

Dynamics and rheology of wormlike micelles emerging from particulate computer simulations

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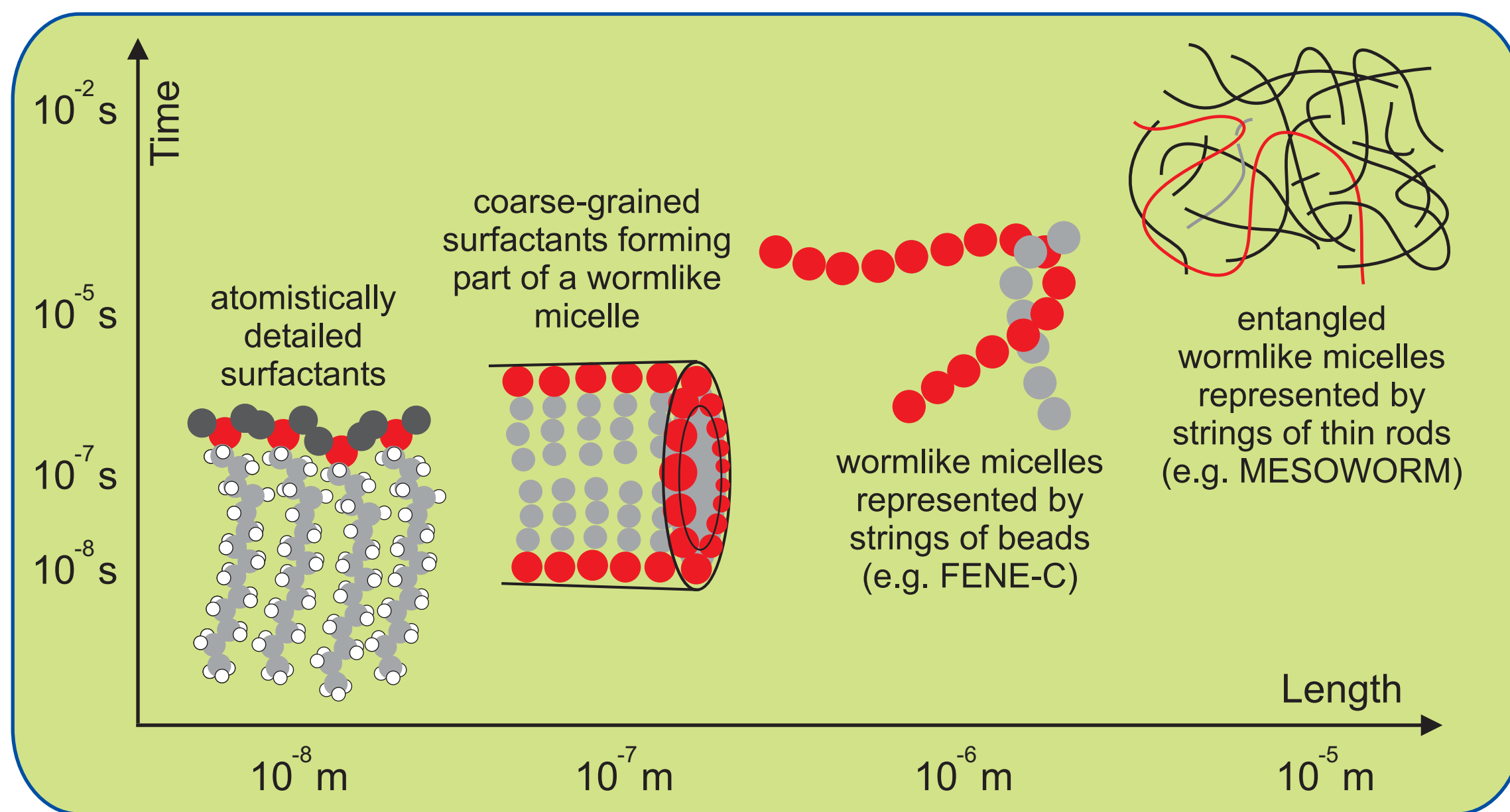
Abstract

We study the large scale dynamics and rheology of semidilute wormlike micelles (WLMs) by coarse grained simulations. Specific mechanical properties of individual WLMs, such as the persistence length, diameter and elastic modulus, are determined from atomistic simulations, providing a link with the chemistry. We apply the method to a solution of erucyl bis (hydroxymethyl)methylammonium chloride (EHAC).

Different scission energies lead to unentangled and entangled WLMs. We can explain the relaxation modulus of unentangled samples with a simple breakable Rouse chain theory. Increasing the shear rate leads to a decrease of the contour length and increase of the breaking rate. The stress is constant at intermediate shear rates. At high shear rate the stress is proportional to (shear rate)^{1/3}, as confirmed by experiments. [1]

From self-assembling molecules to rheology

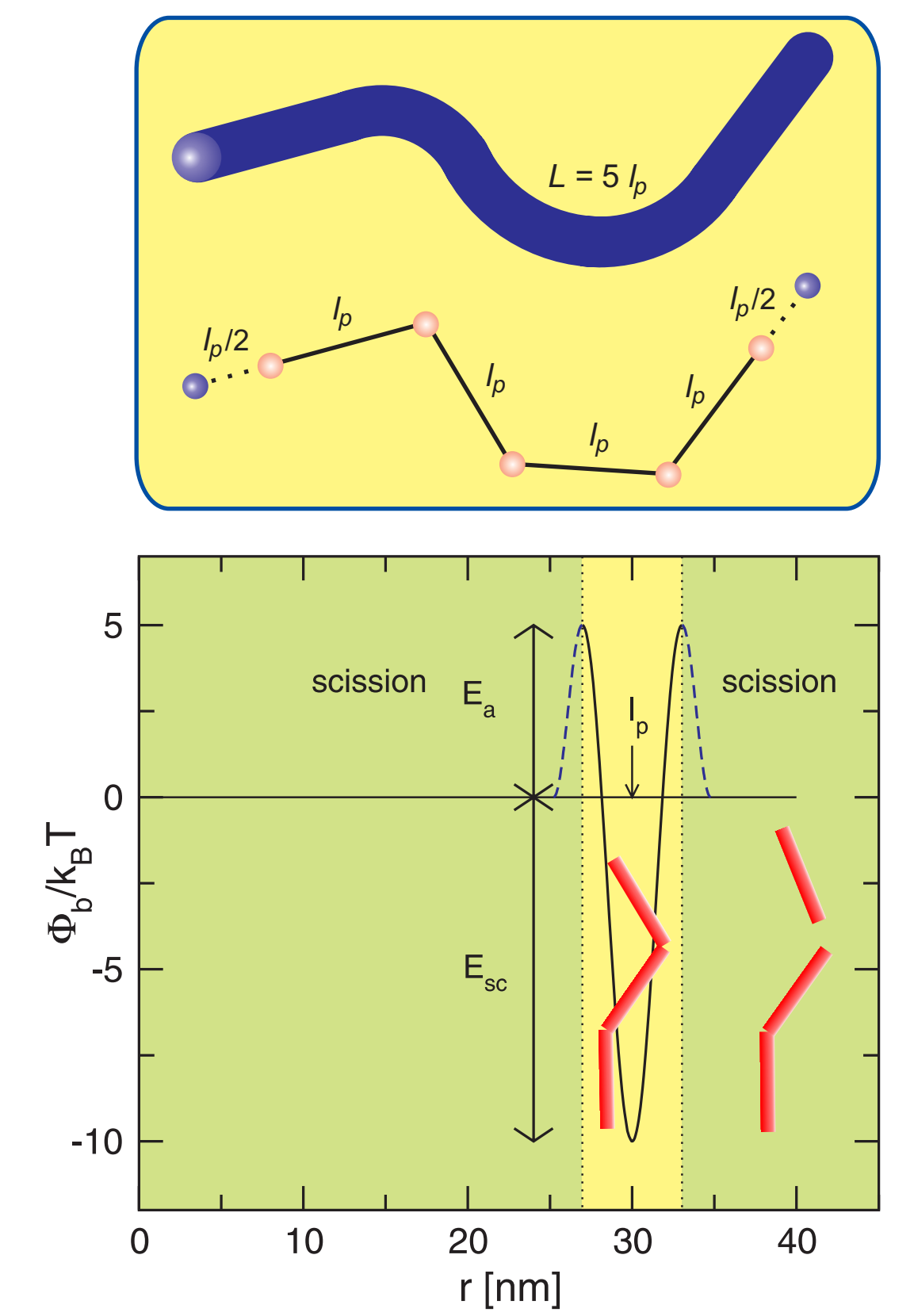
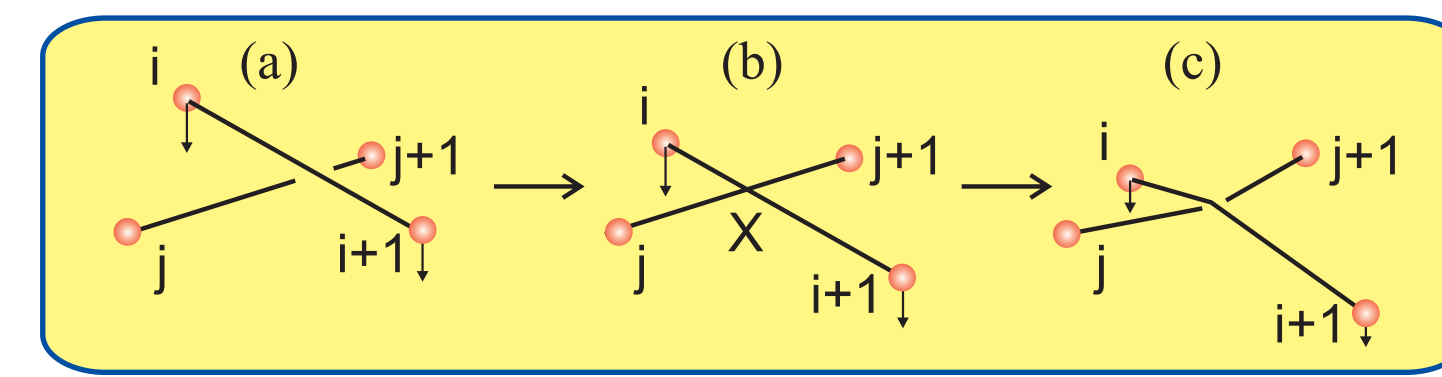
Amphiphilic molecules sometimes self-assemble into elongated structures called wormlike micelles (WLMs). Particle based simulations of WLMs may be performed on many different time and length scales, as indicated in the figure below. Our goal is to **predict the large scale dynamics and rheology** of solutions of wormlike micelles, while **retaining the link with the particular chemistry** of the surfactants [1,2].



Method: Brownian dynamics with Twentanglement

We developed a mesoscale Brownian dynamics model, with the following characteristics:

- Each unit represents one persistence length l_p of wormlike micelle.
- A realistic worm compressibility K is used.
- The bonds are breakable, with an energy cost E_{sc} (cost to create 2 end-caps).
- Recombination is reaction limited due to an additional activation barrier of height E_a .
- The friction on each unit is determined by the friction on an equivalent rod of length l_p and diameter d in a solvent of viscosity η_s .
- Entanglements are conserved by the 'Twentanglement' algorithm [3] (below).

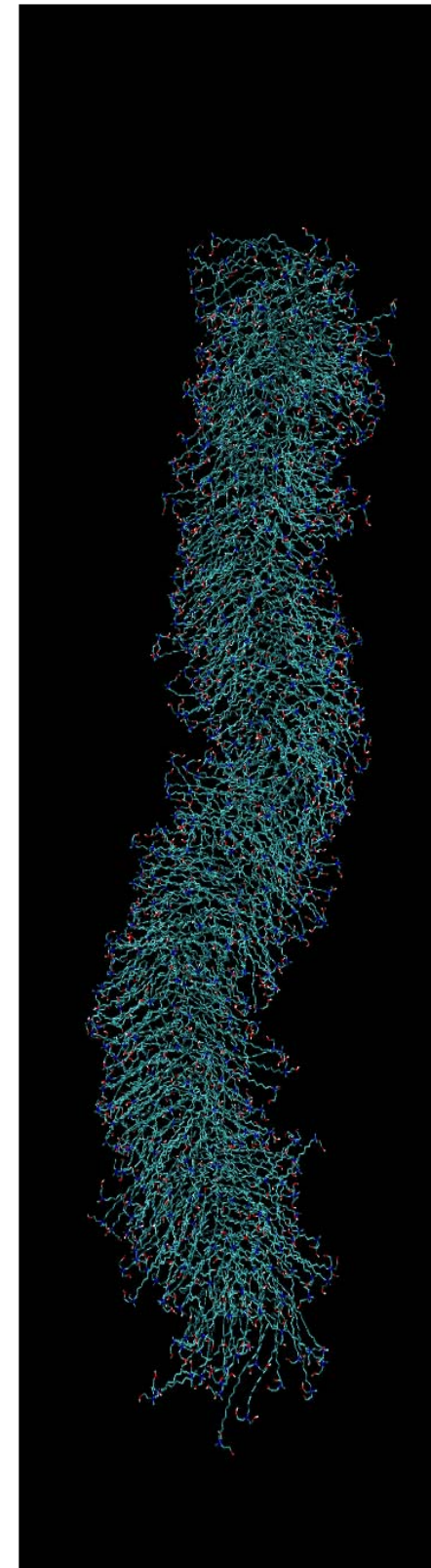


1. Single worm mechanical properties

The mechanical properties which enter the mesoscale model can be determined from more detailed simulations or targeted experiments. In this case we model a solution of erucyl bis (hydroxymethyl) methylammonium chloride (EHAC). We have determined the following parameters by atomistic molecular dynamics simulations:

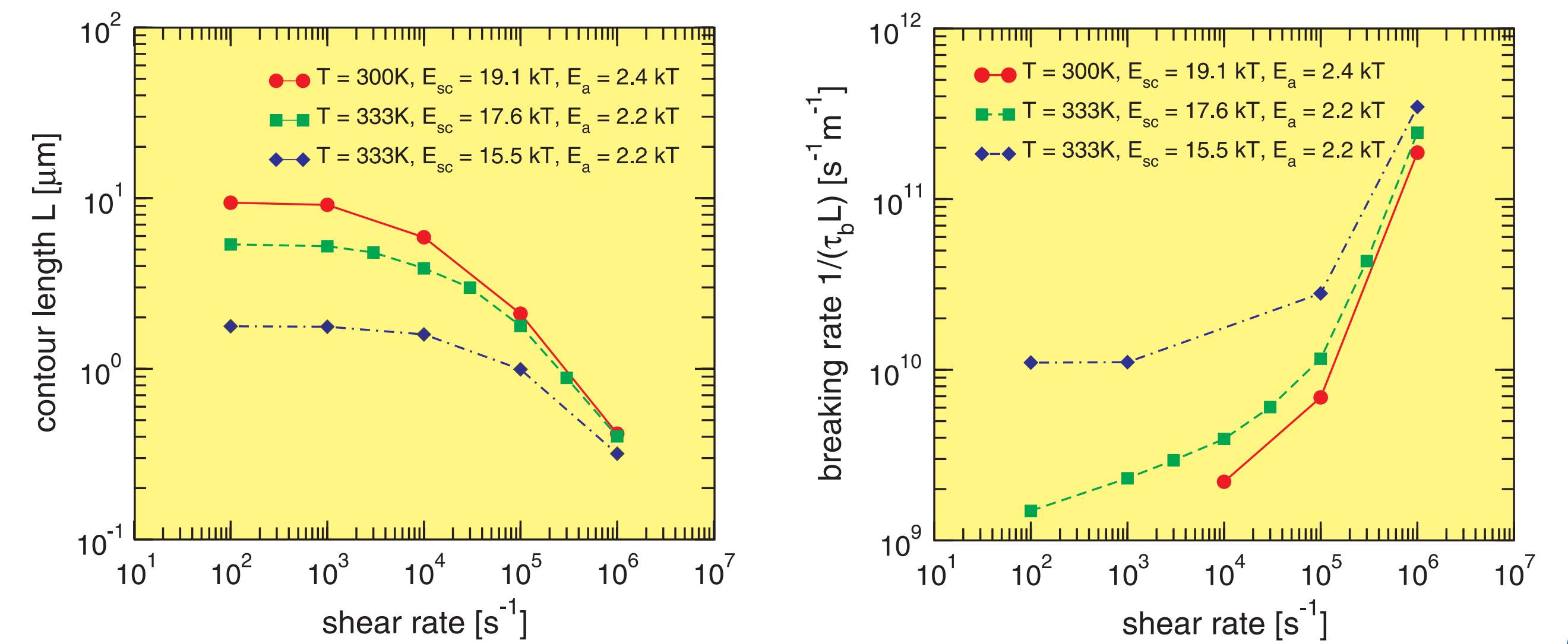
Property	Symbol	Value
Persistence length	l_p	30 nm
(Hydrodynamic) diameter	d	4.8 nm
Elastic modulus	K	0.2 nJ/m
Scission energy [*]	E_{sc}	0.05 or 0.06 aJ
Fusion activation energy [*]	E_a	0.01 aJ
Solvent viscosity	η	1 mPas

^{*} For scission and activation energies we do not yet have values from atomistic simulations. In this work these are adjustable parameters.



2. Contour length and breaking rate in shear flow

In mesoscale simulations of 8% EHAC we find an exponential distribution of contour lengths. Its average L increases rapidly with scission energy, in agreement with theory and experiment [2]. Under shear flow, L decreases (left figure) and the average breaking rate per unit length increases (right figure).

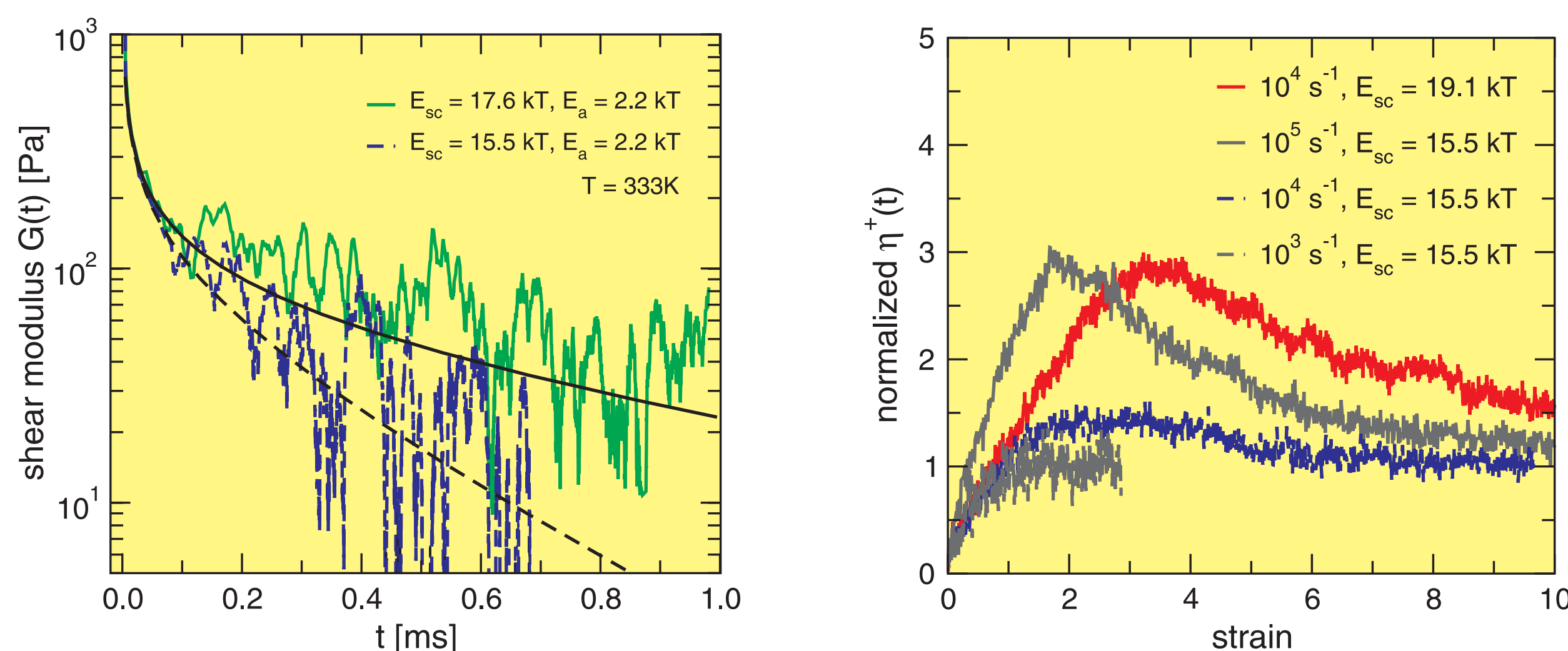


3. Linear and non-linear rheology

For unentangled samples the zero-shear relaxation modulus agrees well with a simple theory of breakable Rouse chains [1], yielding the prediction

$$G(t) \approx \frac{ckT}{N} \sqrt{\frac{\pi\tau_l}{6t}} \exp(-t/\tau) \quad \text{with} \quad \tau = 0.42\tau_l^{1/3}\tau_b^{2/3}$$

(black lines in left figure). Here τ_l is the longest relaxation time of a hypothetical unbreakable WLM and τ_b is the average breaking time of a WLM of average length. For all samples stress overshoots are observed under fast shear flow (right figure).

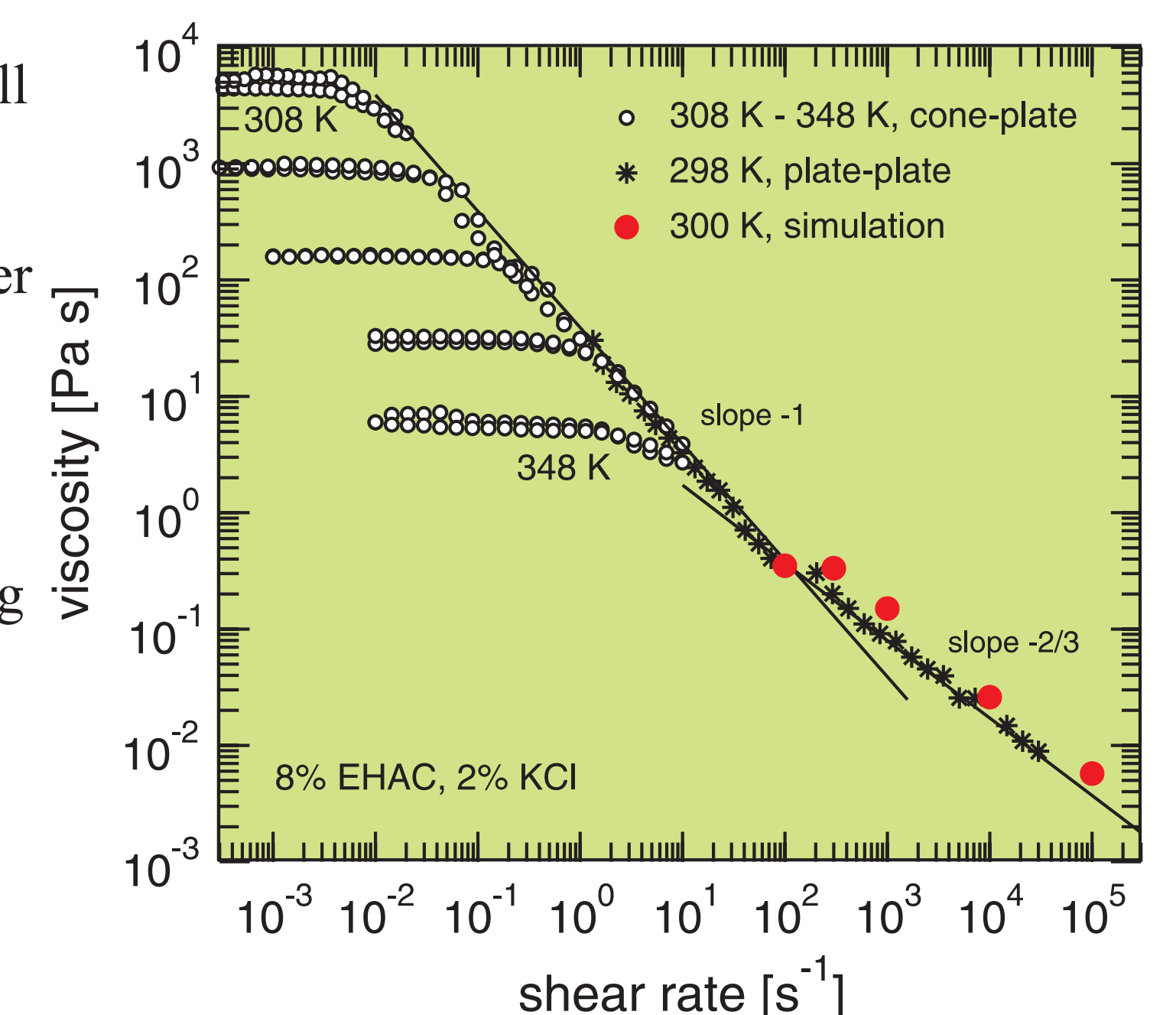


4. Shear thinning: comparison with experiment

Experimentally, EHAC solutions display **strong shear thinning**. Shear thinning with an exponent -1 starts at a certain **critical shear rate**. Because the contour length and (equilibrium) stress relaxation time τ depend on the temperature of the sample, the zero-shear viscosity and this critical shear rate are also temperature dependent.

Interestingly, the flow curves of all temperatures tend to the **same** limiting curve at high shear rates. This allows simulations with lower scission energies than the actual experimental values.

At a **second critical shear rate** (approx. 100 s⁻¹) the shear thinning exponent is observed to change from -1 to -2/3. Our simulations (red circles) are in quantitative agreement with the experimental data (circles and stars).



References

- [1] J. T. Padding, E.S Boek and W.J. Briels, J. Chem. Phys. **129**, 074903 (2008).
- [2] J.T. Padding, W.K. den Otter and W.J. Briels, *Computer Simulations of Wormlike Micelles*, in *Giant Micelles: Properties and Applications*, Surfactant Science Series Vol. **140**, edited by R. Zana and E. Kaler (Taylor&Francis, New York, 2007).
- [3] J.T. Padding and W.J. Briels, J. Chem. Phys. **115**, 2846 (2001).

Conclusion

We can now study the dynamics and rheology at millisecond timescales, while still retaining the specific mechanical properties of individual wormlike micelles. The majority of these mechanical properties can be determined from more detailed molecular dynamics simulations, providing the link with the chemistry of the surfactants. This enables a **rational design of new visco-elastic surfactant systems**.