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Dynamics and rheology of wormlike micelles emerging from particulate computer simulations

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We perform coarse-grained computer simulations of solutions of semidilute wormlike micelles and study their dynamic and rheological properties, both in equilibrium and under shear flow. The simulation model is tailored to the study of relatively large time and length scales (micrometers and several milliseconds), while it still retains the specific mechanical properties of the individual wormlike micelles. The majority of the mechanical properties (persistence length, diameter, and elastic modulus of a single worm) is determined from more detailed atomistic molecular dynamics simulations, providing the link with the chemistry of the surfactants. The method is applied to the case of a solution containing 8% (by weight) erucyl bis(hydroxymethyl)methylammonium chloride (EHAC). Different scission energies ranging from 15.5k_BT to 19.1k_BT are studied, leading to both unentangled and entangled wormlike micelles. We find a decrease in the average contour length and an increase in the average breaking rate with increasing shear rate. In equilibrium, the decay of the shear relaxation modulus of the unentangled samples agrees with predictions based on a theory of breakable Rouse chains. Under shear flow, transient over- and undershoots are measured in the stress tensor components. At high shear rates we observe a steady-state shear stress proportional to \( \dot{\gamma}^{1/3} \), where \( \dot{\gamma} \) is the shear rate. This is confirmed by our high shear rate experiments of real EHAC in a parallel-plate geometry. © 2008 American Institute of Physics. [DOI: 10.1063/1.2970934]

I. INTRODUCTION

In this paper we will focus on the dynamics and rheology of amphiphilic molecules forming elongated structures called wormlike micelles. Rheological experiments produce a wealth of data and theories that can explain some of the experimental findings.1–10 Most macroscopic experiments, however, do not provide us with a detailed fundamental understanding of the underlying processes that lead to the emergent rheology. Often their interpretation is based on theories which contain uncontrolled approximations, and their range of applicability is limited to certain flow conditions. Simulations may contribute to our understanding of the peculiar rheology of wormlike micelles. With simulations we have the possibility to "zoom in" on the detailed processes, study their influence on the rheology, and test the approximations made in theories. This will contribute to a rational design of new viscoelastic materials based on wormlike micelles.

Particle based simulations of wormlike micelles may be performed on many different lengths and time scales, from the atomistic to the mesoscopic. An overview is given in Fig. 1. To realistically simulate the rheology, one would ideally use an atomistic model11–13 or a model in which each amphiphilic molecule is individually represented by a properly coarse-grained version of it.14–16 However, using such models and current-day computing power, it is impossible to determine the macroscopic rheology of a solution of entangled wormlike micelles. Prohibitively long computation times are needed because of the (1) very large length scales and (2) very long time scales involved.

Focusing first on the length scales, it must be realized that the stress tensor is a collective property of a sufficiently large portion of fluid. In a molecular dynamics simulation, the instantaneous stress components are generally given by

\[ \sigma_{ij} = \frac{1}{V} \sum_{a} \left( F_i^{(a)} \right) \left( r_j^{(a)} - r_i^{(a)} \right) \]

where \( V \) is the system volume, \( \mathbf{F}_i \) the force on particle \( a \) with position \( \mathbf{r}_i \), and \( \mathbf{r}_j \) the position of particle \( j \). At steady state, the mean values of \( \sigma_{ij} \) are needed because of the

\[ \left< \sigma_{ij} \right> = \frac{1}{V} \sum_{a} \left< F_i^{(a)} \right> \left< (r_j^{(a)} - r_i^{(a)}) \right> = \frac{1}{V} \sum_{a} \left< F_i^{(a)} \right> \mathbf{R}_j^{(a)} \]

where \( \mathbf{R}_j \) is the position of the center of mass of particle \( j \). To determine the mean stress tensor, \( \left< \sigma_{ij} \right> \), we need an ensemble average over many configurations. Such an average is very difficult to perform with a molecular dynamics simulation, which is why the instantaneous stress is computed and used to calculate the stress

\[ \left< \sigma_{ij} \right> = \frac{1}{N} \sum_{n} \left( \frac{1}{V} \sum_{a} \left( F_i^{(a)}(n) \right) \left( r_j^{(a)}(n) - r_i^{(a)}(n) \right) \right) \]

where \( n \) is the configuration number and \( N \) the number of configurations.

FIG. 1. Particle based simulations may be performed on many different lengths and time scales. With atomistic force fields (lower left) we can capture the influence of the specific surfactant chemistry on the properties of a piece of wormlike micelle. By coarse graining the surfactant molecules these calculations are greatly accelerated. More macroscopic properties, such as the chain length distribution and rheology, can only be calculated with higher-level models, such as the FENE-C and MESOWORM models (upper right).
Conversely, chains can break if any of the bonds are at the chain ends or by recombination with other chain ends. Like micelles are represented by flexible chains of relatively long characteristic relaxation time. Most entangled wormlike micelles have a longest characteristic relaxation time \( \tau \) ranging from \( 10^{-4} \) to \( 10^3 \) s (although entangled wormlike micelles can have smaller relaxation times). In order to simulate the rheological properties of entangled wormlike micelles, one must be able to reach time scales of the order of at least milliseconds. For example, for models with coarse-grained amphiphiles a typical time step is \( 10^{-14} \) s, leading to a total of \( 10^{11} \) time steps. Usually the maximum attainable number of time steps in molecular dynamics is of the order of \( 10^8 \). So, even when the simulation is sped up by coarse graining surfactant molecules to a few beads, this presents us with an unsurmountable amount of computational work.

The above discussion shows clearly that the only way forward is to coarse grain even further, to the point where each unit represents several surfactant molecules. This will, of course, be at the cost of losing detailed information about the surfactant molecules. One important development in this direction is the generic FENE-C model. In FENE-C the wormlike micelles are represented by flexible chains of relatively hard spheres. Chains can grow by the addition of monomers at the chain ends or by recombination with other chain ends. Conversely, chains can break if any of the bonds are stretched because of thermal fluctuations or tension. The FENE-C model was studied extensively by Kröger et al.\(^{21-23} \) and Padding and Boek.\(^{24,25} \) In the original model\(^ {21,22} \) solvent beads were included to account for solvent effects, but the solvent effect may be mimicked through Brownian dynamics as well.\(^ {25} \) The resulting worm length distribution is found to agree well with the theoretical (mean-field) prediction \( c(L) \propto \exp(-L/L) \), and shear thinning of the viscosity is observed, although not as strong as in the experiment.\(^ {22,25} \)

In the FENE-C model, being a generic model, no reference is made to any specific real wormlike micellar system. This may be an advantage, since this allows the simulator of the freedom to scale the simulation results onto experimental results. However, in our opinion great care must be taken if realistic and quantitative results for the dynamics and rheology of wormlike micelles are required. First, there are always multiple relevant length scales. Scaling one of them onto experimental values does not guarantee that the other length scales will be described correctly as well. For example, the persistence length of a typical wormlike micelle is several times its diameter,\(^ {26} \) whereas in the flexible FENE-C model these are more or less the same. Second, the kinetics of breakup and fusion of chain ends may not be as fast as predicted by the FENE-C model. In the original FENE-C model, recombination is relatively easy because chain ends can fuse instantaneously if their separation is smaller than some critical distance. In reality, before two chain ends can fuse, there may be specific demands on the conformations of the surfactants in the end caps, giving rise to a considerable free energy barrier. Chain recombination, like scission, may therefore be an activated process.\(^ {24,25} \)

These disadvantages may be alleviated by introducing a (strong) bending potential between the spherical beads and an additional radial interaction mimicking the activation barrier (as in the FENE-CB model\(^ {26} \)) or some Monte Carlo equivalent.\(^ {27} \) Unfortunately, this remains very CPU-intensive because many beads will be required to represent one entanglement length of a realistic wormlike micelle, while the integration time step will still be limited by the relatively hard interactions at the scale of the beads.

In this paper we will use and study a coarse-grained model called MESOWORM (mesoscale wormlike micelles). Preliminary descriptions of this model have been published elsewhere.\(^ {19,26,28} \) This model is coarse grained to the level of a persistence length, but is still able to capture (most of) the specific mechanical properties of a real wormlike micelle.

II. THE MODEL

The philosophy behind the MESOWORM model\(^ {26} \) is that the material properties of individual wormlike micelles can in principle be measured from more detailed simulations or targeted experiments. Relevant material properties include the worm diameter, persistence length, elastic modulus, and scission and activation free energies for fusion and breaking. Allowing the model to have these parameters as input, the rheology can be predicted from realistic input, with as few assumptions as possible. This enables us to create a hierarchy of simulation models, ultimately linking the chemical details of the surfactants and other components of the solution to its macroscopic rheology.
Of course, some assumptions still have to be made. First, it is assumed that the stress is dominated by the network of wormlike micelles and that hydrodynamic interactions are relatively unimportant. This allows for an implicit treatment of solvent effects by means of Brownian dynamics (of rigid rods). The model therefore does not apply to dilute solutions, where the micelles are relatively short and do not overlap. Second, it is assumed that excluded volume interactions are relatively unimportant. This allows us to treat the interactions between wormlike micelles as chains of infinitely thin lines (but note that the friction with the solvent will be based on the true aspect ratio, vide infra). Treating the wormlike micelles as thin lines is allowed if the ratio of persistence length to diameter is much larger than 1 and if the concentration is low enough to have an isotropic equilibrium distribution. The model should therefore not be used for very high concentrations either, where excluded volume effects may lead to spontaneous nematic ordering of the wormlike micelles. There is a large range of concentrations between dilute and concentrated where the model does apply. Indeed, the semifluid regime is of most practical interest, since the viscosity can be greatly enhanced by adding a relatively low amount of surfactant.

In the MESOWORM model, each persistence length of wormlike micelles is represented by one unit, see Fig. 2. This degree of coarse graining is as large as possible to allow for a large integration time step and few particles, while it is still small enough to allow an accurate description of the overall conformation of the wormlike micelle. The midpoints of bonded units interact with each other through the following radial potential:

$$\varphi_{\text{bond}}(r) = \frac{1}{2}(E_a - E_{sc}) - \frac{1}{2}(E_a + E_{sc})\cos\left(\frac{r - l_p}{w}\right)$$

for \( \, r \in [l_p - \pi w, l_p + \pi w] \),

$$w = \sqrt{\frac{(E_a + E_{sc})l_p}{2K_L}},$$

where \( E_{sc} \) is the scission energy, \( E_a \) the (additional) activation energy associated with the fusion-recombination process, \( l_p \) the persistence length, and \( K_L \) the elastic modulus of the wormlike micelle. The width parameter \( w \) of the potential well has been chosen such that the second derivative in the vicinity of the minimum of the well equals \( K_L/l_p \), as required by the elastic response to compression of a wormlike micelle of length \( l_p \). \( \varphi_{\text{bond}}(r) \approx (1/2)(K_L/l_p)(r - l_p)^2 - E_{sc} \) for small extensions. The correct stiffness of the wormlike micelle is implemented by means of an angular potential between each bonded triplet (see Fig. 2),

$$\varphi_{\theta}(\theta) = k_B T \theta \tan(\theta/2).$$

In the limit for small angles this reduces to the often-used potential \( k_B T \theta^2 / 2 \), while the potential diverges for \( \theta \to \pi \), which prevents problems with the entanglement algorithm (vide infra).

As soon as a bond is stretched or compressed beyond its limits \( (l_p + \pi w, l_p - \pi w) \), the bond is broken. Equation (2) shows that when a bond is broken, its potential energy is not zero but equal to \( E_{sc} \), the activation barrier associated with the fusion-breaking process. Conversely, before two chain ends are allowed to fuse, they must overcome an energy barrier of height \( E_{sc} \). There are many ways in which such an energy barrier may be implemented. In the current model it is implemented as a smooth repulsive barrier,

$$\varphi_{\text{rep}} = \begin{cases} \frac{1}{2}E_a \left[ 1 + \cos\left(\frac{x - \pi w}{w'}\right) \right] & \text{for } x \in [\pi w, \pi(w + w')] \\ 0 & \text{for } x > \pi(w + w'), \end{cases}$$

$$w' = \sqrt{\frac{E_{alp}l_p}{2K_L}}.$$  

Here \( x \) is the distance between the endcaps of the wormlike micelle. The position of the endcap of a wormlike micelle is approximated as the extension of the last bond vector, over a length \( l_p/2 \), i.e., if \( \mathbf{r} \) is the position of the midpoint of the last unit and \( \mathbf{u} \) is the orientation of the last bond vector, then the endcap position is calculated as \( \mathbf{r}_{\text{end}} = \mathbf{r} + l_p/2\mathbf{u} \). When the distance \( x \) between two endcaps is smaller than \( \pi w \), and the distance \( r \) between the midpoints is within the range \( [l_p - \pi w, l_p + \pi w] \), two chain ends are allowed to fuse. Because the width \( w \) is usually much smaller than the persistence length \( l_p \), this means that two wormlike micelles will fuse only when their extremal bonds are more or less aligned, leading to a smooth transition from being unbounded at energy 0, via the activation barrier at energy \( E_{sc} \), to being bonded at energy \( -E_{sc} \), as schematically depicted in Fig. 3.
Note that also in the case of the FENE-CB model, chains tend to recombine in the aligned state.

The fusion energy barrier is purposely not a function of the distance between the midpoints of the units at the extremes of the wormlike micelles because this would lead to far too long wormlike micelles when using realistic values of the scission energy $E_{sc}$. The average wormlength is actually greatly overpredicted in the case of both the FENE-C model and mean-field theory. In the latter, a wormlike micelle is treated as a random walk on a lattice, with an energy penalty $E_{sc}$ for each pair of chain ends. The random walk lattice model is usually justified by identifying each occupied lattice space with one persistence length of wormlike micelle. By variationally minimizing the free energy, under the constraint of fixed volume fraction $\phi$, the theory then predicts an average length of $\bar{L}=c\phi^{1/3} \exp \left[ E_{sc}/(2k_B T) \right]$ persistence lengths, where the prefactor $c$ is of the order of $1$. Although the scaling with $E_{sc}/T$ has been confirmed, the prefactor is unrealistic. For example, experimental estimates of the scission energy of erucyl bis(hydroxymethyl)methylammonium chloride (EHAC) wormlike micelles vary between $25k_BT$ and $50k_BT$.\cite{29,30} Mean-field theory then predicts an average wormlength of $O(10^3-10^4)$ persistence lengths, corresponding to a contour length of $O(10^3-10^4)$ m. These estimates would make wormlike micelles truly giant! It is important to realize that wormlike micelles are relatively thin. By letting the fusion process take place within a small volume at the endcap positions, instead of a large volume associated with a sphere of diameter $O(l_p)$ around the midpoint of the extremal units, the average length of the wormlike micelles is brought down to realistic proportions. In Appendix A we will describe the effect of coarse graining the possible breaking points to just one per persistence length. This yields an additional correction of order $\frac{k_BT}{2l_p} \ln(l_p/D)$ to the scission energy.

In the model as described up to this point, there is no excluded volume between the worm segments. In other words, the wormlike micelles would be able to pass through each other like ghost chains, whereas the dominant stress contribution is expected to arise from entanglements between the wormlike micelles. To remedy this, the TWENTANGLE-MENT technique is applied. In this technique, originally designed for polymer melt simulations,\cite{17,18,31,32} an imminent bond crossing is detected and prevented by the introduction of a new coordinate (an entanglement point) at the crossing point. From that time onward, until the entanglement is removed again, the interaction between bonded units is a function of the path length measured via the entanglement points, instead of the usual distance between the units, see Fig. 4. Entanglements are allowed to jump over the (central) position of a unit, and so can slide along the backbone of a wormlike micelle.

We use (overdamped) Brownian dynamics to update the positions of the particles. The solvent friction on each particle is anisotropic to reflect its rodlike shape of dimensions $l_x \times D$. More precisely, we track the centers of mass $r_i$ of individual rodlike particles. The orientation $\hat{u}_i$ of rod $i$ follows from an average of the connectors to the previous and next particle, i.e.,

$$\hat{u}_i = \frac{r_i - r_{i-1}}{|r_i - r_{i-1}|} + \frac{r_{i+1} - r_i}{|r_{i+1} - r_i|},$$

(7)

The position of rod $i$ is updated according to

$$r_i(t + \Delta t) = r_i(t) + \bar{E}^{-1}_i \cdot F_i(t) \Delta t + v_{\text{flow}}(y) \Delta t + \Delta r^R_i,$$

(8)

where $\Delta t$ is the integration step, $F_i$ the total conservative force on $i$, $v_{\text{flow}}(y)$ the background flow velocity (in the $x$ direction) at height $y$, and $\Delta r^R_i$ the random displacement of $i$, which is linked to the inverse friction (or mobility) tensor $\bar{E}^{-1}_i$, according to $\langle \Delta r^R_i \Delta r^Y_j \rangle = 2k_BT \bar{E}^{-1}_i \delta_{ij} \Delta t$. We note that the friction tensor $\bar{E}_i$ of rod $i$ depends on its orientation $\hat{u}_i$, with the friction parallel to the rod given by $\xi_i = 2\pi \eta l_p / \ln(l_p/D)$ and the friction perpendicular to the rod twice as large. Here $\eta$ is the solvent viscosity. A derivation can be found in Ref. 33.

In order to study shear flow, Lees–Edwards (“sliding-brick”) boundary conditions are implemented.\cite{34} The possibility of nonaffine flow is included. This is not trivial for Brownian dynamics simulations where a friction with a static background flow $v_{\text{flow}}(y)$ is assumed. We solved this by introducing a dynamic background flow, with a velocity coupled to the wormlike micelles through an overdamped feedback mechanism. The feedback is accomplished by measuring, at each timestep and height $y$, the average “velocity” (excluding random displacements) $\langle v_{\text{flow}}(y) \rangle$ of the wormlike micellar material. The background flow velocity field $v_{\text{flow}}(y)$ reacts to this by accelerating or decelerating according to $dv_{\text{flow}}(y)/dt = 1/\tau_f \langle (v_{\text{flow}}(y) - v_{\text{flow}}(y)) \rangle$, where $\tau_f$ is the flow reaction time, which must be set sufficiently fast not to interfere with intrinsic timescales of the wormlike micelles.

The parameters of the model used in this work, chosen to represent EHAC, are given in Table I. We have determined most parameters from the results of more detailed atomistic molecular dynamics simulations.\cite{12,26} Only for the scission and activation energies we do not yet have values from atomistic simulations. Very recently, Pool and Bolhuis\cite{35} suggested a way to estimate such energies by transition path sampling. Note that we have decreased the elastic modulus $K_L$ by a factor of 10 relative to the experimental value to allow a time step of 1 ns. This low value of $K_L$ does not lead to a significant change in rheological properties because the rheology is dominated not by the elasticity between successive units but rather by the overall conformations of the
wormlike micelles and the entanglements between them. The large time step of 1 ns is sufficient to reach the time scales of interest (milliseconds or more). One of the goals of this work was to investigate the influence of the dimensionless scission energy $E_{sc}/k_BT$ on the behavior of the system. We have therefore investigated the model at $E_{sc} = 5 \times 10^{-20}$ J ($T = 333$ K) and at $E_{sc} = 6 \times 10^{-20}$ J ($T = 333$ and 300 K). Including the aforementioned correction of $\frac{1}{2}k_BT \ln(l_p/D)$, this corresponds to experimental scission energies of 15.5$k_BT$, 17.6$k_BT$, and 19.1$k_BT$, respectively. Experimentally, the scission energy can be tuned by changing the salt concentration of the solution, see, e.g., Refs. 29, 30, and 36.

All systems simulated contained 16 384 persistence length segments, corresponding to 10.6 $\times 10^6$ EHAC amphiphilic molecules.26 These were placed in a periodic box of dimensions of 1212 $\times$ 303 $\times$ 303 nm, corresponding to an experimental wormlike micellar system of 8% (by weight) EHAC. The large system dimensions were chosen purposely to accommodate the radius of gyration of wormlike micelles inside the length of one periodic box, even when they are elongated in the $x$-direction by shear flow.

III. RESULTS

A. Contour length

We first study the contour lengths of the wormlike micelles. The contour length distribution in a wormlike micellar solution is very broad—in equilibrium it is exponential—and mainly characterized by its average $L$. Figure 5 shows $L$ as a function of shear rate $\dot{\gamma}$ for all systems studied. At low shear rates all curves show a constant contour length, the scaling of which agrees with the theoretical expectation $L \sim \exp(E_{sc}/(2k_BT)).$ We also observe that beyond a certain critical shear rate the average contour length gradually decreases. The critical shear rate decreases with increasing scission energy. This may be expected because wormlike micelles with a higher scission energy are longer; therefore they are more easily influenced by the shear flow.

B. Breaking times

Next we measure the average breaking time $\tau_b$ of a wormlike chain. In equilibrium, detailed balance requires that the average rate of breaking a bond in a wormlike micelle is equal to the average rate of forming a new bond with another wormlike micelle. When a shear flow has just started up, however, we enter a transient region where these two rates may be very different, causing the average contour length to change. When measuring the average breaking time, we have made sure that steady-state conditions apply. In such a steady state the average breaking time is again equal to the average time for a newly formed chain end to form a bond with another chain end, but its value may be different from the one under equilibrium conditions.

In Fig. 6 we show the average breaking rate per unit length of wormlike micelle as a function of shear rate. We choose to represent the breaking rate per unit length because a longer wormlike micelle, having more bonds to break, will have a higher average breaking rate. Effectively, we are measuring the breaking rate constant $c_1$ which appears in the theory on the rheology of wormlike micelles by Cates et al.37 as $\tau_b = 1/(c_1L)$. In the theory of Cates et al., $c_1$ is assumed to be constant. This constant may, of course, differ from one type of wormlike micelle to another. Because an escape over a barrier of height $E_{sc} + E_{sl}$ is involved, it will certainly decrease with increasing scission and activation energies. The theory of Cates et al. applies to the case of linear rheology, where flow rates are infinitesimally small. Indeed, our results for the wormlike micelles with lowest scission energy (dia-
FIG. 7. The shear relaxation modulus \( G(t) \), calculated from the stress-stress autocorrelation in an equilibrium simulation. The smooth lines are not fits, but theoretical predictions for a breakable Rouse chain, Eqs. (9) and (10).

FIG. 8. Same as Fig. 7 but on a semilog scale to emphasize the near-exponential relaxation at larger correlation times.

mons in Fig. 6) suggest that, at the lowest shear rates studied, the breaking rate per unit length is constant. At higher shear rates, however, the assumption of constant breaking rate (per unit length) is clearly invalid. We observe an increase in the breaking rate over more than two decades. Qualitatively similar but less strong increases in the breaking rate are obtained through a combined effect of breaking and the termination of the average length of wormlike micelles.

The observed accelerated breaking under shear is a large effect. From this we learn that one must be careful in applying Monte Carlo-type mechanisms to mimic the activated effect. From this we learn that one must be careful in applying Monte Carlo-type mechanisms to mimic the activated effect.

C. Linear rheology

By analyzing the fluctuations of the microscopic stress tensor in equilibrium simulations, we obtain the zero-shear relaxation modulus as \( G(t) = V/(k_B T)^{-1} \langle \sigma_{xx}(t) \sigma_{xx}(0) \rangle \), where \( \sigma_{xx} \) is given by Eq. (1). Other property characteristic of linear rheology can be derived from \( G(t) \). For example, the storage and loss moduli \( G'(\omega) \) and \( G''(\omega) \) are obtained through a Fourier transform, and the zero-shear viscosity is given by the infinite time integral, \( \eta_0 = \int_0^\infty G(t) dt \).

It is notoriously difficult to measure stress autocorrelation functions. Indeed, in the system of highest scission energy, the stress correlation turned out to be too noisy to make any definitive conclusions. The other two systems gave sufficiently converged results. Figure 7 shows the measured relaxation modulus \( G(t) \) for these two systems (squares and diamonds).

For unentangled Rouse chains, in the limit where breaking of an average chain is faster than the longest relaxation time of an equivalent unbreakable chain, the relaxation modulus arises from a combined effect of breaking and the usual Rouse stress relaxation of a chain. In Appendix B we give an explicit derivation, including all prefactors. The resulting expression is

\[
G(t) \approx \frac{c k T}{N + 1} \left( \frac{\pi \tau_b}{6 l_p} \right) \exp\left( -\frac{t}{\tau_b} \right) \quad (t > \tau_b/N),
\]

where \( c \) is the number of Kuhn segments per unit volume, \( \tau_b \) the longest relaxation time of an unbreakable chain of length equal to the average wormlike micelle, and \( N \) the number of Kuhn segments in this average chain. In fact, a precise determination of the average length of wormlike micelles is not necessary, as only the combination \( \tau_b/(N+1)^2 \) matters. For a Rouse chain \( \tau_b/(N+1)^2 = \xi b^2/(3 \pi^2 k T) \), with \( b \) the Kuhn length and \( \xi \) the (average) friction on a segment. The stress relaxation time \( \tau \) in Eq. (9) is given by

\[
\tau = 0.42 \tau_0^{2/3} \tau_b^{2/3}.
\]
transition from Rouse to entangled behavior is confirmed when we study the stress in sheared systems in the next subsection.

D. Nonlinear rheology

When a shearing motion is suddenly applied to an initially quiescent solution of wormlike micelles, one often observes a characteristic overshoot in the induced shear stress before it attains a stationary value. This is also observed in our simulations. Figure 9 shows the shear stress $\sigma_{xy}$, the first normal stress difference $N_1 = \sigma_{xx} - \sigma_{yy}$, and the second normal stress difference $N_2 = \sigma_{yy} - \sigma_{zz}$ as a function of time after a sudden application of shear flow at a rate of $\dot{\gamma} = 10^4$ s$^{-1}$ in the $E_a = 19.1kT$ system. A clear overshoot occurs in the shear stress. At the given shear rate, the first normal stress difference is larger than the shear stress and also displays a maximum, but occurring at a later time. Interestingly, the second normal stress difference, although much smaller in magnitude than the first normal stress difference, shows an initial positive overshoot, after which we find a negative undershoot and finally a relaxation to a negative value. Such normal stress differences give rise to quite peculiar viscoelastic effects, collectively known as Weissenberg effects.39

Similarly to the case of polymer melts and solutions, it is generally believed that the overshoots in the stress components occur because the wormlike micelles resist the chain stretch induced by the onset of fast flow, an effect which diminishes once the wormlike micelles become oriented toward the flow direction. An important dimensionless parameter determining the magnitude of this effect is the Deborah number, defined as $De = \dot{\gamma} \tau$, where $\tau$ is the longest relaxation time of the chain in equilibrium. For (unbreakable) polymers, the Doi–Edwards tube model predicts that for $De > 1$ a maximum overshoot in the shear stress occurs at a total strain $\gamma = \dot{\gamma} t$ value of 2.33 It is well known that at very high shear rates, starting roughly at $De \approx 10^2$, the strain at which the maximum in the overshoot occurs actually increases with shear rate. This is predicted, at least qualitatively, by reptationlike theories which include the convective constraint release mechanism.40,41 At present these theories have not been adapted to the case of nonlinear flow of breakable polymers, but we expect overshoot to occur for shear rates higher than the inverse stress relaxation time $1/\tau$. This is tested for the system with lowest scission energy in Fig. 10. Here, we plot $\eta(t)$, the transient growth of the viscosity upon onset of shear, normalized by the steady-state viscosity, against total strain $\gamma$ for three different shear rates. In this system the equilibrium stress relaxation time is approximately $\tau = 4 \times 10^{-4}$ s. Indeed, we find no overshoot for a shear rate of $10^3$ s$^{-1}$, which corresponds to a Deborah number of 0.4, but an increasing overshoot is observed for shear rates of $10^4$ and $10^5$ s$^{-1}$ ($De = 4$ and 40), respectively. Because $De < 10^2$, the location of the peak always lies at strain of 2. For higher scission energies, the stress relaxation time $\tau$ increases, and consequently we reach higher Deborah numbers. Indeed, Fig. 10 also shows that, at fixed shear rate of $10^4$ s$^{-1}$, the strain at which the maximum in the stress overshoot occurs increases with increasing scission energy.

We now turn to the steady-state rheological properties. Figure 11 shows the steady-state shear stress and (first) normal stress components of the three systems studied here, each versus the applied shear rate on a double-logarithmic scale. At low shear rates the shear stress increases linearly with shear rate, $\sigma_{xy} \propto \dot{\gamma}$, with exponent $\alpha = 1$. This linear regime persists up to a shear rate $\dot{\gamma} = 1/\tau$, after which the slope in the double-logarithmic plot decreases ($\alpha < 1$). For the system with lowest scission energy (diamonds in Fig. 11) the decrease is gradual, to a value which is close to $\alpha = 1/3$. For the system with highest scission energy (circles) the slope first decreases from 1 to a value a bit lower than 1/3, and then up again to $\alpha = 1/3$. This indicates that the system with the shortest wormlike micelles still is unentangled, whereas the system with the longest wormlike micelles is entangled. In many experiments on fully entangled wormlike micelles a shear-banding transition is observed.1,8,9,36 Rheologically, shear banding manifests itself as a constant or slowly increasing shear stress (a stress plateau) between two critical shear rates $\dot{\gamma}_{c1}$ and $\dot{\gamma}_{c2}$, often accompanied by a linear in-

![FIG. 9. Time dependence of various stress components measured after start-up of shear flow with shear rate of $10^4$ s$^{-1}$. Overshoots are observed in the shear stress $\sigma_{xy}$ and the first normal stress difference $N_1$. In the case of the second normal stress difference $N_2$ we observe an initial overshoot, followed by an undershoot and a relaxation to a negative value.](image-url)

![FIG. 10. Transient growth of viscosity normalized by the steady-state viscosity as a function of total strain after startup of steady shear flow. Three curves are for $T = 333$ K, $E_a = 15.5kT$, and $E_a = 2.2kT$ at shear rates of $10^3$, $10^4$, and $10^5$ s$^{-1}$. One additional curve is given for $T = 300$ K, $E_a = 19.1kT$, and $E_a = 2.4kT$ at shear rate of $10^4$ s$^{-1}$.](image-url)
crease in the (first) normal stress difference. Our wormlike micelles are entangled, but only just so. They are therefore not yet long enough to be in the fully entangled regime where shear banding could be observed. Moreover, the shear rates which we apply are larger that for 8% EHAC the transition from the −1 scaling to the −2 scaling regimes takes place at a shear rate of approximately \( \dot{\gamma}_c \approx 100 \text{ s}^{-1} \). All simulations were performed at shear rates equal to or higher than this, which explains why shear banding was not observed.

Within the accessible range of shear rates, the simulation results (filled circles) tend to systematically overestimate the experimental viscosities (stars), but only by a factor of 1.5. Given the crude friction model used for the rodlike segments, the overall agreement with the experimentally determined results is very satisfactory. In fact, after the simulations had completed we realized the agreement would have been even better if we had used a friction model for a finite rod, with \( \xi_i = 2 \pi \eta L / (\ln(l_p/D) + \nu_i) \) instead of the employed \( \xi_i = 2 \pi \eta L / (\ln(l_p/D) \nu \nu_i) \) for the parallel friction, and a similar correction \( \nu \nu \) for the perpendicular friction. Estimates for the factors \( \nu \nu \) and \( \nu \nu \) can be found in Ref. 42. The corrections lead to an essentially unaltered parallel friction for our aspect ratio, but to a perpendicular friction which is 1.5 times lower, leading to a lower viscosity.

IV. CONCLUSION

In this paper we have presented a particle based simulation model for solutions of wormlike micelles. We have
shown that with this model we can study the dynamics and rheology at millisecond time scales, while still retaining the specific mechanical properties of the individual wormlike micelles. The majority of these mechanical properties have been determined from more detailed atomistic molecular dynamics simulations, providing the link with the chemistry of the surfactants. We have used this model to study the behavior of both unentangled and slightly entangled wormlike micelles under shear flow. We have made the following observations.

- With increasing shear rate, beyond a certain critical shear rate, the contour length decreases and the breaking rate per unit contour length decreases. The critical shear rate decreases with increasing scission and/or activation energy.

- The linear rheology (shear relaxation modulus) of unentangled samples is in good agreement with a theory of breakable Rouse chains (see Appendix B).

- Upon startup of shear flow, overshoots occur in the shear stress and first normal stress difference at Deborah numbers larger than 1, if De is based on the typical stress relaxation time $\tau$. The maximum overshoot occurs at strain of 2 for Deborah numbers lower than 100.

- At high shear rates $\dot{\gamma}$, beyond the stress plateau, the steady-state shear stress increases like $\dot{\gamma}^{1/3}$. The exponent of 1/3 is confirmed in parallel-plate experiments on an 8% solution of EHAC for shear rates higher than 100 s$^{-1}$.

We expect that, given the ever-growing increase in computing power, more highly entangled wormlike micelles can be simulated in the near future. This will open up the possibility to study the shear-banding phenomenon from a micro-/mesoscopic point of view, complementary to the usual constitutive approach (see, e.g., Refs. 8 and 9).

Furthermore, we note that the simulated values of the activation energy $E_a$ and to a smaller extent also the values of the scission energy $E_{sc}$ are lower than in the actual experimental situation. This is for computational reasons. Figure 13 shows that realistic values would lead to relaxation times which are many orders of magnitude higher. Fortunately, the shear stress converges to a universal curve independent of $E_{sc}$, $E_a$, or $T$, but dependent on other factors such as the persistence length $l_p$, diameter $D$, and wormlike micellar concentration. We found good agreement between the simulated and experimental viscosities at the shear rates that could be studied. We therefore expect that the model can be used, in combination with atomistically detailed simulations to determine the single chain mechanical properties, to design novel wormlike micellar materials.

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**APPENDIX A: CONSEQUENCES OF COARSE GRAINING FOR THE SCISSION ENERGY OF A BREAKABLE GAUSSIAN CHAIN**

Suppose we model a solution of linear wormlike micelles as a collection of breakable bead-spring chains (Gaussian chains). Assuming that all chain lengths are in chemical equilibrium, it can be shown\(^3\) that the average number of beads per chain is given by

$$\langle N \rangle = \frac{1}{2} + \left(\frac{1}{4} + 3\rho \right)^{1/2},$$  \hspace{1cm} (A1)

where $\rho$ is the number density of beads that are able to form breakable chains and $z$ is a quantity with dimensions of volume, defined as

$$z = \left(\frac{2}{3} \pi b^3\right)^{3/2} \exp(E_{sc}/kT),$$  \hspace{1cm} (A2)

where $b$ is the (effective or root-mean-square) bond length between consecutive beads.

We will now calculate the scission energy $E_{sc}$ after coarse graining this model. Suppose we represent the mass of our beads by one new bead. Distinguishing new quantities with a tilde ($\tilde{}$), the number density of beads becomes $\tilde{\rho} = \rho / \lambda$. We demand that the total amount of mass in each chain remains the same, hence a chain which previously consisted of $N$ beads will now be represented by $\tilde{N} = N / \lambda$ new beads. Furthermore, we demand that the overall dimensions of our wormlike micelles, as expressed for example by the radius of gyration, remain the same. For our random walk chain this means that we require that $N b^2 = \tilde{N} \tilde{b}^2$. Hence the effective bond length must increase like $\tilde{b} = \sqrt[4]{\lambda} b$. Now, according to Eq. (A1) the average number of beads per chain in the new situation will be $\langle \tilde{N} \rangle = \frac{1}{2} + \left(\frac{1}{4} + 3\tilde{\rho}\right)^{1/2}$. This must be equal to $\langle N \rangle / \lambda$. As can be seen from Eq. (A2), the term $z\rho$ is approximately equal to the effective volume fraction $b^3$ multiplied by the factor $\exp(E_{sc}/kT)$ and hence will be very much larger than 1 in all practical cases where we deal with long wormlike micelles. We can then safely approximate $\langle N \rangle = (z \rho)^{1/2}$ and find $\tilde{z} = z / \lambda$. Again looking at Eq. (A2) we therefore draw the following conclusion: in order for the further coarse-grained solution of chains to have the same distribution of global dimensions (gyration radii) as present in our original solution, we require that $\tilde{b}^3 \exp(\tilde{E}_{sc}/kT) = b^3 \exp(E_{sc}/kT) / \lambda$ or, using $\tilde{b} = \sqrt[4]{\lambda} b$,

$$\tilde{E}_{sc} = E_{sc} - \frac{5}{2} kT \ln \lambda.$$  \hspace{1cm} (A3)

So the scission energy of a chain coarse grained by a factor of $\lambda$ must be lowered by an amount of $\frac{5}{2} kT \ln \lambda$. Conversely, if one decides to represent each wormlike micelle by more (but smaller) segments, a higher scission energy is needed to get the same distribution of global dimensions.

Finally, we remark that of course there is an upper limit to the number of beads representing a piece of wormlike micelle. In the first place, the random walk approximation used above is no longer valid at scales smaller than the persistence length $l_p$. In the second place, one must ask oneself what is the smallest unit that can break off a real wormlike micelle. This must certainly be at least the thickness of an
amphiphilic molecule. It has recently been shown\textsuperscript{16} that in order to reasonably explain observations of the kinetics of a stretched and breaking wormlike micelle, the smallest unit of breaking must be set equal to the diameter \(D\) of the wormlike micelle. For our coarse-grained simulations this means that, apart from relatively smaller stiffness effects, the experimental scission energy is higher by an amount of \(\frac{1}{2}kT \ln(l_p/D)\) relative to the scission energy used in the simulation.

**APPENDIX B: RHEOLOGY OF UNENTANGLED BREAKABLE CHAINS**

In this Appendix we calculate the rheological properties of a collection of unentangled breakable chains. The treatment is similar to that of Fairey and Gardissat,\textsuperscript{38} but here we give an explicit derivation including the prefactors. We will show that in the fast breaking limit the interplay between relaxation and “breaking” of different normal modes leads to the dominance of a certain length scale. This length scale is independent of the actual length of the chain, so although the results will be derived for a single chain length \(N\), they will apply more generally to a distribution of chain lengths as well.

Let us first consider the case of an unbreakable chain. In the unentangled limit we can treat the dynamics of a selected chain independently of the dynamics of the other chains. In such a case the shear relaxation modulus \(G_N(t)\) can be expressed as a simple sum over normal modes,\textsuperscript{33}

\[
G_N(t) = \frac{c_NkT}{N+1} \sum_{k=1}^{N} C_N^k(t),
\]

where \(N+1\) is the number of segments in one chain, \(c_N\) is the number of chain segments per unit volume (present in chains of length \(N\)), and \(C_N^k(t) = \langle X_N^k(t)X_N^0(t) \rangle / \langle X_N^2 \rangle\) the normalized time correlation function of the \(k\)th normal mode \(X_N^k = (1/(N+1)\sum_{j=0}^{N} R_j \cos[(k\pi/N+1)(n+1/2)]\). From the last expression we see that the \(k\)th normal mode represents the dynamics of a wave with a wavelength containing \(N/k\) bonds. In the case of an unbreakable Rouse chain, the normal modes decay exponentially, \(C_N^k(t) = \exp(-t/\tau_{N,k})\) with relaxation times \(\tau_{N,k} = k^2\tau_1/\zeta\). Here we have defined \(\tau_1\) as the longest relaxation time of a chain of \(N+1\) segments, which for a Rouse chain is given by \(\tau_1 = \zeta b^2 (N+1)^2/(3\pi^2kT)\), with \(b^2\) the mean-square segment bond length and \(\zeta\) the friction on a segment.\textsuperscript{33}

Now let us consider a breakable chain. Assuming breaking is an activated process, the probability that a certain bond will still be in place after a time \(t\) decays like \(\exp(-c_b t)\), where \(c_b\) is a constant characterizing the breaking rate of a single bond. An entire chain, of course, can break anywhere along its contour and will therefore break much faster than any particular bond. The probability for all \(N\) bonds in a chain to survive up to a time \(t\) decays like \(\exp(-c_b N)\), meaning that the average breaking time of the full chain is \(\tau_b = 1/(Nc_b)\). The same reasoning applies also to a subchain. The stress resulting from normal modes \(k\) of all chains of length \(N/k\), or multiples thereof, will continue to decay exponentially as long as they have not yet broken. When they do break, we expect that the contribution to the stress to disappear quickly. In summary, we expect that the shear relaxation modulus will decay like

\[
G_N(t) = \frac{c_NkT}{N+1} \sum_{k=1}^{N} \exp[-(N/k)c_b t] \exp(-2t/\tau_{N,k})
\]

\[
= \frac{c_NkT}{N+1} \sum_{k=1}^{N} \exp\left(-\frac{1}{k\tau_1} + \frac{k^2}{2} t^2 / \tau_1\right),
\]

where in the second line we have used relaxation times of the Rouse model. This expression shows that large wavelength (low \(k\)) modes are “short circuited” by their relatively fast breaking. We can write the effective relaxation rate of mode \(k\) as \(\nu(k) = 1/(k\tau_1) + 2k^2/\tau_1\).

In the fast breaking limit, which applies to most cases of interest (both experimentally and in our simulations), the average breaking time \(\tau_1\) of a chain is much shorter than the longest relaxation time \(\tau_1\) of the (hypothetical) unbreakable chain. We still assume that \(\tau_1\) is much longer than the fastest relaxation time of the unbreakable chain, which is the orientational relaxation time of a single bond. We therefore assume \(\tau_1/N^2 \ll \tau_b \ll \tau_1\). In this case \(\nu(k)\) has a minimum at a certain \(k^* \ll N\), where \(k^*\) is given by \(k^* = (\frac{1}{2\tau_1/\tau_1})^{1/3}\). For \(k\) values smaller or larger than \(k^*\) the effective relaxation rates quickly increase. For long enough times, \(k^*\) will therefore be the dominant mode. The effective relaxation rate and the second derivative at \(k^*\) are given by \(\nu(k^*) = \frac{1}{2} \frac{\pi^2}{3\tau_1} \tau_1^2 b^{-2/3}\) and \(d^2\nu(k^*)/dk^2 \approx 12/\tau_1\). Defining the effective relaxation time of the dominant mode as \(\tau = 1/\nu(k^*)\), we find

\[
\tau = 0.42 \tau_1^{1/3} \tau_1^{2/3}.
\]

It is important to note that, at fixed segment density and fixed interaction parameters, the effective relaxation time \(\tau\) does not depend on the actual chain length because \(\tau_1^{1/3} \ll \tau_1\) \(\propto N^{2/3} \gg N^0\). Approximating the sum over \(k\) by an integral we find

\[
G_N(t) = \frac{c_NkT}{N+1} \int_1^{\infty} \frac{dk}{k} \exp\left(-\frac{1}{k^2 \tau_1} + \frac{6}{\tau_1} (k-k^*)^2 \right)\]

\[
= \frac{c_NkT}{N+1} \exp(-t/\tau_1) \int_{-\infty}^{\infty} dk \exp\left(-\frac{6}{\tau_1} (k-k^*)^2 \right)
\]

\[
= \frac{c_NkT}{N+1} \sqrt{\frac{\pi \tau_1}{6\tau}} \exp(-t/\tau_1) \quad (t \gg \tau_1/\tau_N).
\]

In the second line we have cut off the Taylor expansion at second order and used the fact that the effective rates \(\nu(1)\) and \(\nu(N)\) are much larger than \(\nu(k^*)\) (this follows directly from our assumptions). The zero-shear viscosity can now be calculated as

\[
\eta_0 = \int_0^{\infty} dt G_N(t) = \frac{c_NkT}{N+1} \int_0^{\infty} \frac{dx}{\sqrt{6\pi \tau}} \exp(-x^2/\tau) 2x
\]

\[
= \frac{\pi c_NkT}{\sqrt{6\pi N+1}} \sqrt{\tau_1}.
\]

In the second line we have ignored the fact that for small times \(t \ll \tau_1/\tau_N\) Eq. (B4) is not strictly valid. This is allowed
because the contribution of this regime to the integral is relatively small.

Since $\tau \propto (N + 1)^2$ and $\tau \propto N^0$, both the stress relaxation and the zero-shear viscosity are independent of the actual length $N$ of the chain. The stress in a polydisperse mixture of breakable Rouse chains will therefore also relax as predicted by Eq. (B4), where we have to replace $c_N$ by the overall number density of segments $c$. Similarly, the viscosity will also be given by Eq. (B5).

We warn that the independence of chain length $N$, referred to above, means independence of $N$ at fixed interaction parameters. If the interaction parameters are changed, the rheology of course will change as well. The most important interaction parameters are the scission energy and activation energy. Keeping all parameters other than $E_s$ and $E_a$ fixed, the average chain length $N$ will increase approximately like $N^{\exp\left(\frac{E_s + E_a}{kT}\right)}$. This does not influence the ratio $\tau_0/N^2$ appearing in Eqs. (B4) and (B5). The breaking rate $c_b$ of a single bond, however, is changed. Assuming breaking is an activated process we expect $c_b \propto \exp\left(-\frac{(E_s + E_a)}{kT}\right)$ (see Fig. 3). The stress relaxation time $\tau$ and zero-shear viscosity $\eta_0$ then will increase with increasing $E_s$ and $E_a$ like $\tau \propto \exp\left(\frac{(E_s + E_a)}{kT}\right)$ and $\eta_0 \propto \exp\left(\frac{(E_s + E_a)}{kT}\right)$. We emphasize that these scalings hold only as long as the wormlike micelles behave as unentangled breakable Rouse chains. If the average chain length becomes too short, the chains cannot be viewed anymore as Gaussian chains and/or the average breaking time is no longer much shorter than the longest relaxation time (our main assumption). If the average chain length becomes too large, the chains start to entangle and the description of the relaxation kinetics will need to be changed accordingly.

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