. However, these experiments are difficult to perform and accuracy is relatively low.

**Table C.2:** Original Pom-Pom (OPP) and Pom-Pom with BPW (PP) parameters for fitting of the Lupolen 1810H melt at \( T_r = 150 \, ^\circ \text{C} \).

<table>
<thead>
<tr>
<th>( i )</th>
<th>( G_{0,i} )</th>
<th>( \lambda_{0,i} )</th>
<th>( \sigma )</th>
<th>OPP set</th>
<th>PP set</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.1662 \cdot 10^4</td>
<td>1.0000 \cdot 10^{-1}</td>
<td>2</td>
<td>5.0</td>
<td>3.5</td>
</tr>
<tr>
<td>2</td>
<td>9.9545 \cdot 10^4</td>
<td>6.3096 \cdot 10^{-1}</td>
<td>3</td>
<td>4.5</td>
<td>5.0</td>
</tr>
<tr>
<td>3</td>
<td>3.7775 \cdot 10^4</td>
<td>3.9811 \cdot 10^0</td>
<td>5</td>
<td>4.0</td>
<td>2.8</td>
</tr>
<tr>
<td>4</td>
<td>9.6955 \cdot 10^4</td>
<td>2.5119 \cdot 10^1</td>
<td>8</td>
<td>3.5</td>
<td>9.2</td>
</tr>
<tr>
<td>5</td>
<td>1.1834 \cdot 10^4</td>
<td>1.5849 \cdot 10^2</td>
<td>12</td>
<td>2.0</td>
<td>15.1</td>
</tr>
<tr>
<td>6</td>
<td>4.1614 \cdot 10^9</td>
<td>1.0000 \cdot 10^4</td>
<td>13</td>
<td>1.1</td>
<td>37.6</td>
</tr>
</tbody>
</table>
Figure C.1: Transient (a) and quasi-steady state (b) uniaxial viscosity $\eta_u$, transient (c) and steady state (d) shear viscosity $\eta_s$, and transient (e) and steady state (f) first normal stress coefficient $\Psi_1$ of the PTT model with set 1 for Lupolen 1810H melt at $T = 150 \, ^\circ C$. $\dot{\varepsilon} = 0.0030, 0.0102, 0.0305, 0.103, 0.312, 1.04 \, s^{-1}$. $\dot{\gamma} = 0.001, 0.01, 0.03, 0.1, 0.3, 1, 10 \, s^{-1}$. 
Figure C.2: Transient (a) and quasi-steady state (b) uniaxial viscosity $\eta_u$, transient (c) and steady state (d) shear viscosity $\eta_s$, and transient (e) and steady state (f) first normal stress coefficient $\Psi_1$ of the PTT model with set 2 for Lupolen 1810H melt at $T = 150^\circ$C. $\dot{\varepsilon} = 0.0030, 0.0102, 0.0305, 0.103, 0.312, 1.04 \text{ s}^{-1}$. $\dot{\gamma} = 0.001, 0.01, 0.03, 0.1, 0.3, 1, 10 \text{ s}^{-1}$.
The rheological behaviour of the PTT and original Pom-Pom models

(a) Transient uniaxial viscosity

LDPE melt, BASF Lupolen 1810H at T=150°C

(b) Quasi-steady state uniaxial viscosity

LDPE melt, BASF Lupolen 1810H at T=150°C

(c) Transient shear viscosity

LDPE melt, BASF Lupolen 1810H at T=150°C

(d) Steady state shear viscosity

LDPE melt, BASF Lupolen 1810H at T=150°C

(e) Transient first normal stress coefficient

LDPE melt, BASF Lupolen 1810H at T=150°C

(f) Steady state first normal stress coefficient

LDPE melt, BASF Lupolen 1810H at T=150°C

Figure C.3: Transient (a) and quasi-steady state (b) uniaxial viscosity $\eta_u$, transient (c) and steady state (d) shear viscosity $\eta_s$, and transient (e) and steady state (f) first normal stress coefficient $\Psi_1$ of the PTT model with set 3 for Lupolen 1810H melt at $T = 150$ °C. $\dot{\varepsilon} = 0.0030, 0.0102, 0.0305, 0.103, 0.312, 1.04 \text{ s}^{-1}$. $\dot{\gamma} = 0.001, 0.01, 0.03, 0.1, 0.3, 1, 10 \text{ s}^{-1}$. 

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Figure C.4: Transient (a) and quasi-steady state (b) uniaxial viscosity $\eta_u$, transient (c) and steady state (d) shear viscosity $\eta_s$, and transient (e) and steady state (f) first normal stress coefficient $\Psi_1$ of the eXtended Pom-Pom (XPP), original Pom-Pom (OPP), and Pom-Pom with BPW (PP) models for Lupolen 1810H melt at $T = 150^\circ$C. $\dot{\varepsilon} = 0.0030, 0.0102, 0.0305, 0.103, 0.312, 1.04 \text{ s}^{-1}$, $\dot{\gamma} = 0.001, 0.01, 0.03, 0.1, 0.3, 1, 10 \text{ s}^{-1}$.
Bibliography


Bibliography
Samenvatting

De manier van verwerken van polymere materialen heeft een grote invloed op de resulterende mechanische en optische eigenschappen van het eindprodukt. Zo hangen bijvoorbeeld de dimensie stabiliteit van een precisie-spuigietprodukt en treksterkte, Young’s modulus en zelfs scheursterkte van geblazen folies af van de viscoelastische eigenschappen van de polymere smelt. Het reologisch gedrag van de polymere smelt hangt af van de moleculaire structuur en de moleculaire gewichtsverdeling van het materiaal. Vandaar dat het, onder procescondities, modelleren van de stroming van viscoelastische smelten belangrijk is voor de ontwikkeling van nieuwe materialen en toepassingen. Hiervoor zijn betrouwbare constitutieve modellen en robuuste numerieke methodes nodig. Dit proefschrift levert een bijdrage aan het modelleren van polymere materialen in isotherme, twee- en drie-dimensionale stromingen, gebruikmakend van constitutieve vergelijkingen in differentiaalvorm.

Voor het correct voorspellen van het reologisch gedrag van commerciële polymere smelten zijn meerdere relaxatietijden noodzakelijk. Modellen die gebruik maken van één enkele relaxatietijd zijn slechts in staat de reologie kwalitatief te beschrijven. Een kwantitatieve beschrijving is niet mogelijk omdat de helling in opstart stromingen en het stationaire gedrag in enkelvoudige afschuifstromingen incorrect wordt voorspeld. Voor het bepalen van de niet-lineaire parameters in constitutieve modellen zijn experimentele rekdata van cruciaal belang, vanwege de grotere gevoeligheid in rek ten opzichte van afschuiving.

De grootste moeilijkheid voor constitutieve modellen is het tegelijkertijd goed beschrijven van het niet-lineaire afschuif- en rekgedrag. Conventionele en veel gebruikte modellen als het Phan-Thien Tanner (PTT) en Giesekus model lopen tegen dit probleem aan. Voor hoge reknelheden is het PTT model te zeer rekverslappend (strain thinning), terwijl de stationaire rekkekrmmen voor het Giesekus model zelfs de verkeerde vorm heeft. Schoonen introduceerde in 1998 het Feta model, dat meer flexibiliteit heeft in de onafhankelijke beschrijving van rek en afschuiving. Voor de stroming van polymere oplossingen in een cross-slot geometrie voorspelt het model de spanningen inderdaad beter. Echter, als nadelen heeft het model een te hoog eerste normaalspanningsverschil, het vertoont geen overshoot bij opstartstromingen in afschuiving en voorspelt geen biaxiale rekviscositeit. Het Pom-Pom model, geïntroduceerd door McLeish en Larson ook in 1998, is te beschouwen als een doorbraak op het gebied van de kwantitatieve reologische beschrijving van polymere smelten. We hebben de originele vergelijkingen (in differentiaalvorm) aangepast om drie duidelijke nadelen te vermijden: de stationaire rekviscositeiten vertoonden discontinuïteiten, de hulpvariabele in de oriëntativeringelijking kon ongelimiteerd groeien voor hoge reknelheden en het model voorspelde geen tweede normaalspanningsverschil in afschuiving en planaire
Samenvatting

Het resulterende eXtended Pom-Pom (XPP) model blijkt voor zowel lage (LDPE) als hoge-dichtheid polyetheen (HDPE) voor een breed scala aan reologische stromingen de experimentele data kwantitatief te kunnen beschrijven. Vervolgens zijn de numerieke resultaten voor de PTT, Giesekus en XPP modellen vergeleken met experimentele data voor een LDPE smelt in stromingen met een combinatie van afschuiving en rek, de zogenaamde inhomogene, complexe stromingen ofwel prototype industriële stromingen. Drie typische planaire stromingen zijn hiervoor gebruikt: de contractiestroming, de stroming rond een cilinder en de stagnatiestroming in een cross-slot geometrie. Snelheden zijn gemeten met behulp van een particle tracking techniek, spanningen door middel van stromingsgeïnduceerde dubbele breking. Als numeriek gereedschap is de Discrete Elastic Viscous Stress Splitting (DEVSS) techniek gebruikt in combinatie met de Discontinuous Galerkin (DG) methode, geïmplementeerd in een eindige-elementen pakket. Deze methode is voor zowel twee- als drie-dimensionale geometriën geschikt, is nauwkeurig, robuust en efficiënt wat betreft het gebruik van meerdere relaxatietijden. Alhoewel de techniek gevoelig is voor convergentieproblemen, vertonen wat dit probleem betreft stabielere methodes, die bijvoorbeeld gebruik maken van Streamline Upwind/Petrov Galerkin (SUPG), meer problemen met geometrische singulariteiten. Eventuele convergentieproblemen treden op afhankelijk van de structuur van het gebruikte constitutief model, het reologisch gedrag (dat samenhangt met de keuze van parameters in het constitutief model), de mesh en de tijdstap. Een kleine wijziging in de structuur van het eXtended Pom-Pom model, zoals voorgesteld door Van Meerveld (2001), zorgt voor een sterk verhoogde stabiliteit.

Van de drie onderzochte modellen laat het XPP model de beste overeenkomst zien tussen berekeningen en experimenten in alle drie de geometriën. De verschillen tussen de modellen worden voornamelijk duidelijk in gebieden met aanzienlijke rek. Dit maakt de contractiestroming, alhoewel het meest intensief onderzocht, tot een minder geschikte stromingsgeometrie voor het testen van constitutieve modellen. In de experimentele toegankelijke zone is er amper sprake van het aanspreken van het niet-lineaire rekgedrag van de modellen. De rekcomponent in het stagnatiepunt van een cross-slot geometrie is veel hoger en deze stroming is discriminerender ten opzichte van verschillende modellen en dus idealer.

Al met al ligt er nu een goede basis voor het modelleren van viscoelastische stromingen van polymere smelten: een betrouwbaar constitutief model én een nauwkeurige, robuuste en efficiënte numerieke methode. Er is echter nog genoeg ruimte voor verbeteringen in beide aspecten van de modellering.
Dankwoord

Na vier jaar van onderzoek, ligt het resultaat dan eindelijk op papier voor me. De spreekwoordelijke laatste loodjes waren inderdaad vrij zwaar, vooral in mentaal opzicht. Gelukkig had ik de hulp en ondersteuning van een aantal mensen, die ik bij deze dan ook wil bedanken.

Allereerst mijn copromotor en dagelijkse begeleider Gerrit Peters, bij wie altijd de deur openstaat en vaak ter plekke een gaatje in zijn agenda wist te vinden. Hierdoor konden menige inhoudelijke discussie vrij snel worden gehouden, wat voor mij een heel prettige manier van samenwerken was. Daarnaast wil ik ook mijn promotoren Frank Baaijens en Han Meijer bedanken voor de vrijheid en ondersteuning die ze me hebben gegeven tijdens dit promotieproject, congressen en projectbijeenkomsten. Niet in de minste plaats gaat mijn dank uit naar Arjen Bogaards, die eerst met zijn afstudeerwerk en daarna als collega en 'sparringpartner' in de regelmatige numerieke discussies een grote bijdrage heeft geleverd aan dit promotieproject. Verder nog alle (oud-)collega’s die me hebben geholpen met alle SEPRAN, LATEX, Matlab en anderszins PC-gerelateerde problemen. Marc Mussaeus wil ik bedanken voor het brainstormen over de kaft, en Fleur Flohil voor de eerste en belangrijkste aanzet tot de uiteindelijke versie daarvan.

Naast het boekje en project zelf, zijn de broodnodige sociale activiteiten van cruciaal belang geweest voor de gemoedsrust en stressontlading. (Oud-)kamergenoten bedankt voor de ontspannende en prettige werksfeer: tijdens momenten dat het wetenschappelijk af en toe wat minder voor de wind ging, kwam ik dankzij jullie toch met plezier naar mijn werk. Zaalvoetballers en squashpartners bedankt voor de stressuitdrijvende trainingen en wedstrijden. Familie en vrienden bedank ik voor het delen van de passie voor film en muziek, de gezellige avonden, kampeerwekeinden, en discussies over de zin van het leven en andere filosofische overpeinzingen.

Nog een keer extra wil ik mijn ouders bedanken. Zij hebben me in al die jaren altijd goed weten te steunen en motiveren. Tevens staan ze op de meest onmogelijke momenten voor me klaar.

En als laatste dan natuurlijk Amor. Zij weet uit eigen ervaring wat die laatste maanden inhielden en kon daar dus begrip voor opbrengen. Ook heeft zij ondanks alles de hoop voor ons tweeën niet verloren. Nu is de tijd dan eindelijk aangebroken om wat meer samen door te brengen. ¡Ik ben er aan toe en heb er zin in!

Wilco Verbeeten.
Wilco Verbeeten (1972) studied Mechanical Engineering at the Eindhoven University of Technology, the Netherlands. He received his Master’s degree in August 1996 on the application of spectral elements to multi-mode viscoelastic flows. After a short break working for the hydraulics company Rexroth in Bethlehem, Pennsylvania, USA, he returned to the Eindhoven University of Technology. In April 1997, he started working in the Materials Technology group of Prof.s.dr ir. Frank Baaijens and Prof.s.dr ir. Han Meijer, resulting in this thesis. This work falls within the European BRITE-Euram project Advanced Rheological Tool in collaboration with Dow Benelux N.V., CEMEF (a research laboratory of the Ecole des Mines de Paris), University of Cambridge, Institut für Kunststofftechnologie (an institute of Stuttgart University), DSM Research, BASF A.G. and Polyflow S.A.

Computational Polymer Melt Rheology
The processing of polymer materials has a large influence on the mechanical and optical properties of the end product. For instance, dimensional stability in precision injection moulding or yield strength and Young’s modulus during film blowing are affected by the viscoelastic properties of the polymer melt. In turn, the rheological behaviour is related to specific molecular structures and molecular weight distribution. Therefore, the design of new polymers and processing devices would benefit from predictive modelling of the viscoelastic behaviour of polymer melts at realistic processing conditions. This requires robust numerical analysis tools and reliable constitutive models which are able to quantitatively capture the polymer melt rheology. In this thesis, constitutive models for, primarily, commercial polyethylene melts are analyzed. After implementation of these models in a finite element program, a combined numerical/ experimental analysis is carried out. A quantitative agreement between experimental data and numerical results is obtained, both in well-defined rheological experiments as well as two- and three-dimensional inhomogeneous prototype industrial flows.