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Universality and speedup in equilibrium and nonlinear rheology predictions of the fixed slip-link model

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Synopsis

The discrete slip-link model (DSM) was developed to describe the dynamics of flexible entangled polymer melts. With just three molecular-weight- and chain-architecture-independent parameters—the molecular weight of a Kuhn step \( M_K \); entanglement activity \( b \); and Kuhn step shuffling characteristic time \( \tau_K \)—DSM is able to predict simultaneously the linear viscoelasticity of monodisperse linear, polydisperse linear, and branched systems. Without any adjustment, DSM shows excellent agreement with shear flow experiments and elongational flows with stretch up to \( \lambda^{20} \). Universality observed between entangled melts with the notable exception of high-strain elongations suggests that the average number of entanglements per chain is the primary characteristic of the system. Therefore, theoretical predictions for systems with differing numbers of Kuhn steps per chain but roughly the same number of entanglements should be equivalent when rescaled. In this work, we present a scaling of the DSM parameters, which has no significant effect on model predictions yet reduces greatly computational cost. The idea behind the scaling is clustering several Kuhn steps together. Thus, we call this implementation of the DSM the clustered fixed slip-link model (CFSM). The model is limited to at least one cluster between entanglements. The CFSM assumes two clusters between entanglements on average, which appears to be a reasonable minimum. We find that clustering results in a loss of some of the high frequency modes in \( G' \) predictions, sometimes called “longitudinal modes” in tube models. Matching the low-frequency rubbery plateau height allows us to derive \( M_c \)—the molecular weight of a cluster, as

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a function of the DSM parameters $\beta$, $M_K$. We also find an empirical relationship between timescale parameters $\tau_K$ and $\tau_s$, the characteristic time for shuffling a cluster through the entanglement. We compare $G^*$ predictions of the CFM with predictions of the DSM for monodisperse linear, polydisperse linear, and branched systems, and observe no difference. Comparison with shear flow predictions shows that only rates with a Weissenberg number based on the strand relaxation time $\tau_s$ of 1 and higher are affected. For entanglement flow at high strains and high rates, significant difference can occur, which is perhaps not surprising given the observation above. For the systems shown in this work, we report CFM computational savings of several hundred times. We then apply CFM to the shear flow of a star-branched polymer melt with molecular weight not accessible to DSM without rescaling. Excellent agreement with experimental data is observed. Additionally, we report first normal stress theoretical predictions for this system.

$I. \ \text{INTRODUCTION}$

Universality in relaxation of seemingly different polymer systems was one of the inspirations of entanglement research. Linear melts and solutions were shown to have similar relaxation spectra if they have the same number of entanglements per chain. Accurate comparison can be found in the recent work by Huang et al. (2013). Experimental studies of linear-polymer shear flow are abundant and show qualitatively similar behavior for melt and solutions. Although we are not aware of any detailed studies, shear flow observations suggest that universality holds for at least low and moderate shear rates. In entanglement flow, the universality is currently the subject of concern at high strains (though low strains $\epsilon \leq 2$ appear safe). For both melts and solutions, the steady-state entanglement viscosity decreases with increasing elongation rate for rates smaller than the inverse Rouse time, $\tau_R$. However, Bhattacharjee et al. (2002) saw an upturn in the steady-state viscosity of solutions at rates higher than $\tau_R^{-1}$, whereas Bach et al. (2003) did not. More detailed study of failure of universality in entanglement flow was performed recently by [Huang et al. (2013)], though the nature of the discrepancy remains unknown. The otherwise-observed universality suggests that for a theoretical model, it is not required to contain detailed information of the number of monomers between entanglements to capture the behavior of entangled systems in equilibrium and shear flow. However, the ability of such a model to capture entanglement flow is questionable.

While linear polymers are the simplest subjects of study for entanglement theory, branched polymers are one of the first generalizations. Experimental studies showed that linear chains exhibit much shorter relaxation times than arms of branched polymers with the same molecular weight. It is believed that the limitations that the branch point exerts on chain movement is the source of longer relaxation times. Wide timescale separation can pose a problem for theoretical studies, yet a number of theories were successfully applied to the equilibrium dynamics of branched polymers. Pearson and Helfand (1984) applied the Doi-Edwards theory to star-branched polymers. The theory was further developed by Milner and McLeish (1997) and more recently by Wang et al. (2010) and yields good agreement with experimental $G^*$ data. Watanabe et al. (2000) and Watanabe et al. (2002) applied dynamic tube dilution to star-branched polyisoprene (PI) melts and obtained agreement with mechanical and dielectric equilibrium experiments. Multichain primitive chain network (PCN) simulations were performed by Masubuchi et al. (2006) to study the effect of branch point mobility on step shear strain relaxation of H-shaped polymers. However, there are few nonlinear rheology studies of branched polymers. The main reason is that until recently quantitative agreement with experiments even for linear
chains in shear flow was elusive [Graham et al. (2003); Andreev et al. (2013)]. Recent work by Snijkers et al. (2013) presents accurate transient viscosity measurements of monodisperse star-branched polysisoprene melt, which offer an ideal test for application of entanglement theory to branched polymers.

The discrete slip-link model (DSM) is a single-chain mean-field mathematical model, first proposed by Schieber et al. (2003) and further developed by Khaliullin and Schieber (2009, 2010). In this model, the chain is represented as a random walk with constant step length $a_K$ (the Kuhn step). Entanglements are created and destroyed stochastically. As a result, the number of entanglements $Z(t) - 1$ on the chain fluctuates. The chain is coarse-grained to the entanglement level, which means that we integrate out information about individual Kuhn steps’ positions, and keep information only about the number of Kuhn steps in each strand between entanglements $N_i$, and the connector vector $Q_i$, where $i$ goes from 1 to $Z$—the number of strands. The chain is subject to two dynamic processes: Sliding dynamics (SD) and constraint dynamics (CD). SD corresponds to reallocation of Kuhn steps through entanglements with characteristic time $\tau_K$. SD can also create and destroy entanglements at the ends of the chain. When the last Kuhn step of a dangling end goes through an entanglement, the entanglement is destroyed. The probability to create an entanglement at the end of the chain is connected with the destruction process through detailed balance. CD is the creation and destruction of entanglements due to SD of the surrounding chains. This process takes place along the entire length of the probe chain. We implement CD self-consistently with SD by introducing an entanglement lifetime distribution $p_{\text{CD}}(\tau_{\text{CD}})$. Upon creation, lifetimes are picked from the SD-consistent distribution $p_{\text{CD}}(\tau_{\text{CD}})$. Thus, the DSM has the following set of stochastic variables: \{ $Z$, \{ $N_i$ \}, \{ $Q_i$ \}, \{ $\tau_{\text{CD}}$ \}. There are only three-molecular-weight independent parameters in the model: $M_K$, the molecular weight of a Kuhn step; $\beta$, which is related to the entanglement density as $\beta = \lim_{N_K \to \infty} \langle N_i \rangle + 1$; and $\tau_K$. $M_K$ is determined by chemistry, and we do not treat it as an adjustable parameter, while $\beta$ and $\tau_K$ also depend on solvent concentration, and only $\tau_K$ is a function of temperature. These are fixed by comparison to $G^*$ data. However, atomistic simulations can also be used to predict $\beta$ [Steenbakkers et al. (2014); Schieber and Andreev (2014)]. The equilibrium relaxation modulus can be calculated by using the Green–Kubo expression [Kubo (1957)]

$$G(\tau) = \frac{1}{n_k k_B T} \langle \tau_{xy}(t) \tau_{xy}(t + \tau) \rangle_{eq},$$

where $\langle \cdots \rangle_{eq}$ is an ensemble or time average at equilibrium.

Khaliullin and Schieber (2009) showed that DSM predictions agree with linear viscoelastic data (LVE) at least as well as state-of-the-art tube models. Further papers by Khaliullin and Schieber (2010) and Pilyugina et al. (2012) expanded the DSM applications to binary blends and symmetric star-branched polymers with excellent results. Pilyugina et al. (2012) also studied DSM dielectric predictions and obtained good agreement with existing experimental data, except for a single data set available for bidisperse linear systems with a small volume fraction of long chains. Jensen et al. (2011) applied DSM to an entangled polymer network. An unknown fraction of network imperfections allowed only qualitative agreement with experimental observations. Katzarova et al. (2014) were able to estimate composition and predict nonlinear rheology of swollen network using DSM. Andreev et al. (2013) showed that the DSM can be applied without any adjustments to shear flow and yield agreement over a wide range of deformation rates, while agreement with elongational flow data at large strains remains elusive.
While the DSM is a rigorous stochastic mathematical model, expensive numerical calculations are required to obtain most of the predictions. Calculation for the time evolution of duration $1 \tau_K$ for one chain requires a number of operations proportional to $Z$. We find that the longest relaxation time for a linear chain is

$$\tau_D \approx 0.036(\beta + 2)^{3.07}(\langle Z \rangle - 1)^{3.02}\tau_K.$$  

(2)

Here,

$$\langle Z \rangle_{\text{eq}} = (N_K + \beta)/(\beta + 1)$$  

(3)

is the average equilibrium number of entanglements on the chain with molecular weight $M = N_K M_K$. In order to obtain the full relaxation spectrum [Eq. (1)], we need to simulate the time evolution on an ensemble of chains for several $\tau_D$. Thus, the number of calculations required to calculate the full LVE for linear chains is proportional to

$$N_{\text{cost}} \sim (\beta + 2)^3 \langle Z \rangle^4.$$  

(4)

In practice, we commonly use an ensemble of 100 chains for LVE calculations, each of which evolves for several $\tau_D$. For example, for a polyisoprene linear melt of 90 kDa, Eq. (4) yields $8 \times 10^9$ operations. A bigger ensemble size is required during flow predictions since we can take only ensemble averages, although shorter simulation times are necessary. The exact ensemble size for flow predictions depends on flow rate, average number of entanglements, and disentanglement rate. Typically, we use thousands of chains.

Numerical cost limits the DSM application to some systems. Dependence on $\langle Z \rangle$ prevents DSM application to highly entangled chains. Polymer solutions are typically not accessible since the $\beta$ parameter is large [Eq. (4)]. Generally, chains with bigger molecular weight are more expensive for the DSM. Chain architecture plays an even more significant role. For example for star-branched systems, the longest relaxation time and, respectively, the number of calculations grow exponentially with molecular weight.

The DSM is a robust mathematical model, proven to produce very good results at equilibrium and flow for arbitrary system composition and chain architecture. Reduction of the numerical cost will widen the accessible range for the DSM and allow its application to complex chain architectures.

II. CLUSTERED FIXED SLIP-LINK MODEL

Similarities between seemingly different entangled systems suggest that the average number of entanglements per chain is the primary characteristic of the system, while the average molecular weight between entanglements, or rather average number of Kuhn steps, is secondary. The original idea of the clustered fixed slip-link model (CFSM) comes from an error in Pilyugina et al. (2012). In that paper, the molecular weight of a Kuhn step of polyisoprene was assumed to be 505 Da, whereas 140.5 Da is correct. To obtain the correct plateau, $\beta$ was then incorrectly estimated. Surprisingly, no change in predictions were observed, while significant numerical savings were achieved. Clustering Kuhn steps together is one of the simplest ways to derive a more coarse-grained version of DSM. The CFSM is derived by clustering a maximum number of Kuhn steps.
Mathematically the CFSM is simply the DSM with fixed $\beta = 1$. All details of DSM can be found in previous papers on DSM [Khaliullin and Schieber (2009, 2010); Pilyugina et al. (2012)]. In CFSM, we assume that the chain consists of $N_c$ clusters each containing several Kuhn steps. The average number of strands in CFSM is given by

$$\langle Z_c \rangle_{eq} = (N_c + 1)/2.$$  \hspace{1cm} (5)

This expression can be derived from Eq. (3) using $\beta = 1$ and $N_c$ instead of $N_K$.

By joining $\beta/2$ Kuhn steps into a cluster, we integrate out some relaxation modes associated with Kuhn step fluctuation along the primitive path. Thus, the high-frequency plateau modulus predicted by CFSM has a value a bit different from DSM [Khaliullin and Schieber (2009)]. This does not create a problem, since DSM does not include “Rouse modes” dominating experimental data at high frequencies. CFSM and DSM were designed to capture entanglement-driven dynamics, and the high frequency plateau appears outside this region. The CFSM high-frequency plateau is given by

$$G^0_{N_c} = \frac{\rho RT}{M_w} \left[ (1/2)^{N_c-1} + \frac{N_c - 3}{2} \right].$$ \hspace{1cm} (6)

Since the CFSM plateau modulus is different from DSM plateau modulus

$$G^0_{N_c} \neq \frac{\rho RT}{M_w} \langle H(Z_c - 2) \rangle \neq \frac{\rho RT}{M_w} \langle H(Z - 2) \rangle = G^0_N$$

($H(x)$ is the Heaviside step function), this means that the number of entanglements in CFSM is slightly different from that of the DSM. We conclude that we cannot use the plateau modulus to derive $N_c$ as a function of DSM parameters.

Instead, we examine the DSM ideal cross-linked network predictions by Jensen et al. (2011). A typical $G(t)$ for an ideal cross-linked network (no dangling ends) is shown in Fig. 1. The $G(t)$ curve features a high-frequency equilibrium plateau $G^0_N$ and a low-frequency rubbery plateau $G_0$. In an ideal cross-linked network, there is no entanglement creation/ destruction. The only possible relaxation is that associated with Kuhn step relocation along the primitive path. The low-frequency equilibrium plateau $G_0$ found in an ideal cross-linked network corresponds to a state where complete Kuhn step relaxation has happened, but no entanglement relaxation has taken place. This plateau has the same value in

![FIG. 1. Points: Typical DSM $G(t)$ prediction for ideal cross-linked network: $\beta = 5$, $N_K = 50$. Lines: High-frequency plateau $G^0_N$ and low-frequency plateau $G_0$.](image-url)
DSM and CFSM, though it is not observed directly in the non-network calculation. The value of this plateau has been found empirically by Jensen et al. (2011) for large $\beta$

$$G_0 = \frac{M_w}{\rho RT} (0.74(\langle Z \rangle - 1) + 1), \quad \beta \gg 1. \quad (7)$$

Figure 2 shows a slightly different dependence for the CFSM

$$G_0 = \frac{M_w}{\rho RT} (0.823(\langle Z \rangle) + 0.515). \quad (8)$$

Indeed, the leading-order ratio between the high-frequency plateau and the low-frequency plateau is different between CFSM and DSM. CFSM has a ratio closer to 1, which means less chain relaxation takes place. By matching $G_0$, we can find $N_c$ as a function of $N_K$ and $\beta$

$$M_c \approx 0.56(\beta + 1)M_K. \quad (9)$$

CFSM and DSM $G(t)$ predictions with matching $G_0$ can be combined into one curve, as shown in Fig. 3. The time scale factor $A$ is the ratio between $\tau_K$ and $\tau_c$. A power law approximation for the $A$ factor is shown in Fig. 4. The approximation works well for $\beta \approx 3$. $\tau_c$ as a function of $\tau_K$ and $\beta$ is given by

$$\tau_c \approx 0.265\beta^{8/3}\tau_K. \quad (10)$$

We find that Eq. (10) has accuracy of about 10%. CFSM is identical to DSM with $\beta = 1$, and $M_K$, $\tau_K$ replaced by $M_c$, $\tau_c$. Equations (9) and (10) allow us to map DSM parameters $M_K$, $\beta$, $\tau_K$ onto CFSM parameters $M_c$ and $\tau_c$.

III. DETERMINATION OF CD PARAMETERS

CFSM is a less-detailed version of DSM, thus some mathematical expressions used in DSM can be simplified analytically, granting additional numerical savings. The most important simplifications occur for parameters of the entanglement life-time distribution.

**FIG. 2.** Low frequency equilibrium plateau $G_0$ as function of $\langle Z \rangle$ for $\beta = 1$. Points: CFSM prediction. Line: Linear fit.
Implementation of self-consistent CD in DSM has been described in detail in previous papers [Khaliullin and Schieber (2009); Andreev et al. (2013)]. The same approach can be used for CFSM. For linear chains, we assumed the following form for the life-time distribution probability:

\[ p_{\text{CD}}(\tau) = \frac{1}{C_0} g(\tau a_{s0}) \frac{s_{max}}{C_0} \frac{s_{D}}{C_0} H(s_{max}/C_0) + g(d/s_{D}/C_0), \]

(11)

where \( H(x) \) is the Heaviside step function. In CFSM, the \( p_{\text{CD}} \) parameters \( \{ g, a, s_{0}, s_{\text{max}}, s_{D} \} \) are functions of \( N_c \) only. These are shown in Fig. 5. Analytical approximations also shown in Fig. 5 can be used to determine parameters without expensive preliminary calculations.

IV. RESULTS

We apply the CFSM to several entangled polymer melt rheology data sets: polyisoprene \( G^* \) data sets by Watanabe and coworkers; a linear polyisoprene melt [Matsumiya et al. (2000); Watanabe et al. (2002)] and one set of star-branched polyisoprene melt.

FIG. 3. Superposition of DSM linear chain \( G(t) \) predictions with different \( \beta \). DSM predictions are manually shifted horizontally by factor \( A \) to fall on top of CFSM prediction with \( \langle Z_c \rangle = 12.5 \). \( N_K \) is obtained by matching \( G_0 \).

FIG. 4. DSM \( \tau_K \) scaling. Points: Time scale parameters \( A \) found by superposition of DSM \( G(t) \) predictions. Line: Power law fit.
[Watanabe et al. (2000)]; $G^*$ and shear flow polyisoprene data by Auhl et al. (2008), and shear flow of star-branched polyisoprene melt by Snijkers et al. (2013). For all CFSM predictions, $N_c$ were found using Eq. (9), while $\tau_c$ was fitted.

Figure 6 shows a typical comparison between $G^*$ predictions of CFSM and DSM for linear polyisoprene melt 90 kDa [Auhl et al. (2008)]. CFSM should reproduce DSM prediction approximately up to a frequency $1/\tau_c = 10$ rad/s, but in this region, Rouse modes already dominate in the experimental data. Neither DSM nor CFSM capture the Rouse behavior. Use of a finite-size chain ensemble (100 chains) and using a Baumgaertel-Schausberger-Winter spectrum [Baumgartel et al. (1990)] to convert...
predictions from the time to the frequency domains explains the small difference. We conclude that CFSM and DSM have almost complete agreement, but the cost of CFSM is 387 times less.

CFSM predictions for several linear and star-branched polyisoprenes are shown in Figs. 7 and 8. DSM predictions for these experiments with excellent agreement were reported by Pilyugina et al. (2012). CFSM successfully reproduces those results. We use one \( \tau_c = 4.8 \times 10^{-6} \) s for the entire data set by Watanabe and coworkers, including the star-branched melt since they are taken at the same temperature. \( N_c \) values are linearly proportional to molecular weight.

Shear flow CFSM predictions with comparison to DSM are shown in Fig. 9. A small discrepancy between CFSM and DSM is observed only for the highest experimentally measured shear rates. We estimate the strand Weissenberg number as \( 4 \tau_c \gamma = 0.15 \) for the highest rate. Figure 10 is a comparison of CFSM and DSM for a rate 10 times faster than the highest rate measured by Auhl et al. (2008). CFSM shows a higher steady state value and bigger overshoot. We conclude the discrepancy becomes significant for strand Weissenberg numbers greater than approximately 1.

Elongational flow CFSM predictions with comparison to DSM are shown in Fig. 11. CFSM deviates from DSM for high rates and high strains. For elongational flow, high-frequency “longitudinal” modes are believed to be more important than for shear flow. However, the deviation happens for Hencky strain above approximately three, where
DSM does not agree with the experimental data, and other physics become important [Andreev et al. (2013)]. We conclude that CFSM produces elongational flow predictions similar in quality to DSM. It agrees with experiment until a Hencky strain between two and three, but then it predicts extreme strain softening. CFSM agrees with DSM in the region where they both capture experimental data. The deviation between DSM and CFSM in elongational flow is a result of extreme clustering. Perhaps lowering the molecular weight of a cluster, i.e., setting $b$ larger than unity will bring predictions of the clustered model closer to the predictions of original DSM.

Clustering also fails in ideal cross-linked network elongational flow predictions. Comparison of DSM and CFSM is shown in Fig. 12. Parameters for CFSM were found

![Graph showing elongational flow predictions](image)

**FIG. 9.** CFSM shear flow predictions. Symbols are experimental data by Auhl et al. (2008): Polyisoprene melt 90 kDa, $-35^\circ$C, gray line is DSM predictions: $\beta = 25$, $M_K = 140.5$ Da, $\tau_K = 8 \times 10^{-5}$ s and red line is CFSM prediction: $M_c = 2050$ Da, $\tau_c = 0.1$ s. This figure first appeared in Schieber, J. D., and M. Andreev, “Entangled polymer dynamics in equilibrium and flow modeled through slip links,” Annu. Rev. Chem. Biomol. Eng. 5, 367–381 (2014). Copyright 2014 Annual Reviews.

![Graph showing shear flow predictions](image)

**FIG. 10.** CFSM shear flow predictions. Polyisoprene melt 90 kDa, $-35^\circ$C, $\dot{\gamma} = 3.3$ s$^{-1}$, gray line is DSM predictions: $\beta = 25$, $M_K = 140.5$ Da, $\tau_K = 8 \times 10^{-5}$ s and red line is CFSM prediction: $M_c = 2050$ Da, $\tau_c = 0.1$ s. Note that $\tau_c/\dot{\gamma} = 1.5$. 

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using Eqs. (9) and (10). We believe that the observed deviation is a result of longitudinal modes removed from the model. We mentioned that for an ideal entangled network, longitudinal motion is the only possible relaxation process. For ideal entangled networks, even for slow rates, their contribution to stress during elongation is significant (Fig. 12). However, the true systems are not computationally prohibitive, because the longest relaxation time is much less than \( \tau_D \). \textit{Jensen et al. (2011)} examined relaxation times for several ideal entangled networks. For the most entangled system \((Z) = 20.8\), the longest relaxation time was found to be approximately 1700\( \tau_K \). The longest relaxation time is bigger than \( \tau_e = 4\tau_c \approx 88\tau_K \), but smaller than \( \tau_R = \tau_e(Z)^2 \approx 35\ 000\tau_K \).

Table I shows the numerical savings from using CFSM versus DSM. From Eq. (4), we expect numerical savings to approach \((\beta/3)^3\), which is approximately 700, with \( \beta = 25 \) for PI. In all cases, savings are on the order of hundreds of times, which are close to expected.

We now turn to a system that would be computationally prohibitive for DSM but is easily reached with the CFSM. CFSM predictions for a star-branched polyisoprene melt \((Z) \approx 16.5\) are shown in Fig. 13. Star-branched system with such a molecular weight is inaccessible by DSM due to high computational cost. CFSM shows very good agreement
with the experimental data taken by Snijkers et al. (2013). We also present CFSM predictions for the first normal stress coefficient during inception of shear flow (Fig. 14), which has not yet been measured.

V. CONCLUSION

We showed that rescaling the fixed slip-link model to a universal $\beta = 1$ is able to successfully describe both equilibrium viscoelasticity and shear flow for linear and star-branch polymer melts.

Since the procedure only rescales parameter values, we can use the same code. We found that clustering of Kuhn steps results in loss of some unimportant high-frequency relaxation modes of $G^{*}$ predictions. Thus, matching the high-frequency plateau does not give identical predictions between the CFSM and the more-detailed DSM. Instead, we matched the rubbery plateau, directly observed in $G^{*}$ predictions of cross-linked networks. The height of this plateau gives us the first CFSM parameter $M_c$. The second parameter $s_c$ can be found by fitting just one set of experimental data for a given chemistry, analogous to the DSM $s_K$. With these, the CFSM prediction is surprisingly close to the prediction with the more detailed DSM, but CFSM numerical cost is just a small fraction of that for the DSM. Specifically for polyisoprene, the CFSM requires several hundred times fewer calculations than the DSM. We also obtained empirical relations between the CFSM and the DSM parameters, which makes switching between models simple. Additionally, we derived approximations for linear-chain CD parameters, since in

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CFSM (s)</th>
<th>DSM (s)</th>
<th>Speedup factor</th>
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<td>337</td>
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<tr>
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<td>32</td>
<td>17500</td>
<td>546</td>
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</tbody>
</table>

TABLE I. Comparison of DSM and CFSM numerical cost. For $G^{*}$ entries, we report CPU time required to perform the time evolution of one chain for $10 \tau_0$. For shear flow entries, the time evolution of one chain was performed for the same time as corresponding predictions in Fig. 9. We used Intel® Xeon® E5-2640 CPU.

FIG. 13. CFSM shear flow predictions. Symbols are experimental data by Snijkers et al. (2013): 4-arms star-branched polyisoprene melt 56 kDa, $20^\circ C$, red line is CFSM prediction: $M_c = 2050$ Da, $\tau_c = 5.5 \times 10^{-3}$ s. This figure first appeared in Schieber, J. D., and M. Andreev, “Entangled polymer dynamics in equilibrium and flow modeled through slip links,” Annu. Rev. Chem. Biomol. Eng. 5, 367-381 (2014). Copyright 2014 Annual Reviews.
CFSM, they are functions of just one variable, \( N_c \). Using these approximations allows us to avoid preliminary calculations and further simplifies use of CFSM. For the equilibrium relaxation spectrum, we observe practically identical agreement between the DSM and CFSM. The models show only an insignificant difference in shear flow prediction at the highest strains and strain rates measured experimentally. Discrepancy between CFSM and DSM becomes significant for rates with strand Weissenberg numbers of approximately 1. For elongational flow, significant difference can occur, but only for high strains and high rates, where DSM does not capture experimental data. We also showed failure of clustering for ideal cross-linked networks, where the contribution of high-frequency relaxation modes is significant.

We find that CFSM predictions support the idea of universality in entangled polymer systems. It also shows that for flexible melts and solutions in equilibrium and under moderate shear flows, the number of Kuhn steps between entanglements is an unimportant characteristic of the system. In other words, for sufficiently flexible entangled polymers, the exact degree of flexibility only plays a role at high flow rates and high strains.

Finally, we showed CFSM predictions for transient viscosity and first normal stress during shear flow for star-branched 4-arms 56 kDa polyisoprene melt, which is not accessible to DSM due to high computational cost. The CFSM prediction is in excellent agreement with experimental data for transient viscosity, while we are unaware of experimental measurements of the first normal stress for star-branched polymer melts. We hope that these predictions spur future experimental studies.

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