Conformational and dynamical properties of ultra-soft colloids in semi-dilute solution under shear flow

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Abstract. We investigate structural and dynamical properties of ultra-soft colloids in dilute and semidilute solutions by hybrid mesoscale simulations under linear shear flow. In particular, the influence of functionality on these properties is addressed. Our study combines molecular dynamics simulations for the solute with the multiparticle collision dynamics approach for the coarse-grained solvent. The star polymers exhibit large conformational and orientational changes in shear flow, which we characterize by the radius of gyration tensor and the alignment angle. These quantities show a universal dependence on a concentration- and functionality-dependent Weissenberg number with slight deviations at high shear rates. Moreover, the star polymers display a rotational dynamics with a shear-rate and concentration-dependent rotation frequency. We attribute the concentration dependence to the screening of hydrodynamic interactions in semidilute star-polymer solutions.
1. Introduction

Macromolecular systems are enormously versatile in their structural and dynamical properties. This has led to their wide-spread use as structural and functional materials, as well as fluids with tailored properties. The origin of the versatility is that polymer length, polymer architecture, polymer internal composition (in form of multi-block copolymers) and polymer interactions can be easily tuned, with a strong impact on material properties. The large number of variables and the emergent properties in semi-dilute and dense suspensions imply that a detailed theoretical understanding is required to achieve a knowledge-based design of new materials and their flow properties.

In this article, we focus on a special class of macromolecular architectures, which consist of several linear polymers of equal length, tied together at one of their ends to a common center [1]. These star polymers are technologically important in several applications, such as viscosity modifiers in the oil industry [1], or as novel drug-delivery agents [2–4]. Star polymers have very soft interactions, which increase only logarithmically with decreasing distance between their centers [5–8]. Therefore, star polymers are also known as ultra-soft colloids.

The structural, dynamical, and rheological properties of star polymer solutions strongly depend on the arm number—the functionality $f$—, the lengths of the arms, and the concentration $c$ [9–13]. Experimentally, star polymers have been investigated over a wide range of functionalities, in particular for low and intermediate functionalities $4 \leq f \leq 128$ in Refs. [14–16] and for very large functionality $f = 390$ in Ref. [17]. For concentrations below and moderately above the overlap concentration $c^*$, star polymer solutions are in the fluid phase, while for high concentrations the solution (or melt) becomes glassy [13,17], in particular for large functionalities. These studies mainly focus on the rheological properties. In the fluid regime, the zero-shear viscosity of star polymer solutions interpolates between that of linear polymers and hard spheres at fixed volume fraction—defined by the hydrodynamic radius of an individual macromolecule [15]; here, the viscosity is found to strongly depend on the functionality, but only very weakly on the arm length.

Simulations of star-polymer solutions by mesoscale hydrodynamics methods with a molecularly resolved polymer model have mainly focused on the structural and dynamical behavior of individual stars in dilute solution [18,19], on the dynamic friction between two dragged stars [20], and on rheological behavior of semi-dilute solutions of low-functionality star polymers (with $f = 10$) [21]. In a complementary theoretical description of soft colloids [22–24]—such as block-copolymer micelles, hairy colloids, and star polymers—, each colloid is represented by just one point particle with effective, coarse-grained interactions. This approach with an equilibrium interaction potential has been employed in Ref. [22] to study the nonequilibrium properties of dense solutions of such ultra-soft colloids by mesoscale hydrodynamics simulations. Naturally, such an approach does not capture the flow-induced deformation of the star polymers, and is therefore suitable in the limit of nearly spherical colloids only. As will be illustrated...
in the article, such deformations are quite pronounced even in concentrated systems and determine the rheological properties of the solution. Furthermore, the use of an equilibrium interaction potential does not include the effect of transient entanglements between the polymer arms [23] or the time-irreversible deformation of the corona [20]. Such transient effects can be mimicked by a memory contribution to the (still spherically symmetric) interaction potential [23]; such an approach has been successfully employed, for example, to predict the dynamics of star-polymer solutions with start-up or step-down shear stress [24].

We focus in this paper on the role of concentration and functionality—with $10 \leq f \leq 50$—on the structural and dynamical properties of star polymers in semidilute suspensions. We address the deformation and orientation of individual star polymers and unravel their universal behavior in terms of shear rate and functionality. Moreover, we study the scaling properties of the structure factor of individual arms under shear flow. Similar studies have been performed for linear polymers (a star of functionality $f = 2$) [25]. As shown in Refs. [18,19], star polymers with $f \gtrsim 5$ exhibit a tank-treading-like motion, where individual arms undergo collapse and stretching cycles. This leads to a rotation of the whole star, with a frequency, which depends upon the shear rate. Here, the questions arise, how the star-polymer concentration affects the rotational dynamics, and whether the frequency dependence is similar to the tank-treading motion of vesicles.

The article is organized as follows. In Sec. 2, we introduce the star-polymer model and the mesoscopic hydrodynamics simulation technique, and discuss the choice of model parameters. In Sec. 3, we present our results for the conformational properties, the flow alignment, and the structure factor of star polymers in semi-dilute solution under shear flow. Results for the flow induce rotational dynamics of stars are presented in Sec. 4. Finally, the results are summarized in Sec. 5.

2. Method and Model

2.1. Multiparticle Collision Dynamics

Multiparticle collision dynamics (MPC) is a particle-based hydrodynamic simulation technique [26–28]. In the MPC algorithm, the solvent is modeled by $N_s$ point particles with positions $r_i$ and velocities $v_i$ ($i = 1, \ldots, N_s$). The dynamics proceeds in discrete time increments $h$, denoted as collision time, by alternating streaming and collision steps [27, 28]. In the streaming step, the solvent particles of mass $m$ move ballistically with their respective velocities and their positions are updated as

$$r_i(t + h) = r_i(t) + hv_i(t). \quad (1)$$

In the collision step, the simulation box is partitioned in cubic cells of linear dimension $a$ and the solvent particles are sorted into these cells. Their relative velocities, with respect to the center-of-mass velocity of the cell, are rotated around a randomly oriented axis by an angle $\alpha$, so that

$$v_i(t + h) = v_i(t) + (R(\alpha) - I)(v_i(t) - v_{cm}(t)), \quad (2)$$
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where $\mathbf{R}$ is the rotation matrix, $\mathbf{I}$ is the unit matrix, and $\mathbf{v}_{cm} = \sum_{j=1}^{N_c} \mathbf{v}_j / N_c$ is the center-of-mass velocity of the cell with $N_c$ particles. In this stochastic process mass, momentum, and energy are conserved, which ensures that hydrodynamic behavior emerges on larger length scales.

The transport properties of the solvent depend on the collision time $h$, the rotation angle $\alpha$, and the average number of particles $\langle N_c \rangle$ per cell. Tuning these variables allows us to attain solvents with a high Schmidt number, where momentum transport dominates over mass transport. We use the parameters $h/\sqrt{ma^2/(k_BT)} = 0.1$, $\alpha = 130^\circ$, and $\langle N_c \rangle = 10$, which yields the solvent viscosity $\eta_s = 8.7\sqrt{mk_BT/a^4}$ and the Schmidt number $Sc \approx 17$.

2.2. Star-Polymer Model

A star polymer consist of $f$ linear polymers with one of their ends linked to a common center. A polymer has $N_m$ monomers of mass $M$, which are connected by harmonic springs with the potential

$$V_b = \frac{k_s}{2} (R_{i,i+1} - l)^2,$$  

(3)

where $l$ is the equilibrium bond length, $\mathbf{R}_{i,i+1} = \mathbf{R}_{i+1} - \mathbf{R}_i$ is the bond vector, and $R_{i,i+1} = |\mathbf{R}_{i,i+1}|$. The spring constant $k_s$ is chosen such that even under strong shear flow the change in the equilibrium bond length remains less than a few percent. Excluded-volume interactions between beads are taken into account through the repulsive truncated and shifted Lennard-Jones (LJ) potential

$$V_{LJ}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} + \frac{1}{4} \right] \Theta(2^{1/6}\sigma - r),$$  

(4)

where $\Theta(r)$ is the Heaviside step function ($\Theta(r) = 0$ for $r < 0$ and $\Theta(r) = 1$ for $r \geq 0$).

The equilibrium bond length of each center-arm connection $l_c$ and LJ diameter of the central bead $\sigma_c$ are taken to be twice as large as those for a normal monomer, while the mass of the center bead is the same as for any other monomer. Moreover, we set $\epsilon = k_BT$ and $a = l$. We use the spring constant $k_s/(k_BT/l^2) = 10^3$, the diameter of a bead $\sigma/l = 0.8$ and its mass $M = 10m$. We consider polymer arms with $N_m = 30$ monomers. The velocity Verlet algorithm is used to integrate Newton’s equations of motion of the star polymers with the time step $h_m = 5 \times 10^{-3}\sqrt{ml^2/(k_BT)}$.

The solute-solvent coupling occurs in the collision step, where the velocities of the polymer beads are rotated according to Eq. (2) [28–30], but with the center-of-mass velocity of the cell

$$\mathbf{v}_{cm}(t) = \frac{\sum_{i=1}^{N_c} m \mathbf{v}_i(t) + \sum_{j=1}^{N_m} M \mathbf{v}_j(t)}{mN_c + MN_m}.$$  

(5)

Here, $N^m$ is number of the beads in the considered cell. Thereby, momentum is redistributed between solvent and monomers in the same cell.

Lees-Edwards boundary conditions are applied to impose shear flow [31]. This yields a linear fluid velocity profile $v_x = \dot{\gamma}y$ in the flow direction ($x$-axis) as function of
the particle positions along the gradient direction (y-axis), where \( \dot{\gamma} \) is the shear rate. A local cell-based Maxwellian thermostat (MBS) is applied by which velocities are scaled to maintain the desired temperature of the system [32].

### 3. Structural Properties of Star-Polymers in Shear Flow

We place the star polymers in a cubic simulation box with linear dimension \( L = 100\ell \) and periodic boundary conditions. Their number \( N_{sp} \) depends on concentration and is given in Table 1 together with other parameters. We will present results for the arm length \( N_m = 30 \) and the functionalities \( f = 10, 20, 30, \) and 50. The polymer concentration is measured relative to the overlap concentration, \( c^* \),

\[
c^* = \left[ \frac{4}{3} \pi R_h^3 \right]^{-1},
\]

where \( R_h \) is the hydrodynamic radius, which is obtained from the diffusion coefficient of a star in dilute solution extrapolated to infinite system size [33]. The strength of the shear flow is characterized by the concentration-dependent Weissenberg number \( W_i = \beta \dot{\gamma} \tau_z \), where \( \tau_z = \eta_s N_m^2 \ell^3 / k_B T \) is the Zimm relaxation time of a polymer arm and \( \beta = \beta(c/c^*) \) is a concentration dependent scale factor. We introduce the factor \( \beta \) to account for the concentration dependence of the characteristic relaxation time of a star polymer, i.e., \( \beta \tau_z \) is—up to a constant—equal to the concentration dependent relaxation time. To determine \( \beta \), we map the higher concentration data for different shear rates onto the dilute solution data given in Table 1. This idea has been also applied in Refs. [21, 34] to study concentration-dependent rheological properties of linear and star-polymer solutions for stars with \( f = 10 \). Several independent simulation runs are performed for fixed solution conditions in order to obtain reliable averages of the properties of interest.

#### 3.1. Conformational properties

Typical conformations of star polymers in semi-dilute solution under shear flow are shown in Fig. 1 for \( f = 10 \) and \( f = 50 \). Comparison of the two functionalities

Table 1. Simulation parameters for \( N_{sp} \) star polymers of functionality \( f \). \( R_{g0} \) and \( R_h \) are the equilibrium radius of gyration and hydrodynamic radius in dilute solution, respectively, and \( c \) indicates the range of considered concentrations, with \( c^* \) denoting the overlap concentration.

<table>
<thead>
<tr>
<th>( f )</th>
<th>( N_{sp} )</th>
<th>( R_{g0}/\ell )</th>
<th>( R_h/\ell )</th>
<th>( c/c^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>100 − 750</td>
<td>7.1</td>
<td>7.1</td>
<td>0.15 − 1.13</td>
</tr>
<tr>
<td>20</td>
<td>50 − 375</td>
<td>7.9</td>
<td>9.1</td>
<td>0.16 − 2.37</td>
</tr>
<tr>
<td>30</td>
<td>34 − 250</td>
<td>8.5</td>
<td>10.7</td>
<td>0.17 − 2.57</td>
</tr>
<tr>
<td>50</td>
<td>20 − 150</td>
<td>9.2</td>
<td>13.2</td>
<td>0.19 − 2.92</td>
</tr>
</tbody>
</table>
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Figure 1. Simulation snapshots of star-polymer solutions with (a) functionality \( f = 10 \) and concentration \( c/c^* = 1.13 \) as well as (b) \( f = 50 \) and \( c/c^* = 1.46 \) for the same Weissenberg number \( \text{Wi}_L \approx 10^2 \). Only star polymers with their centers in a slice of thickness of 3\( R_g^0 \) parallel to the flow-gradient plane are shown. Multiple colors are used to distinguish the various star polymers more easily. Movies are provided as supplemental material.

Figure 1 demonstrates that large-functionality stars are less deformed and less aligned with the flow direction than low-functionality star polymers.

The conformational properties of the star polymers can be characterized quantitatively by the radius of gyration tensor, which is defined as

\[
G_{\gamma \gamma'} = \frac{1}{N} \sum_{i=1}^{N} \Delta r_{i,\gamma} \Delta r_{i,\gamma'},
\]

where \( \Delta r_i \) is the position of the \( i^{th} \) monomer relative to the star center of mass, \( \gamma, \gamma' \in \{x, y, z\} \), and \( N = fN_m + 1 \) is the total number of monomers in a star. At equilibrium, all diagonal components of \( G_{\gamma \gamma'} \) are equal, i.e., \( \langle G_{\gamma \gamma} \rangle = \langle G_{0 \gamma}^0 \rangle \), where the superscript indicates the equilibrium value at the particular concentration. In the dilute regime \( \langle G_{\gamma \gamma} \rangle = \langle G_{0 \alpha}^0 \rangle = R_g^2/3 \), where the radius of gyration \( R_g^2 \) follows the scaling relation \( R_g^2 \approx l^2 N_m^{2\nu} f^{1-\nu} \) in terms of arm length and functionality [5,9,35,36], with the exponent \( \nu \approx 0.63 \) for our system. Our scaling exponent is slightly larger than that for polymers in dilute solution due to the relatively short arm length. Longer arms would lead to the same exponent as for linear chains (\( \nu \approx 3/5 \)) [37].

In linear shear flow, polymers become deformed, which is measured by the relative deformation

\[
\delta G_{xx}(c/c^*) = \frac{\langle G_{xx}(c/c^*) \rangle - \langle G_{xx}^0(c/c^*) \rangle}{\langle G_{xx}^0(c/c^*) \rangle}
\]

in terms of the gyration tensor. Simulation results of \( \delta G_{xx} \) for star polymers of various
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Figure 2. Relative deformation $\delta G_{xx}$ of star polymers along the flow direction as a function of the functionality-dependent Weissenberg number $\phi_f Wi_c$. (a) Dilute solution data at the lowest concentrations given in the table for $f = 10$ (bullets), $f = 20$ (squares), $f = 30$ (diamonds), and $f = 50$ (triangles). The inset presents the relative deformations as function of $Wi_c$ only. (b) Simulation data for all concentrations and functionalities.

Functionalities in dilute solution are displayed in the inset of Fig. 2(a). It is clear that $\delta G_{xx}$ decreases with increasing functionality at a given shear rate, or $Wi_c$, due to difference in the shear resistance, which increases for larger functionalities.

The star polymer relaxation time depends on its arm number. The relative dependence of the relaxation time on the functionality can be estimated by shifting the $\delta G_{xx}$ curves to the highest-functionality curve in the inset of Fig. 2(a). Figure 2(a) itself shows the scaled curves as function of the $\phi_f Wi_c$, where $\phi_f$ is a $f$-dependent scale factor. Clearly, the scaled data follow a common curve within the accuracy of the simulations, which indicates universal behavior of this structural property.

Relative deformation ratios for various concentrations, above and below the overlap concentration, are displayed in Fig. 2(b). Evidently, a universal curve is obtained.
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Figure 3. Concentration-dependent scale factor $\beta$ for the relaxation time $\tau(c) = \beta(c/c^*)\tau_z$ obtained from the scaling of the radius-of-gyration tensor and the alignment along the shear direction. The inset shows the functionality dependence of the scale factor $\phi_f$. The line indicates the power-law dependence $\phi_f \sim f^{-2/3}$.

as function of $\phi_f W_i c = \phi_f \beta Wi$ over a wide range of Weissenberg numbers. At low $\phi_f W_i c < 1$, a quadratic dependence of the relative deformation on Weissenberg number is found for all concentrations and functionalities [18, 21, 34, 38]. At high shear rates, the deformation of the polymers saturates and $\delta G_{xx}$ assumes a maximum value, which depends on the length of polymer arms as well as on the functionality. This finite-polymer-length effect breaks the universality as reflected in the figure. Note that the equilibrium value of the radius of gyration increases with increasing functionality, which partially accounts for the decrease of $\delta G_{xx}$ at high Weissenberg numbers.

Figure 3 displays the concentration dependence of the scale factor $\beta(c/c^*)$. We find a universal curve for the various considered functionalities [21]. As emphasized, $\beta$ measures the concentration dependence of the star polymer characteristic relaxation time. Evidently, this time increases significantly with concentration. The inset of Fig. 3 shows the functionality dependence of $\phi_f$, which decreases with increasing $f$ in a power-law manner, with an exponent of $-2/3$. This is surprising, because it implies that the relaxation time of a star polymer determining the Weissenberg number decreases with increasing functionality. This is in contradiction with the relaxation time of an individual polymer arm, which is predicted [10] to follow the dependence $f^{(2-3\nu)/2}$, with $(2 - 3\nu)/2 \simeq 0.1$ for $\nu = 0.6$, i.e., this relaxation time increases with increasing functionality.

The radius of gyration tensor components along the gradient direction are displayed in Fig. 4 for dilute systems and star polymer concentrations well above $c^*$ as function of $\phi_f W_i c$. The star polymer size $\langle G_{yy} \rangle$ decreases with increasing shear rate. Thereby, a weak dependence on functionality is revealed—beyond the effect captured by $\phi_f$. At large Weissenberg numbers, higher-functionality star polymers exhibit a somewhat smaller deformation. More importantly, low- and high-concentration systems show a
qualitatively different dependence on shear rate, expressed by the different slope of the corresponding data sets. Dilute systems exhibit a stronger shrinkage than concentrated systems at the same value of \( \phi_f W_i c \). This might be explained by the fact that the equilibrium radius of gyration of star polymers in concentrated systems is smaller than that of dilute systems. The associated denser packing of monomers of individual stars is maintained even at high shear rates and leads to smaller deformations compared to the dilute case. Along the vorticity direction, the conformations of the star polymers are less affected by the flow, as already shown in Ref. [18] for dilute systems.

In equilibrium, a star polymer is a spherically symmetric object on average. As it is evident from the above results, this symmetry is broken under shear flow. We characterize the shear-induced asphericity of a star polymer by the ratio of the largest and smallest eigenvalues of the average gyration tensor \( \langle G_1 \rangle \) and \( \langle G_3 \rangle \), i.e., \( \langle G_1 \rangle / \langle G_3 \rangle - 1 \). For a spherically symmetric object, this value is zero and increases as the object gets asymmetrically deformed, and diverges for a thin rod. Similarly, for star polymers the asphericity is small at low shear rates, while it increases with increasing shear rates, as displayed in Fig. 5(a). For low and moderate \( \phi_f W_i c \), a universal curve for all functionalities and concentrations is obtained, indicating that the \( f \) and \( c/c^* \) dependence is absorbed in \( \phi_f W_i c \). At large \( \phi_f W_i c \gg 1 \), the asphericity curves split for the various concentrations and functionalities. At large concentrations, the asphericity is smaller. Larger concentrations lead to a slower decrease of \( \langle G_{yy} \rangle \) (see Fig. 4) and to a larger \( \langle G_3 \rangle \).

In addition, we present in Fig. 5(b) the instantaneous asphericity \( \bar{G}_1/\bar{G}_3 - 1 \), where the \( \bar{G}_i \) are obtained by averaging the diagonalized radius of gyration tensor. At high shear rates the instantaneous asphericity is equal to the average one, while at low shear rates plateau values are obtained, which depend on functionality and arm length. These
shear-independent values characterize the deviation of a star polymer from a perfectly spherical object in equilibrium. Thus, stars of low functionality are more aspherical in comparison to those with high $f$. This property reflects a change in the star structure as functionality increases, namely the inner compact region of a star swells, while the outer soft region is reduced, leading to smaller variations in star’s instantaneous shape.

The inset of Fig. 5(b) shows the instantaneous asphericity for the largest considered concentrations. Here, we also find a universal behavior of stars with different functionalities over a wide range of Weissenberg numbers. Only at large $\phi_f W_{i_c}$, curves for the various $f$ split. This could be related to the fact that the packing of monomers increases with increasing functionality. The difference between the various curves...
seems to decrease with increasing concentration and we expect an asymptotic curve for sufficiently large concentrations.

As a measure of the asphericity of star polymers in equilibrium and in dilute solution, we use the quantity [28, 39]

\[ A = \left\langle \frac{(G_1 - G_2)^2 + (G_1 - G_3)^2 + (G_2 - G_3)^2}{(G_1 + G_2 + G_3)^2} \right\rangle. \]  

(9)

Results for the various functionalities are presented in Fig. 6. As expected [40–42], the asphericity decreases with increasing functionality and shows a strong dependence on \( f \). We find a stronger decrease with \( f \) than the theoretically predicted power law \( f^{-1} \) [40, 41]; at large functionalities, our data decay approximately as \( A \sim f^{-3/2} \). However, our data are in good agreement with the Monte Carlo simulations of Ref. [42] for small functionalities. Note that these simulations predict a very weak dependence of \( A \) on polymer length only for the considered low-functionality stars polymers. The discrepancy between our simulation data and theory could be related to the relative short length \( N = 30 \) of the polymer arms and the high monomer packing at large functionalities. The length-independent regime might be accessible for longer polymers only.

3.2. Flow Alignment

Aside from being deformed, star polymers under shear are also aligned with the flow field. The extent of alignment can be characterized by the angle \( \chi_G \) between the largest eigenvalue of the average radius of gyration tensor and the flow direction. It is obtained as

\[ \tan(2\chi_G) = \frac{2 \langle G_{xy} \rangle}{\langle G_{xx} \rangle - \langle G_{yy} \rangle}. \]  

(10)
In Fig. 7, alignment angles are plotted as a function of \( \phi_f \) for various concentrations and functionalities. In the linear response regime \( \langle G_{xy} \rangle \sim \phi_f \) and \( \langle G_{xx} \rangle - \langle G_{yy} \rangle \sim (\phi_f)^2 \), which implies that at low Weissenberg numbers \( \tan(2\chi_G) \sim Wi^{-1} \) [43, 44]. This power-law dependence is approached for \( \phi_f < 5 \). At higher \( \phi_f \), star polymers assume an approximately ellipsoidal shape, and the angle \( \chi_G \) decreases with increasing shear rate. Again, we obtain a universal curve for different concentrations and functionalities over a certain \( \phi_f \) range, where \( \phi_f \beta(c/c^*) \) absorbs any functionality and concentration dependencies. The alignment angle at high shear rates follows the scaling law \( \tan(2\chi_G) \sim (\phi_f)^{-\delta} \) with the exponent \( \delta \approx 0.43 \). As for other properties discussed in Sec. 3.1, the alignment angle data split at high shear rates due to a finite size of the polymers. For \( \phi_f > 50 \), star polymers with a smaller number of arms are slightly more aligned with the flow direction than those with a larger number of arms. We would like to emphasize that for \( \tan(2\chi_G) \) only the shear rate needs to be scaled to obtain a universal curve. The obtained universality for \( \phi_f \leq 50 \) confirms that \( \phi_f \beta(c/c^*) \) is a suitable combination of the functionality and concentration dependence of the relaxation time.

3.3. Static Structure Factor

Structural changes of a star polymer under flow at different length scales are reflected in its static structure factor

\[
S(q) = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} \langle e^{-iq(r_i-r_j)} \rangle.
\]

(11)

Figure 8(a) displays equilibrium structure factors along the flow direction for various functionalities in dilute solution. At small wave vectors \( q_x l \ll 1 \), \( S(q_x) \) is approximately
Figure 8. (a) Equilibrium structure factors $S(q_x)$ of star polymers and of (b) individual arms $S_a(q_x)$ for the functionalities $f = 10$ (black), 20 (red), 30 (green), and 50 (blue). The straight lines indicate the power-law $q^{-1/\nu}$ with $\nu = 0.63$.

constant. It then decays very rapidly for $q_x R_{g0} > 1$ according to the power law $q^{-4}$ for large functionalities, corresponding to the behavior of a spherical particle. In the range $4l/R_{g0} < q_x l < \pi$, the internal structure of the ultrasoft polymer is reflected. For low functionality, we find the approximate power-law decay $S(q_x) \sim q^{-1/\nu}$ with $\nu \approx 0.63$. At higher functionalities, additional features appear and no clear power-law regime is visible. The decrease of $S(q)$ with increasing functionality at $q_x l \approx 1$ indicates a stretching of the polymers due to the increased packing at larger functionalities. At $q_x l \approx 2\pi$, a peak appears by scattering from nearest neighbor monomers.

Figure 8(b) presents the structure factors $S_a$ of the individual arms within a star. The curves for the various functionalities show small differences at $q_x R_{g0} \approx 1$ caused by the increase of the radius of gyration with increasing functionality. In the range $6l/R_{g0} < q_x l < \pi$, we find a universal, self-similar behavior with a power-law regime corresponding to the scaling behavior of an individual polymer of similar length.
The deformation of a star polymer under shear flow is also reflected in the structure factor. Since a star is anisotropic, we determine the structure factors along the flow, gradient, and vorticity direction separately. An example of structure factors along the flow direction for various shear rates is provided in Fig. 9. The increase of the radius of gyration $\langle G_{xx} \rangle$ leads to a shift of the curves to smaller $q_x$ values. More importantly, the power-law exponent $\nu$ in $S(q_x) \sim q_x^{-1/\nu}$ depends on shear rate. The inset of Fig. 9 shows the exponents $\nu$ for various functionalities as a function of the Weissenberg number. $\nu$ increases with increasing Weissenberg number and seems to saturate at large $Wi_c$, which indicates a stretching of the individual polymers. Since some of the polymers are stretched and others are in a coiled state, we expect the exponent to be always smaller than unity. Evidently, there is a only a very weak dependence on functionality. As shown in Fig. 4, the polymers shrink along the gradient direction. Here, we find a very minor change of the power-law exponent $\nu$ toward smaller values. A similar behavior is observed along the vorticity direction.

A comparable change in the scaling behavior of the structure factor of linear polymers under shear flow has been found in Ref. [25] by molecular dynamics simulations. In contrast to our star polymers, however, a significantly modified scaling behavior is obtained for linear polymers along the minor axis. The exponent $\nu$ along this axis decreases significantly below the equilibrium value.
4. Rotational Dynamics of Star Polymers in Shear Flow

4.1. Angular Rotation Frequency and Tank-Treading

Under linear shear flow the vorticity is non-zero, which implies a rotational motion of a star with a non-zero rotational frequency. The dynamics of a star polymer is quite different from that of a linear polymer. A linear polymer exhibits tumbling motion [38, 44–47], whereas star polymers show a tank-treading-like rotation for functionalities \( f \gtrsim 5 \) [18, 19], where individual arms are subject to a cyclic stretching and collapse motion. The rotational dynamics can be characterized by the rotational frequency \( \omega \) of the star, which is obtained from the angular momentum [19, 48, 49]

\[
L = \sum_{i=1}^{N} M \Delta r_i \times \Delta \dot{r}_i
\]

and the inertia tensor \( \Theta \), with its components

\[
\Theta_{\gamma \gamma'} = \sum_{i=1}^{N} M (\Delta r_i^2 \delta_{\gamma \gamma'} - \Delta r_{i, \gamma} \Delta r_{i, \gamma'})
\]

via the relation \( L = \Theta \omega \). For a rigid body, this yields the average frequency

\[
\omega_z = \left\langle \sum_{\gamma} \Theta_{\gamma \gamma}^{-1} L_{\gamma} \right\rangle
\]

for a rotation around the vorticity axis. Since a star polymer is not a rigid body, we neglect terms containing fluctuations in \( \omega_i \) of the individual monomers around the mean value \( \omega \). If we neglect the off-diagonal elements of the inertia tensor (13), and replace \( \Theta_{zz} \) by its average, we find

\[
\langle L_z \rangle \approx \langle \Theta_{zz} \rangle \omega_z^L = M \left( \langle G_{xx} \rangle + \langle G_{yy} \rangle \right) \omega_z^L.
\]

Another approximation for the angular momentum is obtained, when the local velocity of a particle is replaced by the flow field, i.e., \( \Delta \dot{r}_i \approx \mathbf{v}(r_i) \). With \( \mathbf{v}(r_i) = (\dot{\gamma} \Delta y_i, 0, 0)^T \) follows

\[
\langle L_z^G \rangle = -\dot{\gamma} \langle G_{yy} \rangle,
\]

where the superscript indicates an approximation in terms of the radius of gyration tensor component \( G_{yy} \). Hence, we obtain the frequencies

\[
\omega_z^L = \frac{\langle L_z \rangle}{M(\langle G_{xx} \rangle + \langle G_{yy} \rangle)},
\]

\[
\omega_z^G = -\dot{\gamma} \frac{\langle G_{yy} \rangle}{M(\langle G_{xx} \rangle + \langle G_{yy} \rangle)}.
\]

Figure 10 shows an example of rotational frequencies obtained by the various definitions at low and high star-polymer concentrations. The data obtained by Eqs. (14), (17) are hardly distinguishable, whereas Eq. (18) yields somewhat larger frequencies \( |\omega_z^G| \) at large shear rates. Remarkably, the differences between the various definitions are smaller at larger concentrations.
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Figure 10. Shear-rate dependence of angular frequencies $|\omega_z|$ of star polymers with $f = 50$ and the concentrations $c/c^* = 0.19$ (full triangles) and $c/c^* = 2.92$ (open triangles). Results are compared for the definitions Eq. (14) (black), Eq. (17) (red), and Eq. (18) (green).

Figure 11(a) presents reduced rotational frequencies $|\omega_z|/\dot{\gamma}$ calculated according to Eq. (14) for systems in dilute solution and various functionalities. For weak flow strengths $\phi_f W_i c \ll 1$, the expected dependence $|\omega_z| = \dot{\gamma}/2$ is recovered. At higher shear rates, the reduced frequency decreases with increasing Weissenberg number according to the power-law $|\omega_z|/\dot{\gamma} \sim (\phi_f W_i c)^{-1}$, which implies that the angular frequency is independent of $\dot{\gamma}$. The figure also demonstrates that the reduced frequency essentially follows a universal curve. Figure 11(b) shows $|\omega_z|/\dot{\gamma}$ for various concentrations and the functionality $f = 50$. Interestingly, a strong concentration dependence is obtained, with reduced slopes for frequency curves at higher concentrations. Starting from the power law $W_i c^{-1}$ at low concentrations, the rotational frequency curves approach a $W_i c^{-2/3}$ dependence for high concentrations. Such a dependence has also been found in Ref. [19] in flow simulations of individual stars without hydrodynamic interactions. Hence, we attribute the concentration dependence to the screening of hydrodynamic interactions at concentrations $c/c^* > 1$. A similar screening of hydrodynamic interactions was found for semidilute solutions of linear polymers in Refs. [34,47]. The comparison in Fig. 10 shows that the dynamical quantity $\omega_z$ can be equally well obtained by any of the proposed definitions at high concentrations. Since Eq. (18) uses stationary state properties only, this might be expected to be applicable when correlations in the fluid are negligible, which is the case at large concentrations where hydrodynamic interactions are screened. At low concentrations, we expect dynamical quantities to be governed by hydrodynamic interactions beyond a simple rescaling of relaxation times, although the effect may be small as for linear polymers in shear flow [47].
4.2. Comparison of Star Polymer and Vesicle Rotational Dynamics

The tank-treading dynamics of star polymers in shear flow has a striking resemblance with the tank-treading behavior of lipid vesicles [50]. To describe the tank-treading motion of a vesicle in shear flow, Keller and Skalak [50] proposed a model (KS model) for a viscous tank-treading ellipsoid. The details of the model are presented in the Appendix. The KS model predicts the time dependence of angle $\phi$ between a material point on the ellipsoid and the $x$-axis to describe tank-treading, and of the inclination angle $\theta$ between the main ellipsoidal axis and the $x$-axis. To compare the predictions of the KS model for tank-treading with our results on star polymers, we identify the ellipsoidal axes $a_i$ ($i = 1, 2, 3$) to be the main axes of the star radius of gyration tensor, i.e., $a_i = \sqrt{<G_i>}$ . The only unknown parameter is the inner-to-outer fluid viscosity.
ratio $\lambda$ in the KS model, which slows down the rotational tank-treading frequency as it increases for a fixed shear rate. It is plausible to expect $\lambda$ to be greater than unity, because polymer arms in a star contribute to the star inner viscosity. We vary $\lambda$ in the range $\lambda = 1 - 6$ in order to fit the relative rotational frequency of star polymers at low concentration and the functionality $f = 10$, and achieve the best fit for $\lambda = 4$. This value compares well with the ratio $\eta_G/\eta_s = 2.6$ of the viscosity coefficient $\eta_G$ of a polymer globule in bad solvent and the solvent viscosity $\eta_s$, which has been determined in Ref. [51] by Brownian dynamics simulations.

Figure 12 shows the comparison of the reduced angular frequency $|\omega_z|/\dot{\gamma}$ calculated according to Eq. (14) (full symbols) of star polymers at low concentration with the predictions by the Keller-Skalak model (open symbols) for a tank-treading ellipsoid in shear flow. The ratio of inner-to-outer viscosity is assumed to be $\lambda = 4$ for all cases.

Figure 12. Comparison of the reduced angular frequency $|\omega_z|/\dot{\gamma}$ calculated according to Eq. (14) (full symbols) of star polymers at low concentration with the predictions by the Keller-Skalak model (open symbols) for a tank-treading ellipsoid in shear flow. The ratio of inner-to-outer viscosity is assumed to be $\lambda = 4$ for all cases.
5. Conclusions

We have studied the conformational and dynamical properties of star polymers under shear flow for various functionalities and concentrations. With increasing functionality, star polymers become more spherical and less deformable. Therefore, high-functionality stars are less elongated and less aligned with the flow direction at a given shear rate. The main result of our simulations is that the dependence of many static and dynamic properties of semi-dilute star-polymer solutions on concentration and functionality can be absorbed into an effective Weissenberg number, which can be factorized into a Weissenberg number $W_i = \dot{\gamma}\tau$ of a single polymer arm, a concentration-dependent factor $\beta(c/c^*)$, and a functionality-dependent factor $\phi_f$.

Interestingly, the factor $\phi_f$ is found to be a decreasing function of $f$. In contrast, the equilibrium relaxation time $\tau_f$ of an individual star polymer in solution has been predicted [9]—based on the Daoud-Cotton approach—to display a power-law dependence $f^{(2-3\nu)/2}$, with $(2 - 3\nu)/2 = 0.1$ for $\nu = 0.6$; this would imply an effective Weissenberg number which is slowly increases with $f$. There is an obvious contradiction between these two results. A possible explanation for the discrepancy is that our simulation results are derived for moderate arm lengths and functionalities, while the scaling arguments apply to very long arms and large functionalities. It would certainly be interesting to investigate star-polymer relaxation times in equilibrium in more detail to clarify this issue.

A second intriguing result is that a comparison of the star-polymer rotation dynamics with the dynamics of fluid vesicles shows a very similar tank-treading behavior for small and intermediate shear rates. This comparison can be used to extract an effective internal viscosity of a star, which is about a factor four larger than the solvent viscosity. It will be interesting to see whether it is possible to predict the viscosity of a dilute star-polymer solution based on this effective internal viscosity.

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Appendix: Keller-Skalak Theory

The Keller-Skalak (KS) theory [50] describes tank-treading motion of a vesicle membrane in shear flow. The membrane is assumed to move along a fixed ellipsoidal path. The
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tank-treading motion is defined by the equations

\[
\frac{\partial \phi}{\partial t} = -\frac{\dot{\gamma} \cos (2\theta)}{z_1 (z_2 (\lambda - 1) + 2)},
\]

\[
\frac{\partial \theta}{\partial t} = -\frac{\dot{\gamma}}{2} - z_0 \frac{\partial \phi}{\partial t} + \frac{\dot{\gamma}}{2} z_0 z_1 \cos (2\theta),
\]

where \(\phi\) is the angle between a material point on the ellipsoid and the \(x\)-axis to describe tank-treading, \(\theta\) is the inclination angle between the main ellipsoidal axis and the \(x\)-axis to define orientation of the ellipsoid, \(t\) is time, and \(\lambda\) is the inner-to-outer fluid viscosity ratio. The parameters \(z_i\) (\(i = 0, 1, 2\)) are determined by geometrical characteristics of the ellipsoid and are given by

\[
z_0 = \frac{2a_1 a_2}{a_1^2 + a_2^2}, \quad z_1 = \frac{a_1^2 - a_2^2}{2a_1 a_2}, \quad z_2 = g \left(\alpha_1^2 + \alpha_2^2\right), \quad \alpha_i = \frac{a_i}{(a_1 a_2 a_3)^{1/3}},
\]

\[
g = \int_0^\infty \left(\alpha_1^2 + s\right)^{-3/2} \left(\alpha_2^2 + s\right)^{-3/2} \left(\alpha_3^2 + s\right)^{-1/2} ds,
\]

where the \(a_i\) (\(i = 1, 2, 3\)) are the semiaxes of the ellipsoid. This model predicts tank-treading motion of a viscous ellipsoid (vesicle) with the inclination angle

\[
\cos (2\theta) = \frac{z_1}{z_0} \left(\frac{2}{z_2 (\lambda - 1) + 2}\right)^{-1}
\]

and the angular frequency

\[
\frac{\omega}{\dot{\gamma}} = \frac{\cos (2\theta)}{z_1 (z_2 (\lambda - 1) + 2)}.
\]

The dependence of \(\omega/\dot{\gamma}\) on shear rate, which is displayed in Fig. 12, arises from the implicit dependence of the \(z_i\) on \(\dot{\gamma}\). Note that at low \(\lambda\) values the ellipsoid shows tank-treading, while at high \(\lambda\) the ellipsoid may exhibit tumbling dynamics.

References

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