Chapter 5. Flow properties of dendrimers under shear

5.1. Introduction

The flow of incompressible Newtonian fluids can be characterised by the material constants of density \( \rho \) and viscosity \( \eta \). In the case of macromolecular melts that exhibit non-Newtonian behaviour, more complex functions have to be used to describe their flow. The rheological properties of molecular melts are typically analysed using standard material functions such as the shear viscosity and the first and second normal stress coefficients (see Chapter 4). In general, the flow properties of complex systems depend on the strain rate, frequency, time and other variables. This work concentrates on the steady-state flow properties of polymeric melts under shear, therefore the material functions depend only on the shear rate.

To characterize the rheological properties of dendrimer and linear chain polymer melts from the trajectories obtained in the NEMD simulations, the shear viscosity \( \eta(\dot{\gamma}) \), the first \( \Psi_1(\dot{\gamma}) \), and second \( \Psi_2(\dot{\gamma}) \) normal stress coefficients were derived. All material functions are expressed in terms of the components of the pressure tensor given by:

\[
P = \begin{pmatrix}
P_{xx} & P_{xy} & P_{xz} \\
P_{yx} & P_{yy} & P_{yz} \\
P_{zx} & P_{zy} & P_{zz}
\end{pmatrix}
\]  

(5.1)

The atomic pressure tensor can be calculated using the virial theorem (Edberg et al. 1986; Edberg et al. 1987):

\[
P^{\alpha \nu} = \left\{ \sum_{i=1}^{N} \sum_{\alpha=1}^{N_a} \frac{p_{i\alpha}}{m_{i\alpha}} \right\} - \frac{1}{2} \sum_{i=1}^{N} \sum_{\alpha=1}^{N_a} \sum_{j=1}^{N} \sum_{\beta=1}^{N_a} r_{i\alpha j\beta} \mathbf{F}_{i\alpha j\beta} - \sum_{i=1}^{N} \sum_{\alpha=1}^{N_a} \sum_{\beta=1}^{N_a} r_{i\alpha\beta} \mathbf{F}_{i\alpha\beta} \right\}
\]  

(5.2)

where \( r_{i\alpha j\beta} \) is the separation between bead \( \alpha \) in molecule \( i \) and bead \( \beta \) in molecule \( j \), \( p_{i\alpha} \) is the atomic momentum, and \( \mathbf{F}_{i\alpha j\beta} \) is the force acting on the bead \( \alpha \) in molecule \( i \) due to bead \( \beta \) in molecule \( j \). The first sum in the equation calculates the kinetic part of the pressure tensor, whereas the second and third sums correspond to the intermolecular and intramolecular virial, respectively. The angled brackets \( \langle \rangle \) denote a time average over
the nonequilibrium steady state. In the case of the central two-body interactions between
the interacting beads, the atomic pressure tensor is symmetric at all times.

Alternatively, the molecular pressure tensor can be derived as (Edberg et al. 1986;
Edberg et al. 1987; Morriss and Evans 1991):

\[
P^M_{ij} = \left\{ \sum_{i=1}^{N} \frac{p_i p_j}{M_i} - \frac{1}{2} \sum_{j=1}^{N} \sum_{\alpha=1}^{N} \sum_{\beta=1}^{N} r_{ij} F_{\alpha j \beta} \right\}
\] (5.3)

In this case \( p_i \) is the molecular momentum, whereas \( r_{ij} \) is the distance between the
centre of mass of molecules \( i \) and \( j \). In contrast to the atomic representation, the
instantaneous values of the molecular pressure tensor may not be symmetric at every
time. This effect is related to the fact that the total force with which one molecule
interacts with another does not have to be central (parallel to the vector connecting their
centres of mass). However, the time average of the molecular pressure tensor should be
symmetric and equal to the atomic pressure tensor.

At the implementation testing stage, for all systems at steady state a check was made to
ensure that calculated atomic and molecular pressure tensors yielded the same results.
Later, to decrease the simulation time, only the molecular pressure tensor was
calculated.

The hydrodynamic pressure of the simulated systems can be calculated as a trace of the
pressure tensor:

\[
p(\dot{\gamma}) = \frac{1}{3} Tr\left(P^M\right) = \frac{1}{3} \left(P_{xx}^M + P_{yy}^M + P_{zz}^M\right)
\] (5.4)

The non-Newtonian viscosity for planar shear flow is calculated as:

\[
\eta(\dot{\gamma}) = \left\{ \frac{P_{yy}^M + P_{yx}^M}{2\dot{\gamma}} \right\}
\] (5.5)

whereas the first and second normal stress coefficients are obtained from:

\[
\Psi_1(\dot{\gamma}) = \left\{ \frac{P_{yy}^M - P_{xx}^M}{\dot{\gamma}^2} \right\}
\] (5.6)

\[
\Psi_2(\dot{\gamma}) = \left\{ \frac{P_{zz}^M - P_{yy}^M}{\dot{\gamma}^2} \right\}
\] (5.7)
The strain rate dependence of these functions for various dendrimer systems will be presented in the following sections. The flow behaviour of dendrimer melts will be compared to the behaviour of linear chain molecules at the same steady state. Also the effect of branching and molecular architecture on the flow curves will be discussed.

5.2. Simulated systems

In Chapter 4, the coarse-grained model of dendrimers and linear chain polymers applied in this study has been described. Also, nonequilibrium molecular dynamics techniques have been discussed. To perform simulations of dendrimer and linear chain melts under shear, samples of dense fluids have been prepared. Collections of dendrimers with trifunctional end groups \((f = 3)\), spacers composed of two beads \((b = 2)\), and generations 1 - 4 (D2G1, D2G2, D2G3, D2G4) were constructed at low density. The sample consisted of 256 molecules in the case of D2G1 and 125 molecules for higher generations with 19, 43, 91, and 187 beads per molecule for generations 1 to 4, respectively. The systems of dendrimers of each generation were matched with the corresponding systems composed of linear chain polymers of the same size. The total number of beads in the simulation box varied from approximately 5000 to 25000. The isotropic compression, i.e. the SLLOD algorithm with equal negative diagonal elements of the strain rate tensor, was applied to achieve the desired high density of the melt: typically 0.84. Figure 5.1 shows an example of an initial configuration for the melt of dendrimers of generation 4.

Most simulations were performed at constant density of \(\rho = 0.84\) and temperature \(T = 1.25\). At this thermodynamic state point the monomer WCA fluid is a liquid. It suggests that under the same conditions the molecular fluid composed of the WCA beads would also remain in the liquid state. Similar range of parameters was assumed by other workers in the field (Kröger and Hess 2000; Daivis et al. 2003). In the case of constant pressure simulations, the equilibrium pressure was maintained under shear. The equations of motion of the atoms were integrated with a time step \(\Delta t = 0.001\) in reduced LJ units using a fifth-order Gear predictor corrector differential equation solver. This choice of a time step was found to be sufficiently small to ensure that the results of
the simulation did not depend on it. For simulations of shear flow, wide ranges of strain rates were taken into account so that the transition between the Newtonian and non-Newtonian regimes could be captured. In Table 5.1 the summary of all simulations performed in this study is presented.

Figure 5.1. Initial configuration of the dendrimers of generation 4 (D2G4). Beads of the same colour constitute a single molecule.

During the initial several million steps of every simulation, the system was allowed to relax and reach the thermodynamic steady state (or equilibrium when no external field was imposed). Figure 5.2 shows the typical convergence of the hydrodynamic pressure with time to the steady state value. The steady state was determined by observing the time evolution of various thermodynamical variables, like atomic temperature (the molecular one is constrained), pressure etc. After this time the macro- and microscopic properties were accumulated for further analysis.

A block averaging method was applied to derive values and statistical uncertainties of the physical properties of interest. To exclude from the analysis highly correlated values, as well as to improve the performance of the program (decrease an execution
time), the instantaneous values were calculated every 20\textsuperscript{th} integration time step. These were average over blocks of 50000 time steps. Each simulation was composed of at least 20 – 30 of such blocks. The mean value of the block averages was assumed to be the magnitude of the measured properties, whereas an error of the mean value is presented throughout this thesis as a statistical uncertainty.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{convergence_pressure.png}
\caption{Convergence of the pressure to the steady state value in the simulation of dendrimers of generation 1 (D2G1).}
\end{figure}
### Table 5.1. Summary of all simulations performed in the course of this study.

<table>
<thead>
<tr>
<th>System</th>
<th>Number of molecules</th>
<th>Ensemble</th>
<th>Thermodynamic state</th>
<th>Shear rates</th>
</tr>
</thead>
<tbody>
<tr>
<td>D2G1</td>
<td>256</td>
<td>NVT</td>
<td>( \rho = 0.84 )</td>
<td>0.0005 – 0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NpT</td>
<td>( T = 1.25 )</td>
<td></td>
</tr>
<tr>
<td>D2G1</td>
<td>250</td>
<td>NVT</td>
<td>( \rho = 0.4 - 1.1 )</td>
<td>0</td>
</tr>
<tr>
<td>(equilibrium)</td>
<td></td>
<td></td>
<td>( T = 0.8, 1.25 )</td>
<td></td>
</tr>
<tr>
<td>D2G2</td>
<td>125</td>
<td>NVT</td>
<td>( \rho = 0.84 )</td>
<td>0.001 – 0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NpT</td>
<td>( T = 1.25 )</td>
<td></td>
</tr>
<tr>
<td>D2G3</td>
<td>125</td>
<td>NVT</td>
<td>( \rho = 0.84 )</td>
<td>0.001– 0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NpT</td>
<td>( T = 1.25 )</td>
<td></td>
</tr>
<tr>
<td>D2G4</td>
<td>125</td>
<td>NVT</td>
<td>( \rho = 0.84 )</td>
<td>0.0005 – 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NpT</td>
<td>( T = 1.25 )</td>
<td></td>
</tr>
<tr>
<td>19-mers</td>
<td>216</td>
<td>NVT</td>
<td>( \rho = 0.84 )</td>
<td>0.001 – 0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( T = 1.25 )</td>
<td></td>
</tr>
<tr>
<td>43-mers</td>
<td>125</td>
<td>NVT</td>
<td>( \rho = 0.84 )</td>
<td>0.001 – 0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( T = 1.25 )</td>
<td></td>
</tr>
<tr>
<td>91-mers</td>
<td>125</td>
<td>NVT</td>
<td>( \rho = 0.84 )</td>
<td>0.001 – 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( T = 1.25 )</td>
<td></td>
</tr>
<tr>
<td>187-mers</td>
<td>125</td>
<td>NVT</td>
<td>( \rho = 0.84 )</td>
<td>0.001 – 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( T = 1.25 )</td>
<td></td>
</tr>
<tr>
<td>D2G2 solutions:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>33%</td>
<td>27 + 2322</td>
<td>NpT</td>
<td>( p = 5.42 )</td>
<td>0.001 – 0.2</td>
</tr>
<tr>
<td>50%</td>
<td>64 + 2752</td>
<td></td>
<td>( T = 1.25 )</td>
<td></td>
</tr>
<tr>
<td>67%</td>
<td>64 + 1376</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D2G2+43-mers blends:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3:1</td>
<td>32 + 96</td>
<td>NpT</td>
<td>( p = 5.42 )</td>
<td>0.001 – 0.2</td>
</tr>
<tr>
<td>1:1</td>
<td>64 + 64</td>
<td></td>
<td>( T = 1.25 )</td>
<td></td>
</tr>
<tr>
<td>1:3</td>
<td>96 + 32</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5.3. Viscosity

In Figure 5.3, the non-Newtonian viscosity for the dendrimers of generation 1 to 4 is presented. Systems composed of the linear chains of the mass corresponding to the mass of dendrimers were also simulated, and the flow curves are shown in the bottom panel. Various analytical functions were proposed to describe the dependence of viscosity on the shear rate. In Figure 5.3 the Carreau-Yasuda model (Bird et al. 1987) of the form:

\[ \eta = \eta_0 \left[ 1 + (\dot{\gamma} \lambda)^2 \right]^p \]  \hspace{1cm} (5.8)

where \( \eta_0 \) is the zero shear viscosity, \( \lambda \) is a time constant, and \( p \) is the power law exponent, was fitted to the data points. The fitting parameters are presented in Table 5.2.

<table>
<thead>
<tr>
<th></th>
<th>( \eta_0 )</th>
<th>( \lambda )</th>
<th>( p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>D2G1</td>
<td>9.12(12)</td>
<td>63(14)</td>
<td>0.147(18)</td>
</tr>
<tr>
<td>D2G2</td>
<td>16.93(23)</td>
<td>323(58)</td>
<td>0.140(11)</td>
</tr>
<tr>
<td>D2G3</td>
<td>25.63(44)</td>
<td>480(100)</td>
<td>0.165(20)</td>
</tr>
<tr>
<td>D2G4</td>
<td>41.8(11)</td>
<td>1500(430)</td>
<td>0.152(18)</td>
</tr>
<tr>
<td>19-mers</td>
<td>12.49(20)</td>
<td>165(40)</td>
<td>0.172(23)</td>
</tr>
<tr>
<td>43-mers</td>
<td>27.58(24)</td>
<td>731(60)</td>
<td>0.209(8)</td>
</tr>
<tr>
<td>91-mers</td>
<td>77.63(42)</td>
<td>2406(94)</td>
<td>0.296(7)</td>
</tr>
</tbody>
</table>

Table 5.2. Parameters of the Carreau-Yasuda model fitted to the viscosity versus shear rate dependence observed in the NVT simulations (\( \rho = 0.84, T = 1.25 \)).

All of the systems studied exhibit the transition from the Newtonian regime for small strain rates to the non-Newtonian regime for high strain rates (see Chapter 4). The flow curves can be characterised by the zero shear viscosity:

\[ \eta_0 = \lim_{\dot{\gamma} \to 0} \eta , \]  \hspace{1cm} (5.9)

the value of an exponent in the power law region:

\[ \eta \propto \dot{\gamma}^{-n} , \]  \hspace{1cm} (5.10)

and the cross-over shear rate \( \dot{\gamma}_0 \) above which the viscosity becomes shear dependent.

Although the absolute values of the viscosity depend on the actual thermodynamic state point, the flow curves can be superimposed on one master curve (Bird et al. 1987;
McCabe et al. 2002). Therefore, though the simulations were performed only at one single thermodynamic point (single density, temperature), the results obtained are characteristic for the particular molecules composing the fluid.

Figure 5.3. Dependence of shear viscosity on strain rate for dendrimers (top panel) and linear chains of equivalent molecular weight (bottom panel) observed in the NVT simulations ($\rho = 0.84, T = 1.25$). Solid lines represent fitting with the Carreau-Yasuda model. Arrows indicate the approximate onset of shear thinning.
There are several ways in which the zero shear viscosity of a fluid can be obtained through molecular dynamics (MD) simulations (Evans and Morriss 1990). The most commonly used method is to perform Green-Kubo equilibrium MD simulations (Allen and Tildesley 1987) and compute the zero shear viscosity from the stress autocorrelation function. Alternatively, a less widely used method is to compute the shear viscosity as a function of the strain rate via NEMD simulation, and then extrapolate to zero strain rate to extract $\eta_0$. This method was used in this work because it is more computationally efficient. However, the accurate determination of the melt viscosity at very small shear rates can be a tedious and computationally expensive task, especially for systems composed of large molecules. The values obtained are also often associated with a large degree of uncertainty. Several extrapolation schemes have been proposed to derive the value of $\eta_0$ from the flow curve. These include fitting of linear:

$$\eta = \eta_0 - A\dot{\gamma}$$ \hspace{1cm} (5.11)

or quadratic:

$$\eta = \eta_0 - B\dot{\gamma}^2$$ \hspace{1cm} (5.12)

functions (Ryckaert et al. 1988; Pierleoni and Ryckaert 1991) to the values of the viscosity obtained at the smallest shear rates. The latter dependence is also known as the retarded motion expansion (Bird et al. 1987) for a third order fluid. Alternatively, a square root dependence was proposed (Evans et al. 1984):

$$\eta = \eta_0 - C\dot{\gamma}^{1/2}$$ \hspace{1cm} (5.13)

for the asymptotic behaviour of the fluid. Recently it was demonstrated (Ge et al. 2003) that the exponent dependence of the transport properties of simple fluids is a linear function of density and temperature. Such dependence has yet to be determined for more complex molecular fluids. The dependence of the inverse viscosity on the shear stress (Vinogradov and Malkin 1980):

$$\eta^{-1} = \eta_0^{-1} - DP_{xy}$$ \hspace{1cm} (5.14)

can also be used to estimate $\eta_0$. The zero shear viscosity was determined as the average of the values obtained using all four of these extrapolation schemes. Details of this averaging procedure are given elsewhere (Berker et al. 1992; Kröger and Hess 2000). The quality of the fit to the simulation data for these various extrapolation schemes is compared in Figure 5.4 for a generation 1 dendrimer.
Figure 5.4. Comparison of the various extrapolation schemes used to obtain the zero-shear viscosity with simulation data (●) for a generation 1 dendrimer: 
(a) $\eta = \eta_0 - A\dot{\gamma}$ (-----) $\eta = \eta_0 - B\dot{\gamma}^2$ (----), $\eta = \eta_0 - C\dot{\gamma}^{1/2}$ (-------) 
(b) $\eta^{-1} = \eta_0^{-1} - DP_{xy}$. The estimated values of zero shear viscosity are 9.22, 9.09, 9.42, and 9.24, respectively. The average value is 9.24.

Figure 5.5 shows the dependence of the zero shear viscosity on the molecular mass for dendrimers and linear chain molecules. The results for the linear chain molecules were combined with the NEMD results reported elsewhere (Kröger and Hess 2000). For the
short chains, in agreement with the Rouse model (Doi and Edwards 1986), an almost linear dependence \( \eta_0 \propto M^{0.95} \) was observed, which for the larger molecules tends to a power law with the exponent larger than 3 (reptation regime). In contrast, for dendrimer melts a similar crossover has not been observed. Instead, the relationship satisfies a power law with a single exponent that is smaller than that for unentangled chain molecules \( \eta_0 \propto M^{0.646(2)} \). Although the results are in qualitative agreement with experimental observations (Hawker et al. 1995; Farrington et al. 1998; Uppuluri et al. 2000), the absolute value of the exponent is much smaller than the one determined experimentally (approximately 1.1). This discrepancy could be attributed to the assumptions made in the way the dendrimers are modelled (see Chapter 4). The freely-jointed beads (without constraints on the bond angles) result in molecules that are more flexible than the real ones. This means that the model dendrimer is more prone to fold upon itself when sheared in a dense melt. This could result in lower values of the shear viscosity compared to those observed in real dendrimer melts.

The exponents in the power law region were obtained from the linear region in the log-log plot of the viscosity vs. strain rate curve (Figure 5.3). Their values (plotted in Figure 5.6) as well as the zero-strain-rate viscosities for all studied systems are presented in Table 5.3. For both, dendrimers and linear polymers, the exponents in the power law region of the \( \eta \) vs. \( \dot{\gamma} \) relationship increase with molecular mass, but the increase is more rapid for linear polymers. Also the absolute values of the exponents are larger for linear chain molecules. This is in agreement with the results obtained in other studies (Kröger et al. 1993; Xu et al. 1995; Xu et al. 1997), but it is in contrast with more recent results (Kröger and Hess 2000), where invariant exponents were observed. However, it should be noted that the determination of these exponents is extremely sensitive to where on the strain rate curve one assumes the power law region is valid. In the absence of a commonly accepted rule for judging the onset of the non-Newtonian region, there is some ambiguity in comparing values of exponents. Furthermore, these other studies used the atomic SLLOD equations of motion with an atomic thermostat (see Chapter 4) and simulated their fluids at a lower temperature than ours, which could also account for differences in trends. A full discussion on the merits and pitfalls of the various forms of the SLLOD algorithm and thermostatting mechanisms is given elsewhere (Travis et al. 1995b). Daivis et al. (Daivis et al. 2003) also report constant
values of the exponents, but their estimates were performed at constant pressure, in contrast to the constant volume simulations presented here.

Table 5.3. Estimated values of the zero shear viscosity $\eta_0$ and exponent $\eta \propto \dot{\gamma}^{-n}$ in the power law region (shear thinning) for dendrimers and linear chains ($\rho = 0.84$, $T = 1.25$). Statistical uncertainty (from the standard error of the fit) in the last significant digit is given in brackets.

<table>
<thead>
<tr>
<th>Mass</th>
<th>Dendrimers</th>
<th>Chain polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\eta_0$</td>
<td>$n$</td>
</tr>
<tr>
<td>19</td>
<td>9.2(3)</td>
<td>0.275(3)</td>
</tr>
<tr>
<td>43</td>
<td>17.4(9)</td>
<td>0.304(3)</td>
</tr>
<tr>
<td>91</td>
<td>26.9(1)</td>
<td>0.330(3)</td>
</tr>
<tr>
<td>187</td>
<td>43.1(2)</td>
<td>0.360(8)</td>
</tr>
</tbody>
</table>

Figure 5.5. Zero shear viscosity vs. molecular mass for dendrimers and linear chain molecules in NVT simulation ($\rho = 0.84$, $T = 1.25$). Results for chains are combined with those reported elsewhere (Kröger and Hess 2000). Lines with slope 1 (Rouse regime) and 3 (reptation regime) are fitted to the data points for linear chain molecules. A single line is fit to the data for dendrimers with a slope of 0.65.
Figure 5.6. Exponent of the viscosity vs. strain rate curve in the shear thinning region plotted against molecular weight \((\rho = 0.84, T = 1.25)\).

For dendrimers the exponent in the shear thinning region is close to \(1/3\) for all generations taken into account. The same scaling was observed in simulations of dendrimers in solution (Lyulin et al. 2000). Larger power law exponents for linear chain molecules in comparison to branched alkanes were also reported elsewhere (Daivis et al. 1992; Xu et al. 1995; Xu et al. 1997; Jabbarzadeh et al. 2003).

A direct comparison of the viscosity - strain rate curves for dendrimers with those of traditional linear chain polymers of the same size (at the same density and temperature) is shown in Figure 5.7. In all cases, when the fluid is in the Newtonian regime, the viscosity of dendrimer melts is lower than that of the linear molecules. Internal branching and the compact globular structure of dendrimers, resulting in suppression of intermolecular entanglement, are responsible for this decrease in viscosity. From the analysis of the internal structure of dendrimers under shear, it was found that the outermost branches, which might participate in entanglement, often fold back and can be found inside the molecule. Therefore, they can not interact with branches of other molecules, consequently reducing intermolecular entanglement and hence the shear
viscosity. A detailed study of the microscopic properties of dendrimers under shear will be given in the following chapter.

![Graph comparing the flow curves of dendrimers of generation 1 (top panel) and generation 2 (bottom panel) with linear chain molecules of the same size and at the same thermodynamic state point ($\rho = 0.84$, $T = 1.25$).]

Figure 5.7. Comparison of the flow curves for dendrimers of generation 1 (top panel) and generation 2 (bottom panel) with linear chain molecules of the same size and at the same thermodynamic state point ($\rho = 0.84$, $T = 1.25$).

In the non-Newtonian regime, the exponent in the power law region is always smaller for dendrimer melts in comparison to linear chain polymers, leading to lower viscosities for linear chains in comparison to dendrimers of the same molecular weight. In this case

64
the branching of dendrimers prevents the shear-induced alignment of molecules, which therefore slows the shear thinning. Similar behaviour has been reported for star-shaped molecules compared to linear chain molecules of the same mass (Daivis et al. 1992; Kioupis and Maginn 1999, 2000).

The strain rate $\dot{\gamma}_0$ at which the onset of shear thinning is observed is indicated in Figure 5.3 by arrows. It was derived as an inverse of the time constant $\lambda$ in the Carreau-Yasuda model (Equation 5.8) fitted to the experimental data. This time constant is also proportional to the rotational relaxation time $\tau_0$ of molecules composing fluids ($\lambda = 1/\tau_0$), as described in Section 3.1. The latter one increases with the size of the molecule for both dendrimer and linear chain systems. However, for the systems composed of the molecules of the same size, $\dot{\gamma}_0$ is always smaller (rotational relaxation time is larger) for linear chains than for dendrimers. This can be again explained in terms of the molecular architecture and the fact that the beads composing dendrimers are distributed closer to the molecular centre of mass than in the case of linear chains. As a result, dendrimers rotate more freely and entangle less. Figure 5.8 shows the dependence of the estimated relaxation times for dendrimers and linear chains on the molecular mass. For the linear chains they scale as $\tau_0 \propto M^{1.7}$. The Rouse theory for isolated chains predicts $\tau_0 \propto M^2$, whereas the Zimm model for dilute solutions gives $\tau_0 \propto M^{1.5}$ (Doi and Edwards 1986). reptation theory predicts $\tau_0 \propto M^3$ for concentrated solutions and melts. However, it must be noted that the size of the simulated chain polymers places them below the transition to the reptation regime. For dendrimers the characteristic relaxation time scales with the mass as $\tau_0 \propto M^{1.5}$, and the absolute values are approximately three times smaller than for corresponding linear chains of the same size. It should be noted that the estimated values carry large uncertainties due to the procedure used to obtain them, and further work would be required to decrease the statistical uncertainty.
Figure 5.8. Relaxation times for dendrimers and linear chains plotted against the molecular mass ($\rho = 0.84$, $T = 1.25$). The values were obtained from the shear rate at which onset of the shear thinning was observed.

5.4. First and second normal stress coefficients

Normal stress coefficients describe the effect of the normal stress differences exhibited by polymeric fluids. In Figure 5.9 the log-log plot of the dependence of the first normal stress coefficient on strain rate is shown. Figure 5.10 instead illustrates the second normal stress coefficient vs. strain rate. In each case the viscometric functions for dendrimers are compared to those observed in simulation of linear chain systems. For all systems the stress coefficients have large power law regions. Linear functions were fitted to the data in the power law region, and from the slope the exponents of the asymptotic dependences:

$$\Psi_1 \propto \dot{\gamma}^{-\alpha}$$  \hspace{1cm} (5.15)

and

$$|\Psi_2| \propto \dot{\gamma}^{-\beta}$$  \hspace{1cm} (5.16)

were derived. The values obtained are presented in Table 5.4. In the case of dendrimer melts, values of the $\alpha$ and $\beta$ exponents appear to be constant and do not depend on the
molecular mass. In contrast, for linear chain molecules their values increase with the size of the molecules, in agreement with observations in other studies (Kröger et al. 1993). The smaller values of the power law exponents for branched alkanes were also reported in the literature (Daivis et al. 1992).

**Table 5.4.** Estimated values of the exponents in the power law regions of the first \( (\Psi_1 \propto \dot{\gamma}^{-\alpha}) \) and second \( (|\Psi_2| \propto \dot{\gamma}^{-\beta}) \) normal stress coefficients for dendrimers and linear chains \( (\rho = 0.84, T = 1.25) \).

<table>
<thead>
<tr>
<th>Mass</th>
<th>Dendrimers</th>
<th>Chain polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \alpha )</td>
<td>( \beta )</td>
</tr>
<tr>
<td>19</td>
<td>1.089(6)</td>
<td>0.99(2)</td>
</tr>
<tr>
<td>43</td>
<td>1.099(4)</td>
<td>1.03(1)</td>
</tr>
<tr>
<td>91</td>
<td>1.099(4)</td>
<td>1.003(8)</td>
</tr>
<tr>
<td>187</td>
<td>1.065(4)</td>
<td>1.04(1)</td>
</tr>
</tbody>
</table>

The absolute values of the first and second normal stress coefficients are usually smaller for dendrimers than for linear chain molecules. A similar decrease in the normal stresses of branched polymers, compared to linear polymers, was also observed elsewhere (Jabbarzadeh et al. 2003). In Figure 5.12 the ratio \( |\Psi_2|/|\Psi_1| \) is plotted against the strain rate. For linear polymers its value is approximately 5–15% and is in agreement with experimental results for typical polymers (Bird et al. 1987). In contrast, for dendrimers this ratio is about 20%. This could be attributed to the spherical shape of the molecules and internal bond constraints, which prevent large stretching of the molecules and in turn lead to smaller differences between the diagonal elements of the stress tensor.
Figure 5.9. First normal stress coefficient vs. strain rate for dendrimers and linear chain molecules of equivalent molecular weight ($\rho = 0.84$, $T = 1.25$).
Figure 5.10. Second normal stress coefficient vs. strain rate for dendrimers and linear chain molecules of equivalent molecular weight ($\rho = 0.84$, $T = 1.25$).
5. FLOW PROPERTIES OF DENDRIMERS UNDER SHEAR

![Graphs showing ratios of second to first normal stress coefficient vs. strain rate for dendrimers and linear chain molecules of equivalent molecular weight (ρ = 0.84, T = 1.25).]

**Figure 5.11.** Ratio of the second to first normal stress coefficient vs. strain rate for dendrimers and linear chain molecules of equivalent molecular weight (ρ = 0.84, T = 1.25).

**5.5. Equation of state**

The dependence of the pressure of a dendrimer system on density has been analysed by performing a series of simulations of dendrimers of generation 1 (D2G1) at various densities. The simulations were performed at equilibrium and at two different temperatures. The results are presented in Figure 5.12 where the pressure is plotted against the system density. Analogous series of simulations were performed for the
system composed of linear chain polymers (19-mers), and the results were found identical in spite of molecular architecture. Therefore, it can be stated that the equation of state depends only on the nature of beads composing the molecules and a type of interactions between them. For the coarse-grained model applied in this study (see Chapter 5), the repulsive WCA interactions dominate the properties of the low density system at equilibrium.

With decreasing temperature the $p/k_B T$ ratio increases for all densities and approaches the equation of state of hard spheres also shown in Figure 5.12 (Wu and Sadus 2005).

Some work on equations of state for polymer chains, polymer stars and dendritic polymers (solutions dilute and semi-dilute) has been reported earlier by Lue et al. (Lue and Prausnitz 1997; Lue 2000a; Patrickios and Lue 2000).

![Figure 5.12. Equation of state for dendrimers D2G1 at temperatures $T = 0.8$ and $T = 1.25$. For comparison also results for hard spheres of radius 1 (Wu and Sadus 2005) are shown.](image_url)
5.6. Pressure

The pressure of the systems undergoing shear flow, calculated from the diagonal elements of the molecular pressure tensor, is shown in Figure 5.13. Unlike simple fluids, which have been shown to display a simple power law behaviour (Ge et al. 2003):

\[ p = p_0 + b\dot{\gamma}^m, \]  

(5.17)
molecular fluids exhibit a more complex behaviour. The pressure first decreases as a function of \( \dot{\gamma} \) down to a minimum, beyond which it increases with power law behaviour. This effect is more pronounced in the case of linear chain systems, whereas dendrimer melts behave more like systems of soft spherical molecules. A similar drop of pressure with the shear rate was observed earlier in the NEMD simulations of linear chain polymer melts (Kröger et al. 1993; Xu et al. 1995). It was also shown that this effect become less significant with the increase of the degree of branching of the molecules (Khare et al. 1997; Jabbarzadeh et al. 2003). The results obtained for dendrimer are in agreement with this trend.

A power function \( (p \propto b\dot{\gamma}^m) \) was fitted to the data points in the high strain rate region, and the obtained parameters are reported in Table 5.5. The equilibrium pressure \( (p_0) \) was determined by extrapolation of the low strain rate data to zero strain rate.

Table 5.5. Estimated parameters in the shear dependent pressure of the melt given by Equation 5.17.

<table>
<thead>
<tr>
<th>Mass</th>
<th>Dendrimers</th>
<th>Linear polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( p_0 )</td>
<td>( b )</td>
</tr>
<tr>
<td></td>
<td>( p_0 )</td>
<td>( b )</td>
</tr>
<tr>
<td>19</td>
<td>5.546(2)</td>
<td>16.3(1)</td>
</tr>
<tr>
<td>43</td>
<td>5.420(4)</td>
<td>31.5(1)</td>
</tr>
<tr>
<td>91</td>
<td>5.368(3)</td>
<td>74.8(9)</td>
</tr>
<tr>
<td>187</td>
<td>5.350(3)</td>
<td>156(2)</td>
</tr>
<tr>
<td></td>
<td>5.410(1)</td>
<td>25(11)</td>
</tr>
</tbody>
</table>
Figure 5.13. Molecular pressure of melts composed of dendrimers and linear chain molecules plotted against the strain rate from the simulation in the NVT ensemble ($\rho = 0.84$, $T = 1.25$).
5.7. Constant pressure simulations

In most cases real rheology experiments are performed under conditions of constant pressure and constant temperature. The studied fluids have at least one free surface in contact with the atmosphere. The results presented in the preceding chapters were obtained in simulations performed at constant volume (isochoric-isothermal ensemble). The temperature and bead concentration (density) of the systems were kept at constant values $T = 1.25$ and $\rho = 0.84$. Though composed of identical beads, systems behaved differently under shear. For example, the hydrostatic pressure of the systems even at equilibrium differs between systems composed of molecules of different size or architecture (see Table 5.5). The effect can be explained by taking into account the way the connection between the neighbouring beads in the chain is modelled. The FENE potential combined with WCA interactions result in an average bond length shorter that the average separation between nearest non-bonded neighbours in the fluid. Therefore the volume occupied by the molecule composed of the $N$ beads is smaller then the volume occupied by the same number of beads but without FENE interactions between them. This feature of the model results in the decrease of the pressure with increasing size of the molecules composing the melt.

An even more significant effect of performing simulations in the NVT ensemble can be seen in the dependence of the pressure on the strain rate in the case of fluids away from equilibrium. Different internal architectures of the molecules lead to different responses of the system to the deformation (see Figure 5.13). At high strain rates an increase of the pressure can be observed. For dendrimers this seems to be a simple exponential growth, whereas for linear polymers a drop in pressure is observed before this increase at higher strain rates. The latter effect becomes more pronounced for large molecules.

It is also believed that the increase of the shear viscosity (shear thickening) at high strain rates for systems modelled using molecular SLLOD, not observed in real experiments, is a property of the NVT ensemble (Daivis and Evans 1994). The NVT ensemble also creates difficulties in estimating the shear thinning rate in the non-Newtonian regime.
All the size and structure related influences on the thermodynamic properties derived from the simulations, though in most cases not large, make it difficult to compare results of the simulations with experimental data. This can be also an obstacle in quantitative comparison of systems composed of molecules with different sizes or architectures. Maintaining and controlling hydrostatic pressure becomes even more important in simulation of dendrimers in solution at different concentrations or blends of different polymers.

To study the effect of performing simulations at constant pressure, the simulations of dendrimers and some linear chain systems were repeated using the NPT-SLLOD algorithm (as described in Chapter 4).

Dendrimers of generation 1 to 4 and linear chain polymers of corresponding size were taken under consideration. All simulations were performed at constant pressure $p = 5.42$, i.e. the pressure of the D2G2 system at equilibrium. The coupling of the systems with a barostat introduces additional oscillations of the volume of the simulation box. However, in each case the value of the damping factor $Q$ was chosen in such a way as to ensure that the effect on the molecular dynamics is minimised. A typical value of $Q$ is 500. The melts in these simulations were therefore allowed to relax (expand or contract) to compensate the flow-induced changes in the pressure.

Figure 5.14 shows the dependence of pressure on strain rate for dendrimers of generation 2 and corresponding linear chains. This is coupled with the changes of density of the simulated systems, shown in Figure 5.15.
Figure 5.14. A comparison of the pressure versus strain rate for D2G2 and 43-mers observed in the NVT ($\rho = 0.84$, $T = 1.25$) and NpT ($\rho = 5.42$, $T = 1.25$) simulations.

Figure 5.15. Changes of density with the strain rate of dendrimers and linear chains for constant pressure simulations ($\rho = 5.42$, $T = 1.25$).
Figure 5.16 shows the dependence of the viscosity on the strain rate for dendrimers of generation 1 to 4. In Figure 5.17 the same curves for dendrimers of generation 2 and 3 are compared to those obtained from the simulations in the NVT ensemble. In each case the flow curves do not change much for small values of the strain rate; the zero shear viscosity is the same, and so is the strain rate at which onset of the shear thinning occurs. However, the results are different in the non-Newtonian regime. As expected, the shear thickening at high strain rates is not observed any more in the case of NpT. Instead, a monotonic decrease of the viscosity is observed. Consequentially the rate of shear thinning changes and is found to be larger than estimated from the flow curves obtained in the NVT simulations. For dendrimers under NVT simulation conditions, the rate of shear thinning in the non-Newtonian regime varied from 0.28 for D2G1 to 0.36 for D2G4. At constant pressure their values vary in a much narrower range from 0.37 to 0.39.

![Flow curves for dendrimers of generation 1 to 4 derived from the constant pressure simulations (\(\rho = 5.42, T = 1.25\)).](image)

The fact that shear thickening observed earlier in the NVT simulations (see Section 5.3) is absent when the isobaric ensemble is considered indicates that this effect is related to the thermodynamical ensemble rather than being an artefact of the molecular SLODD algorithm. Similar absence of shear thickening due to changing thermodynamic
ensemble from NVT to NpT was reported in simulations of decane under shear (Daivis and Evans 1994; Mundy et al. 1995) and other linear polymer melts (Daivis et al. 2003).

In Figure 5.18 and Figure 5.19, the first and second normal stress coefficients for selected dendrimer systems are compared to the relationships observed in NVT simulations. In every case the slope of the function in the linear regime (high strain rates) is larger than reported earlier for systems kept at constant density. The values of these exponents obtained from the linear fits to the log-log plots are presented in Table 5.6. The first normal stress coefficients typically decrease with the exponent ~1.27 (it was ~1 in NVT), whereas the slope of the second normal stress coefficients is approximately 1.23 (in contrast to ~1 for NVT).

Except for the highest shear rates, the microscopic properties of the simulated systems like radius of gyration, molecular alignment and rotation, distribution of mass, etc. are not affected by the change from isochoric to isobaric ensemble.

Table 5.6. Values of the exponents in the power law regions of the first and second normal stress coefficients for dendrimer systems at constant pressure ($\rho = 5.42$, $T = 1.25$) and constant volume ($\rho = 0.84$, $T = 1.25$, as in Table 5.4).

<table>
<thead>
<tr>
<th></th>
<th>NpT</th>
<th></th>
<th>NVT</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha$</td>
<td>$\beta$</td>
<td>$\alpha$</td>
<td>$\beta$</td>
</tr>
<tr>
<td>D2G1</td>
<td>1.207(6)</td>
<td>1.08(2)</td>
<td>1.089(6)</td>
<td>0.99(2)</td>
</tr>
<tr>
<td>D2G2</td>
<td>1.270(5)</td>
<td>1.23(2)</td>
<td>1.099(4)</td>
<td>1.03(1)</td>
</tr>
<tr>
<td>D2G3</td>
<td>1.301(3)</td>
<td>1.23(1)</td>
<td>1.099(4)</td>
<td>1.003(8)</td>
</tr>
<tr>
<td>D2G4</td>
<td>1.278(6)</td>
<td>1.26(2)</td>
<td>1.065(4)</td>
<td>1.04(1)</td>
</tr>
</tbody>
</table>
Figure 5.17. Comparison of the viscosity vs. strain rate dependencies for D2G2 and D2G3 obtained in NVT ($\rho = 0.84$, $T = 1.25$) and NpT ($\rho = 5.42$, $T = 1.25$) simulations.
Figure 5.18. Comparison of the first normal stress coefficient for D2G2 and D2G3 observed in NVT ($\rho = 0.84$, $T = 1.25$) and NpT ($\rho = 5.42$, $T = 1.25$) simulations.
Figure 5.19. Comparison of the second normal stress coefficient for D2G2 and D2G3 observed in NVT ($\rho = 0.84$, $T = 1.25$) and NpT ($\rho = 5.42$, $T = 1.25$) simulations.
5. FLOW PROPERTIES OF DENDRIMERS UNDER SHEAR

5.8. Mixtures

5.8.1. Dendrimers in solution

A primary objective of this work is to study the rheology of dendrimers in the melt. In addition, a series of simulations of dendrimers in solution were performed to determine the influence of solvents on the flow properties and conformation of molecules under shear. The solvent molecules were included explicitly in the model as spherical WCA beads, the same as those used to construct dendrimer molecules. Interactions between solvent molecules and dendrimers are also maintained unchanged, i.e. no interaction preferences between different components of the system were incorporated. Therefore, in accordance with the rest of this study, the main interest is in the conformational changes of the system caused by the solvent rather then in the particular type of solvent and its chemical properties. In Figure 5.20 an example of a simulation box containing dendrimers of generation 2 in solution at concentration 0.5 is shown. The concentration used in this section is defined as the mass fraction of dendrimers to the mass of the whole system. Therefore, assuming that the mass of the solvent molecules equals the mass of the beads constituting dendrimers, a concentration of 0.5 (50%) indicates that half of all beads in the simulation box are not chemically bonded and represent the solvent.

Dendrimers of generation 2 (D2G2) were generated in solution at concentrations 33%, 50%, 67%, and 100% (melt). The systems were equilibrated and subjected to planar shear flow. Simulations were performed using the NPT-SLLOD algorithm, and all systems were maintained at the same pressure $p = 5.42$. The obtained flow curves (viscosity versus shear rate) are presented in Figure 5.21. The viscosity of solutions at any shear rate increases with increasing content of dendrimers. All systems exhibit transition from Newtonian to non-Newtonian regimes. However, the rate of shear thinning decreases with the decrease of concentration from 0.39 for melt (100%), through 0.26, 0.20, down to 0.13 for 67%, 50%, and 33%, respectively. A similar behaviour was observed experimentally for solutions of highly branched poly(ether-imide)s (Sendjarevic and McHugh 2000). At low concentrations the systems exhibited shear independent properties, whereas at higher concentrations (>30%), when the
entanglement and contribution from interactions between molecules became more significant, the non-Newtonian viscosity was reported.

Similar to the viscosity, the normal stress coefficients of the solutions also decrease with the decrease of the concentration of dendrimers. In Figure 5.22 the dependence of normal stress coefficients (as defined in Equations 5.6 and 5.7) on shear rate is shown.

Figure 5.20. Simulation box containing 50% solution of dendrimers of generation 2. Molecules of solvent are represented by beads, whereas dendrimers are represented by interconnected cylinders. Different colours correspond to different molecules.
Figure 5.21. Viscosity of dendrimers of generation 2 in solution at various concentrations plotted against shear rate \((\dot{\gamma} = 5.42, T = 1.25)\).

Although the melts and mixtures were kept at the same pressure (therefore similar densities), the structure of dendrimers is strongly affected by the presence of molecules of the solvent. In the melt entanglement and interpenetration between dendrimers is suppressed due to the high density and level of branching of their arms. As a consequence dendrimers are found in compact globular conformations (detailed analysis of microscopic structural properties of dendrimers in the melt is given in Chapter 6). In contrast, small solvent molecules can easily penetrate the interior of dendrimers. This phenomenon is sometimes referred to as swelling of the molecule in solution. In polar solvents the configurational effects can be strongly enhanced in the case of hydrophilic systems or suppressed in hydrophobic ones. In this study the latter effects are not taken into account. Figure 5.23 shows the variation of the radius of gyration of dendrimers with concentration, where a monotonic decrease of the size with the decreasing separation between the molecules is observed. In Figure 5.24 the flow-induced changes in the radius of gyration is shown. At highest strain rates the molecules are fully stretched, thus their size does not depend on the concentration any more and is the same.
as for the melts. A full discussion on the behaviour of the radius of gyration of dendrimers in the melt will be presented in Section 6.6.

Figure 5.22. First and normal stress coefficients of dendrimers of generation 2 (D2G2) at various concentrations plotted against the shear rate ($\rho = 5.42$, $T = 1.25$).
5. FLOW PROPERTIES OF DENDRIMERS UNDER SHEAR

![Graph showing the dependence of the radius of gyration of dendrimers of generation 2 (D2G2) on the concentration of the solvent. Results obtained from simulations at equilibrium ($p = 5.42$, $T = 1.25$).](image1)

Figure 5.23. Dependence of the radius of gyration of dendrimers of generation 2 (D2G2) on the concentration of the solvent. Results obtained from simulations at equilibrium ($p = 5.42$, $T = 1.25$).

![Graph showing the dependence of the radius of gyration on shear rate of solutions of dendrimers of generation 2 (D2G2) at various concentrations ($p = 5.42$, $T = 1.25$).](image2)

Figure 5.24. Dependence of the radius of gyration on shear rate of solutions of dendrimers of generation 2 (D2G2) at various concentrations ($p = 5.42$, $T = 1.25$).
5.8.2. Blends of dendrimers with linear chain polymers

Dendrimers are considered to be potential candidates to use as rheology modifiers. Due to their unusual flow properties, they could be used as additives to modify and tune properties of polymeric blends. Throughout this chapter, the flow properties of dendrimer melts were compared to those of linear chain systems. In this section preliminary results of the explicit modelling of blends are presented. At this stage only blends of molecules of the same molecular weight are taken into account. In Figure 5.25 an example of a configuration of a mixture of dendrimers of generation 2 (D2G2) and linear chains of the same size (43-mers) in the 1:1 ratio is shown. Three different ratios were considered: 1:3, 1:1, and 3:1 resulting in blends containing 25%, 50%, and 75% of dendrimers, respectively (weight fraction). The results obtained for these systems are compared to those for pure dendrimer or linear chain melts presented earlier in this chapter.

![Figure 5.25. Configuration of the blend of dendrimers of generation 2 (D2G2) and 43-mers at 1:1 ratio.](image)
In Figure 5.26 the viscosity of the blends is plotted against the shear rate. The properties of the systems change gradually with the composition and are between those of pure systems. In the Newtonian regime the viscosity decreases with the amount of dendrimers in the system, whereas in the non-Newtonian regime the trend is opposite, and the addition of dendrimers increases viscosity of the blends. Also the onset of shear thinning shifts towards larger strain rates with the increase of the dendrimer fraction. A similar decrease of the Newtonian viscosity was observed experimentally in blends of linear polymer with hyperbranched polyesters (Nunez et al. 2000) or with highly branched polyphenylenes (Kim and Webster 1992).

![Graph showing viscosity of blends of dendrimers of generation 2 (D2G2) and linear chains of the same size (43-mers) in the shear thinning regime (ρ = 5.42, T = 1.25).]

Figure 5.26. Viscosity of blends of dendrimers of generation 2 (D2G2) and linear chains of the same size (43-mers) in the shear thinning regime (ρ = 5.42, T = 1.25).

Figure 5.27 shows the effect of composition on the normal stress coefficients. Due to the statistical uncertainty at lower strain rates, only the high shear rates are taken into consideration. In case of the first normal stress coefficient, the pressure difference (between the x and y diagonal elements of the pressure tensor) is stronger for linear chain polymers than for dendrimer systems, and it monotonically decreases with the amount of dendrimers in the blends. For the second normal stress coefficient the effect of compositions is less profound. However, the trend can be observed in which addition...
of dendrimers to the linear chain system increases the normal pressure difference (between \( y \) and \( z \) components of the pressure tensor).

Figure 5.27. First and second normal stress coefficients of blends of dendrimers of generation 2 (D2G2) with the linear chain molecules of the same molecular weight (43-mers) at various ratios \( (\rho = 5.42, \ T = 1.25) \).