

Review of multi-scale particulate simulation of the rheology of wormlike micellar fluids†

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We provide a review of our recent work on the development of a multi-scale simulation methodology to calculate the rheology and flow of wormlike micelles. There is a great need for understanding the link between the detailed chemistry of surfactants, forming wormlike micelles, and their macroscopic rheological properties. We show how this link may be explored through particle simulations. First, we calculate the mechanical properties of small units of wormlike micelles from atomistic molecular dynamics simulations. These mechanical properties are subsequently used in a coarse-grained Brownian dynamics model, where the persistence length is the smallest length scale. We show that the non-Newtonian rheology of wormlike micellar systems can be accurately determined from our simple mesoscopic simulation model. Finally, we show that this mesoscopic model can be used to study the flow of wormlike micelles in contraction–expansion geometries.

I. Introduction

Surfactant molecules self-assemble reversibly into micelles with a variety of morphologies.¹ In aqueous salt solutions, they may assemble into wormlike micelles. Several books and review

articles^{2–4} present state-of-the-art of theoretical and experimental studies of wormlike micellar systems. Above the overlap concentration, the combination of entanglement and reversible dynamics of micellar self-assembly and disassembly (by end-to-end recombination and scission) provides these solutions with useful viscoelastic properties. For example, highly viscous and shear thinning micellar fluids,^{5,6} may be applied to hydraulic fracturing operations in the oilfield.⁷ The advantage of using wormlike micelles is that they disassemble as soon as oil is produced, resulting in a low viscosity Newtonian fluid which easily flows out of the fractures.

In this paper, we review our attempts at linking the chemistry of the surfactant molecules to the viscoelastic properties of the self-assembled wormlike micelles by means of particulate simulation methods. One of our goals is to explain the flow of

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J. T. Padding

Johan Padding received his PhD (cum laude) in Physics in 2003 from the University of Twente on the subject of coarse-grained computer simulations of entangled polymer melts. During a three-year postdoc at the University of Cambridge, he worked with Dr Ard Louis on efficient simulations of colloidal suspensions including hydrodynamic interactions, and with Dr Edo Boek (at Schlumberger) on simulations of the dynamics of wormlike micelles and

asphaltene particles. After this he received a Dutch 'VENT' award to continue his work on hydrodynamic interactions in colloidal and polymeric soft matter.



W. J. Briels

Wim Briels received his PhD from the University of Utrecht in 1981. His early research concerned the dynamics of molecular crystals. He introduced a method to calculate bare growth coefficients of crystals using interphase fluctuations. Together with Wouter den Otter he presented the first correct method to calculate free energies from constrained simulations. Since 2000 he holds a chair on Computational Biophysics in the University of Twente. Since then

his research has focused on simulating slow dynamics and rheology of soft matter. He has contributed several new ideas to dynamical coarse-graining of polymers, wormlike micelles and core-shell systems.

wormlike micellar fluids in porous media. It is observed that the apparent viscosity (pressure drop) in porous media does not decrease monotonically with apparent shear (flow) rate.⁸ A possible explanation is that elongational effects lead to an increased extensional viscosity.

Some of the constitutive models for wormlike fluids^{2,8–10} indeed predict a greatly enhanced extensional viscosity for certain extension rates. A practical problem with most constitutive models, however, is that they capture the microscopic features of the wormlike micelles in a grossly simplified way, for example by coupling the stress tensor to structural order parameters such as the average micellar length. In most cases, the parameters appearing in these models depend in an unknown fashion on the particular chemistry of the surfactants, concentration and temperature. Therefore, despite the large amount of experimental data on particular surfactant systems, there is no systematic way to design fluids with a particular desired rheology.

A rational design of surfactant fluids may become possible by using particulate simulation methods to predict the rheology from first principles. Ideally, one would like to obtain the rheology directly from atomistically detailed simulations, see Fig. 1. Unfortunately, it is impossible to simulate more than a part of one wormlike micelle with this level of detail. As depicted in Fig. 1, the only way forward is to coarse-grain, not only to the level where each surfactant is represented by a few beads, but even further to the level 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 and co-workers^{11–13} and by some of us.^{14,15} In the original model^{11,12} solvent beads were included to account for solvent effects, but the solvent effect may be mimicked through Brownian dynamics as well.¹³ The resulting worm length distribution is found to agree well with the theoretical mean-field prediction $c(L) \propto \exp(-L/\bar{L})$, and shear thinning of the viscosity is observed, although not as strong as in the experiment.^{12,15}

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 provides the simulator 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

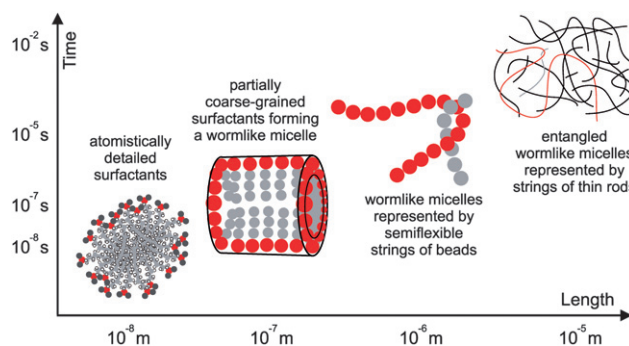


Fig. 1 Particle based simulations of wormlike micelles may be performed on many different length and time scales. With atomistic force-fields (lower left) we can capture the influence of specific surfactant chemistry on the properties of a piece of wormlike micelle. By coarse-graining the surfactant molecules these calculations are greatly accelerated. More macroscopic properties, such as the length distribution and rheology, can only be calculated with higher-level models, such as the bead-based FENE-C model or the rod-based model considered in this review.



M. R. Stukan

His current research is dedicated to fundamental studies of fluid flow in porous media.

Mikhail Stukan obtained his diploma degree in physics in 2000 at the Moscow State University, Russia, where he also obtained his PhD in 2003. He has worked as a postdoctoral researcher at the Max Plank Institute for Polymer Research in Mainz, Germany, and then at Schlumberger Cambridge Research, UK. He is now a research scientist at Schlumberger Dhahran Carbonate Research Center, Saudi Arabia.



E. S. Boek

Very recently, he has accepted a position as Senior Lecturer at the Dept. of Chemical Engineering at Imperial College, London, working on complex fluids, flow in porous media, CO₂ capture and storage in combination with Enhanced Oil Recovery.

Edo Boek received his MSc (cum laude) from the University of Utrecht and his PhD from the University of Twente on the subject of particulate computer simulations of crystal growth. After a post-doc at the University of Nijmegen, he obtained a position as senior research scientist at Schlumberger Cambridge Research (SCR) in the U.K. At SCR, he has developed a research programme on complex fluids, including clay suspensions, wormlike micelles

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,¹⁶ 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.^{14,15} 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 model¹³). In a series of papers,^{17–19} Huang *et al.* have shown how the activation barrier can also be incorporated in the FENE-C model by introducing a Monte Carlo-like move which switches between bound and unbound pair potentials. The switching rate is determined by (among other things) the height of the activation barrier. They were able to follow the influence of the scission–recombination kinetics on various relaxation processes at equilibrium and on the stress and structural features when these solutions are sheared.¹⁹ Unfortunately, all bead-based methods remain 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.

We have used a different approach and developed a mesoscopic Brownian dynamics (BD) simulation model in which the smallest unit is one persistence length of wormlike micelle. This degree of coarse-graining is as large as possible to permit a large integration step (10^{-9} s) and fewer particles, while it is still small enough to allow an accurate description of the overall conformation of the wormlike micelle. In contrast to generic coarse-grained models, the input parameters for this BD model are derived from chemically specific atomistic molecular dynamics (MD) simulations.

The key issue is to identify the key properties of a wormlike micellar solution that determine its rheology. In our work we have assumed that these key properties are the mechanical properties that characterise a single wormlike micelle, such as its

persistence length, radius, and the free energies associated with fusion and breaking, combined with micellar concentration, temperature and solvent viscosity. The simulations can offer new insights because the theory available for the dynamics of wormlike micelles²⁰ makes assumptions that cannot be directly validated by experiments. For example, the average break-up time per unit length of worm is assumed to be constant and independent of stress or shear rate. Another approximation in the theory is that recombination after scission takes place with any of the other available chain ends in the system instead of predominantly with the previous scission partner.^{14,17,21} Our mesoscopic simulation approach can check and go beyond such assumptions for realistic systems.

In the next section we will describe how the parameters that go into the BD model can be measured from MD simulations. Then we will give an introduction to and results of the BD model. Finally, we show that this mesoscopic model can be used to study the flow of wormlike micelles in contraction–expansion geometries.

II. Mechanical properties from molecular dynamics simulations

Using atomistic MD simulations, we can find relationships between the chemistry and mechanical properties of a wormlike micelle. To this end, we carry out simulations of a small segment of a wormlike micelle, consisting of a limited number of surfactant molecules, in this example EHAC.⁷ The worm is immersed in water containing the required concentration of salt (NaCl) ions. Typically, the MD simulation box has dimensions of the order of 10 nm and contains $\mathcal{O}(10^5)$ atoms. Periodic boundary conditions are applied in 3 dimensions so that effectively we are considering an infinite segment of a wormlike micelle. Typically, the simulations require of the order of 10 nanoseconds of simulation time to obtain statistically meaningful ensemble averages. A simulation snapshot is shown in Fig. 2. This system contains 640 surfactant and 40 000 water molecules together with Na^+ and Cl^- ions corresponding to a 3% (by weight) NaCl solution. Coulomb interactions are treated by Ewald summations.

First, we calculate radial distribution functions as ensemble averages over the particle coordinate trajectories. From these functions, we find a radius of the worm $r = 2.3$ nm. Then, we determine the tensionless state. This is achieved by a series of MD simulations, where we compress/stretch the worm at

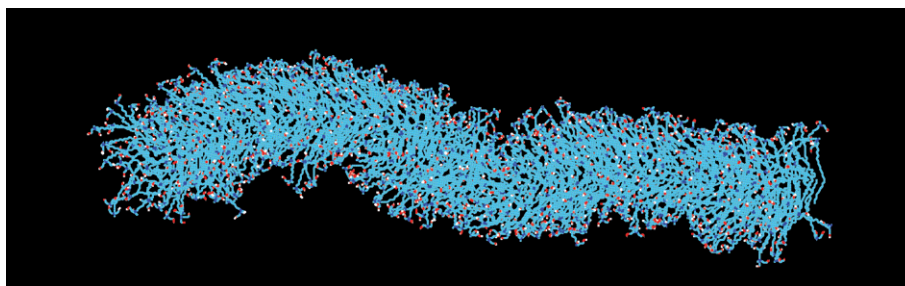


Fig. 2 Snapshot of an MD simulation of an EHAC wormlike micelle in a 3% NaCl solution. Only the surfactant molecules are shown: carbon (light blue), oxygen (red), nitrogen (dark blue) and head-group hydrogens (white). Reproduced from Padding *et al.*¹⁶ with permission of *Institute of Physics Publishing Ltd.*

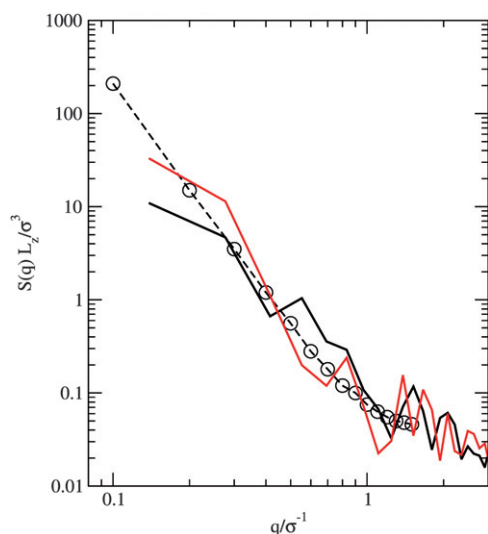


Fig. 3 Structure factors $S_\alpha(q)$ of a tensionless EHAC worm; $\alpha = x, y$ in black and red respectively. The dashed line shows the $S(q)$ for a coarse-grained worm simulation,²³ using $\sigma = 0.6$ nm. Reproduced from Padding *et al.*¹⁶ with permission of *Institute of Physics Publishing Ltd.*

constant volume.²² We observe that the difference in pressure parallel and perpendicular to the worm, ΔP , decreases linearly with the length of the worm segment L_z . The elastic modulus K_L is then calculated from

$$-\Delta P \frac{V}{L_z} = \frac{K_L}{L_{z0}} (L_z - L_{z0}) \quad (1)$$

where L_{z0} is the box z dimension in the tensionless state. Both K_L and L_{z0} have been determined²² from a graph of $-\Delta P/V/L_z$ as a function of L_z . From a linear fit of all data points, we find $L_{z0} = 15.10$ nm and $K_L = 1.9$ nJ/m. Note that it is difficult to determine the elastic modulus of a single wormlike micelle experimentally.

The persistence length l_p of the worm in the tensionless state is calculated from the position fluctuation spectrum perpendicular to the worm (z -axis), as shown in Fig. 3:

$$S_\alpha(n) = \langle c_{\alpha,n} c_{\alpha,n}^* \rangle = \frac{1}{L_z l_p} q_n^{-4}, \quad \text{where } q_n = \frac{2\pi}{L_z} n; \quad \alpha = x, y \quad (2)$$

where $c_{\alpha,n}$ are the coefficients of the Fourier decomposition.²³

Qualitatively, we find that the low q modes follow a q^{-4} scaling behaviour, as expected.²³ We try to fit the low q modes to the fluctuation spectrum of a coarse-grained worm simulation,²³ in which each surfactant is represented by one head bead and four tail beads of diameter σ . We find quantitative agreement for $\sigma = 0.6$ nm. The coarse-grained worm simulations yielded a radius of 4σ and persistence length of 38σ . The radius agrees well with our previous measurement of 2.3 nm from the radial distribution function, and suggests that the persistence length must be of the order of $38\sigma = 23$ nm. Of course the ratio of persistence length to radius can be different for the coarse-grained model and the fully atomistic model. After longer atomistic simulations of EHAC we found that the persistence length is probably somewhat higher, closer to 30 nm. These values are in agreement with experimental values for wormlike micellar persistence lengths reported in the literature.^{3,24}

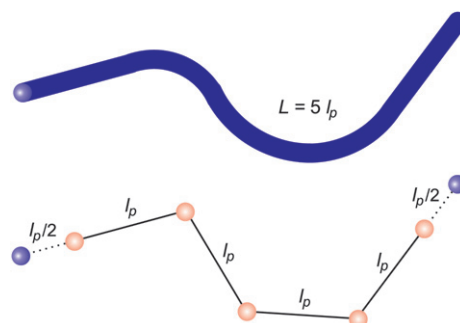


Fig. 4 Example of coarse-graining a wormlike micelle to a sequence of units (red spheres), each representing the centre of one persistence length. The end-caps of the wormlike micelle are assumed to be located at the blue spheres.

III. Rheology from Brownian dynamics simulations

A. Model and assumptions

The collective dynamics and rheology of a semidilute solution of wormlike micelles are determined by the interactions between different micelles. In order to reach the large length and time scales associated with these phenomena, a coarse-grained model is employed in which each unit represents one persistence length of wormlike micelle,^{16,25} see Fig. 4. Chemical specificity is maintained by allowing the coarse model to have relevant single-micelle mesoscale properties which are determined from atomistic molecular dynamics simulations. These properties (and their specific values in the EHAC simulations), are the worm radius ($r = 2.3$ nm), persistence length ($l_p = 30$ nm), elastic modulus ($K_L = 2 \times 10^{-10}$ J/m), and scission and activation energies E_{sc} and E_a for fusion and breaking, where the last two are used as adjustable parameters, see Section IIIB. We note that, instead of atomistic molecular dynamics simulations, targeted experiments such as depolarized light scattering, ultra small-angle neutron scattering, small-angle X-ray scattering or Brillouin scattering may also be used to provide single-micelle properties. We refer the reader to ref. 3 for an excellent overview of the many experimental techniques that have been used to date.

It is assumed that the stress is dominated by the network of wormlike micelles and that hydrodynamic interactions (HIs) are relatively unimportant. This allows for an implicit treatment of solvent effects by means of (overdamped) Brownian dynamics of rigid rods in a liquid of viscosity η_s (in our work we use the water viscosity $\eta_s = 10^{-3}$ Pa s). The friction parallel to the rod is chosen equal to $\xi_{\parallel} = 2\pi\eta_s l_p / \ln(l_p/2r)$ and the friction perpendicular to the rod $\xi_{\perp} = 2\xi_{\parallel}$.²⁷ The magnitude of these frictions sets the relaxation times of the wormlike micelles, whereas the anisotropy reflects the rodlike shape of each coarse-grained particle.

We note that whether or not HIs may be neglected is a subtle point. For colloidal hard spheres at volume fractions similar to those studied here (of the order of 10%), HIs are very important and significantly change the dynamics, especially in non-equilibrium.²⁶ Also for dilute polymeric systems HIs are very important.²⁷ On the other hand, it is believed that HIs are effectively screened in concentrated polymer suspensions and to a certain extent also in semidilute suspensions in equilibrium situations.^{27–30} The onset of the semidilute regime already occurs

at lower concentrations for semiflexible chains than for flexible chains of equal contour length.²⁷ This corresponds to a smaller dynamic correlation length in a semidilute suspension of semiflexible chains than in an equally concentrated suspension of flexible chains. Wormlike micelles can be viewed, hydrodynamically, as semiflexible polymers. At the concentration considered in this work (8%), they are already quite deep in the semidilute regime. Under these conditions HIs are expected to only slightly perturb large scale dynamical properties such as the diffusion coefficient and linear rheology.^{28,29} It may be possible that HIs do become more important in non-equilibrium. Such effects are however ignored in this work. The influence of HIs on the dynamics of semidilute suspensions of semiflexible polymers in non-equilibrium is a topic of current research.³⁰

Another assumption is that excluded volume interactions between different (parts of) wormlike micelles are relatively unimportant. This is the case as long as the concentration remains far below the concentration corresponding to the isotropic–nematic transition (which is the case for the systems studied here). This allows us to treat the interactions between wormlike micelles as chains of infinitely thin lines, where the uncrossability of these lines is taken into account by the Twentanglement method. In this method, originally designed for polymer melt simulations,³¹ 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.

Flow in the x -direction with a velocity gradient $\dot{\gamma}$ in the y -direction is generated by applying Lees–Edwards boundary conditions for particles moving through the upper or lower boundaries of our simulation box.³² The y -dependence of the (implicit) solvent flowfield in the x -direction is dynamically updated by coupling it to the motion of the wormlike micellar segments with an averaging time of 10^{-6} s, as described in detail in ref. 25,33,34. The advantage of this algorithm is that no affine flow (constant uniform shear rate) is imposed, but that any y -dependent flowfield is allowed to form.

B. The scission energy and entanglement length

In our applications the parameters of the model were chosen to represent an 8% solution of EHAC wormlike micelles. It was found that, despite the coarse-graining step, we still had to use relatively low values for the scission energy. Experimentally, the scission energy can be tuned by changing the salt concentration of the solution, see *e.g.* ref. 6,35,36, leading to scission energies between 25 and $50 k_B T$. The average breaking times of wormlike micelles with such high scission energies lie beyond the simulation time (several milliseconds) possible with this model. Our simulations were restricted to lower scission energies, up to $19.1 k_B T$. We made it one of our goals to investigate the influence of the dimensionless scission energy $E_{sc}/k_B T$ on the behaviour of the system.

We found that for scission energies up to $16 k_B T$ the wormlike micelles are essentially unentangled. In this regime the linear shear relaxation modulus can be described quantitatively by

a theory of breakable Rouse chains (see the Appendix of ref. 25 for a derivation). Similar observations were made in the work of Huang *et al.*^{17,19} For higher scission energies we observed a transition to dynamics dominated by entanglements. Looking at the contour length measurements in the next section, this suggests that in our 8% EHAC system the entanglement length lies between 2 and 6 micrometres. Note that this corresponds to 60 to 180 persistence lengths.

C. Contour length and breaking rates

We studied the contour lengths of the wormlike micelles and found that its distribution is very broad—in equilibrium it is exponential—and that the scaling of the average contour length L agrees with the theoretical expectation $L \propto \exp(E_{sc}/(2k_B T))$.³ This has also been confirmed in FENE-C type simulations.^{11–13,17–19} At sufficiently low shear rates the average micellar contour length (Fig. 5) and breaking rate per unit contour length (not shown) are independent of shear rate. This observation lies at the core of most extensions of reptation theory to breakable chains.²⁰ Beyond a certain critical shear rate, however, the contour length decreases and the breaking rate increases with increasing shear rate. In this regime, breaking of the wormlike micelles is enhanced by the additional tension on the micelles. The effect will be larger for larger micelles. Indeed, the critical shear rate decreases with increasing scission energy and shear induced breaking may therefore become important for real wormlike micelles already at moderate shear rates. The observed accelerated breaking under shear is a large effect. From this we learn that one must be careful in applying Monte Carlo mechanisms to mimic the activated breaking of bonds in simulations of wormlike micelles under flow. If one single breakup probability (independent of tension) is used, the breaking rates will be severely underestimated at high shear rates. This will also lead to an overestimation of the contour lengths at high shear rates. In the work of Huang *et al.*,¹⁹ the tension effect is included because their breakup probability increases when the energy in the bond between two bonded beads increases.

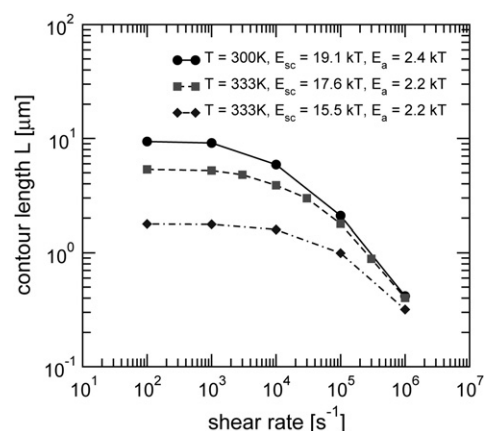


Fig. 5 Average micellar contour length *versus* shear rate for EHAC wormlike micelles with different scission and activation energies. Note that one micrometre contour length consists of approximately 33 persistence lengths. Reproduced from Padding *et al.*²⁵ with permission of the American Institute of Physics.

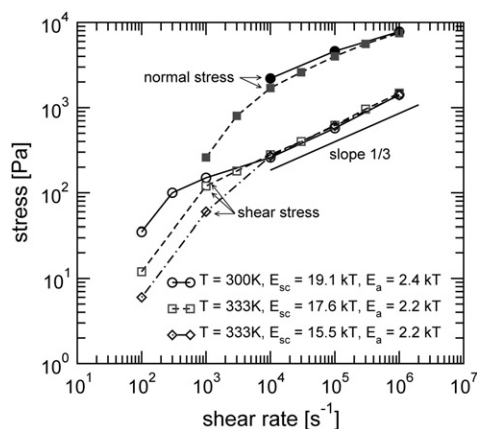


Fig. 6 Predicted steady-state shear stress (open symbols) and normal stress (closed symbols) *versus* shear rate for EHAC wormlike micelles with different scission and activation energies. Reproduced from Padding *et al.*²⁵ with permission of the *American Institute of Physics*.

D. Non-linear shear rheology

Fig. 6 shows the shear stress and normal stress as a function of shear rate for three different scission and activation energies. An important observation is that these stresses converge towards the same curves at high shear rates, independent of scission energy, activation energy or temperature, but dependent on other mesoscale properties such as the persistence length, micellar radius, and concentration. This justified, *a posteriori*, the use of lower scission energies to study the rheology of wormlike micellar solutions at medium and high shear rates. At high shear rates of the order of 1000 s^{-1} and higher, the simulations predicted a steady state shear stress which increases with shear rate like $\dot{\gamma}^\alpha$, with an exponent $\alpha = 1/3$, see Fig. 6 (open symbols). The reason for this exponent is currently unknown, but we believe it is related to a balance between the large shear forces, tending to break up the wormlike micelles into pieces smaller than the entanglement length, and strong alignment, reducing the ‘grip’ of the flow on these micelles. This is a topic of current research. It is important to note that FENE-C models show a much stronger increase of shear stress in the non-linear regime (*i.e.* a weaker shear thinning of the viscosity), with an approximately two times as large exponent, $\alpha \approx 0.6$.^{15,19}

To test the predictive power of our simulations, we performed cone-plate experiments on a solution of 8% EHAC with 2% KCl³⁷ at a variety of temperatures between 308 and 348 K (Fig. 7, circles). At high shear rates the normal forces tend to expel the sample out of the cone-plate geometry. We therefore also studied shear rates from 1 s^{-1} to $3 \times 10^4 \text{ s}^{-1}$ by using a parallel plate geometry. With such a geometry much higher shear rates can be studied (stars). Note that the results of the two types of experimental measurement coincide perfectly in the range of shear rates where they overlap. These experiments confirmed that the viscosities in the non-linear regime converge to a universal curve, independent of temperature (indicated by the solid lines in Fig. 7). This must be contrasted with the viscosities in the linear regime, *i.e.* the Newtonian plateau values, which are in fact very sensitive of the temperature because of the Arrhenius-like dependence on temperature of the average equilibrium contour length of the wormlike micelles. The experiments show that for

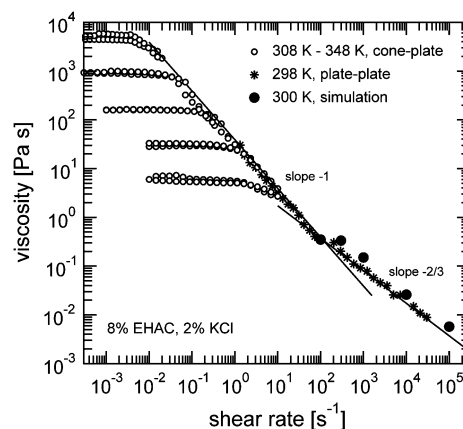


Fig. 7 Experimental and simulated shear viscosities *versus* shear rate of an 8% EHAC, 2% KCl wormlike micellar solution. Cone-plate experiments were performed at 308, 318, 328, 338 and 348 K, respectively (open circles, from top to bottom), parallel-plate experiments were performed at 298 K (stars). Simulation data (solid circles) are for $T = 300 \text{ K}$, $E_{sc} = 19.1 k_B T$, $E_a = 2.4 k_B T$. Solid lines with slope -1 and $-2/3$ indicate the universal non-linear behaviour. Reproduced from Padding *et al.*²⁵ with permission of the *American Institute of Physics*.

intermediate shear rates the universal non-linear viscosity curve decays like $\dot{\gamma}^{-1}$, indicating a stress plateau ($\alpha = 0$), while for high shear rates it decays like $\dot{\gamma}^{-2/3}$, with a change of slopes near a shear rate of 100 s^{-1} .

The stress plateau at intermediate shear rates is probably accompanied by shear banded flow,³⁸ but in these particular experiments we did not attempt to prove or measure this. The slope of $-2/3$ in the viscosity curve at high shear rates confirms our simulation predictions that the stress increases like $\dot{\gamma}^{1/3}$ at higher shear rates. Even better, within the accessible range of shear rates, the simulation results (filled circles) are in almost quantitative agreement with the experiments. The simulations systematically overpredict the viscosity, 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 were complete, we realised the agreement would have been even better if we had used a friction model for a finite rod, instead of an approximation valid for very long rods.^{25,39} This would have resulted in an essentially unaltered parallel friction and a perpendicular friction which is 1.5 times lower than the friction used in these simulations.

We note that, because of the lower scission energy used in our simulations, the transition to the Newtonian plateau already occurs at a shear rate of several hundred reciprocal seconds. This explains the apparent ‘deviation’ of the first simulation point. As computers get faster, we will be able to use higher scission energies, with longer wormlike micelles, that go deeper into the entangled regime. We therefore expect that in the near future it will be possible to also quantitatively study the extreme shear thinning (with a slope -1) at lower shear rates. This will give us a unique opportunity to study shear banding from a microscopic point of view. In this regard it is important to stress again that the simulated equations of motion do not bias towards a linear profile by construction. Indeed shear banding has clearly been observed, in solutions of resin particles³³ and telechelic polymers,³⁴ in simulations which use exactly the same boundary and

flow conditions as in the current work. We do not observe shear banding here, simply because our wormlike micelles are not yet long enough to be in the fully entangled regime.

IV. Wormlike micelles in contraction–expansion geometries

When wormlike micelles flow through porous media, the convoluted three-dimensional shape of the pore space subjects the fluid to a combination of shear and elongation with the result

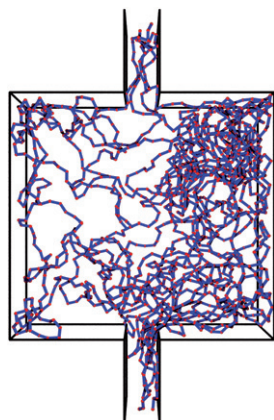


Fig. 8 Example of a simulated pore space containing a particularly long wormlike micelle consisting of 1601 persistence length units. The background solvent flux is directed from top to bottom.

that the overall relationship between flowrate and pressure gradient is difficult to predict.⁴⁰ In order to shed some light on the relevant processes, we have applied the model described in the previous section to flow through a stepwise contraction–expansion geometry, representing a single pore in a rock,^{41,42} see Fig. 8. The Brownian dynamics approach requires knowledge of the background solvent flowfield with which the wormlike micelles are pumped through the pore space. In a first approach this flowfield was determined by numerically solving Stokes' equation for a Newtonian solvent.⁴¹ Although such a flowfield is clearly not compatible with the viscoelastic character of the wormlike micellar solution, we have used this as a reference case for comparison with results using a non-Newtonian flowfield, as explained in the next paragraph. We found that if the size of the pore is comparable to the radius of gyration of the (average) wormlike micelle, the permeability is constant for micelles of different lengths. The reason is that, for relatively small pores, a wormlike micelle can sample many different regions of the flowfield simultaneously, both fast and slow. Parts of a micelle residing in a region of slow flow are pulled along by connected micellar parts residing in regions of fast flow. This prevents accumulation of the micelle in a region of low flow rate. Fig. 8 shows an extreme example of a very large micelle spanning the entire simulated system.

Next we increased the size of the pore so that it is much larger than the radius of gyration of the micelle⁴² and we extended the work to include the non-Newtonian flowfield obtained experimentally by particle image velocimetry experiments.³⁷

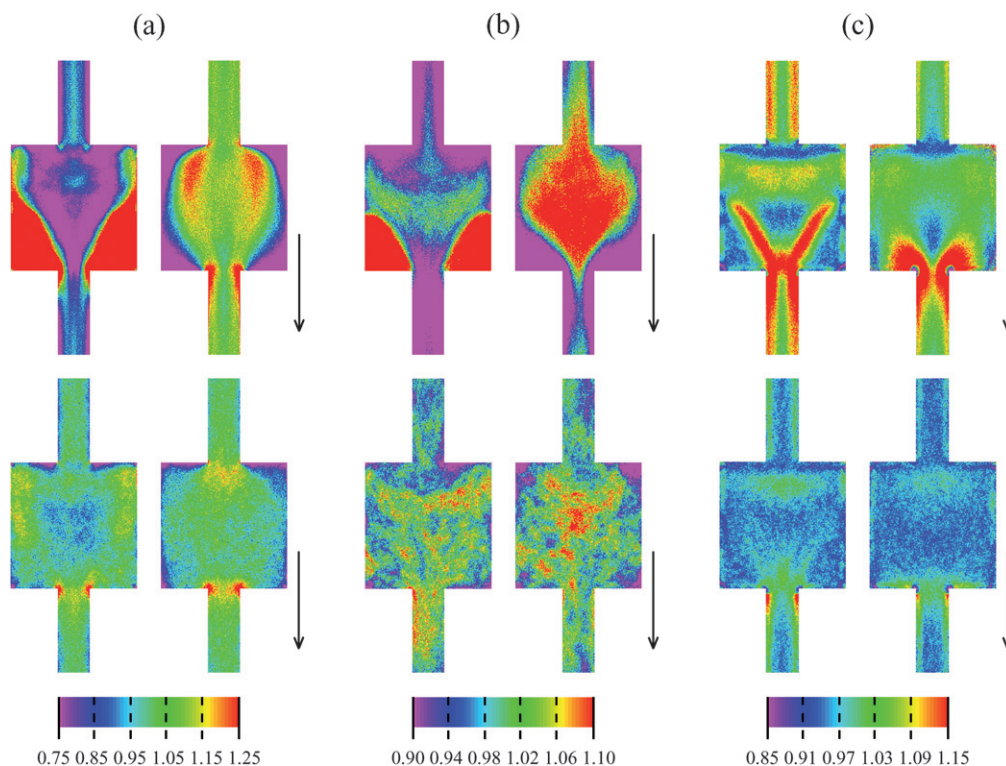


Fig. 9 Normalised density (a), normalised worm length (b) and normalised orientation parameter (c). Results obtained in a (experimentally determined) non-Newtonian flowfield are shown on the left, and results obtained in a Newtonian flowfield on the right. For “fast” flow (top) the apparent Deborah number is of order 1, while for “slow” flow (bottom) it is 10 times lower. The arrows indicate the flow direction. Reproduced from Stukan *et al.*⁴² with permission of Springer-Verlag.

Note that this approach is still an approximation because the experimental rather than the simulated rheology is used to determine the flowfield. An important dimensionless parameter is the ratio of the characteristic (stress) relaxation time τ of the (unperturbed) wormlike micelle and a characteristic time of this experiment t_c , which defines an apparent Deborah number:

$$De = \frac{\tau}{t_c} \quad (3)$$

As the characteristic time of this experiment we chose the typical time for the worm segments to pass through the main volume. We have investigated “fast” flows for which De is of order 1 and “slow” flows for which De is of order 0.1. Fig. 9 shows that in “fast” flow (top figures), the distribution of micellar density, length and orientation become markedly non-uniform, especially for the non-Newtonian flow field. This is caused by the more extreme differences in local shear and extension rates, to which the micellar length and orientation respond quickly. In “slow” flow (bottom figures) the density, length and orientation are more uniform.

We also studied smaller systems than depicted in Fig. 9 and confirmed that as soon as the shoulders of the contraction–expansion geometry become comparable to or smaller than the radius of gyration of the wormlike micelles, the density and orientation profiles become more homogeneous. In those cases the type of background flowfield becomes less relevant.⁴²

V. Conclusion

In this paper we have reviewed a Brownian dynamics simulation method to calculate the rheology of wormlike micellar fluids. As an input for this mesoscopic model, we use mechanical properties such as the persistence length and elastic modulus, which are obtained from atomistic molecular dynamics simulations. For computational reasons we are limited to scission energies lower than those estimated from experiments, but fortunately this does not influence the high shear-rate rheology. Indeed, we find that the experimentally observed nonlinear rheology at high shear rates of a specific wormlike micellar fluid (EHAC) can be predicted quantitatively. We have also studied, using strong approximations, less idealised flow conditions occurring in contraction–expansion geometries.

A few limitations of the method have been pointed out, which may direct future development of the model. First, the method neglects hydrodynamic interactions. We have argued why this may be a valid assumption for our chosen concentration (8%) and for low deformation rates. The fact that the predicted viscosities at high shear rates are in quantitative agreement with experiments suggests that hydrodynamic interactions are relatively unimportant for high shear rates too at this concentration. However, what role hydrodynamic interactions play for lower (but still semidilute) concentrations and/or different types of deformation flow remains to be tested. Work along these lines has been started by using stochastic rotation dynamics in simulations of semidilute semiflexible chains.³⁰

Second, excluded volume interactions between different wormlike micelles have been neglected. Therefore the model cannot be used for concentrations close to or higher than the isotropic–nematic transition.

Last, despite the large gain in time and length scales by coarse-graining to a persistence length, we have been able to simulate wormlike micelles which are only slightly entangled: the average contour length of the system with highest scission energy ($19.1k_B T$) was of the order of $L = 10 \mu\text{m}$, while the entanglement length was estimated to be 2 to 6 μm . Fortunately, given the ever-growing increase in computational power, more highly entangled wormlike micelles with higher scission energies can be simulated in the near future. This will open up the possibility to study the shear-banding phenomenon from a microscopic point of view.

Our hope is that, in conjunction with atomistically detailed simulations to determine the single chain mechanical properties, the model presented here can aid in the design of novel wormlike micellar materials for realistic applications.

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