Gel point in CNC dispersion from FT Rheology

Gel point in CNC dispersion from FT Rheology

Sylwia Wojno[1,3], Gunnar Westman[2,3], and Roland Kádár[1,3]

[1] Chalmers University of Technology, Department of Industrial and Material Science, Division of Engineering Materials, SE-412 96 Gothenburg, Sweden
[2] Chalmers University of Technology, Department of Chemistry and Chemical Engineering, Division of Chemistry and Biochemistry, SE-412 96 Gothenburg, Sweden
[3] Wallenberg Wood Science Center, Chalmers, SE-412 96 Gothenburg, Sweden

ABSTRACT
A non-linear analysis via Fourier-Transform Rheology (FT-Rheology) and Large Amplitude Oscillatory Shear (LAOS) of cellulose nanocrystals (CNC) dispersions is presented. Dynamic frequency and strain sweep measurements were performed for different CNC concentrations with various parameters (ω, γ). The relevance of nonlinear material rheological parameters on flow-field-CNC interactions are initially investigated. This preliminary analysis is mainly formed on the magnitude of the stress response nonlinearities. Dependence of concentration on phase transition in CNC while applying strain was investigated. A comparison between the linear viscoelastic dynamic moduli and nonlinearities a steep increase in nonlinear response around the gel point.

INTRODUCTION

Cellulose is one of the most abundant natural resource on earth with wide presence in wood, plants, tunicates, algae, bacteria.[14]Cellulose nanocrystals (CNC) are stiff, highly crystalline and rod like shaped cellulose structures obtained by removing the amourphous part of cellulose nanofibrils through acid-catalysed hydrolysis.[1]CNC in aqueous suspensions can behave as a liquid crystalline or gel-like depending on the concentration, CNC dimensions, ionic strength and type of counter-ion.[7]The interest in nanocellulose is generally motivated by its wide occurence and possibility of new applications. It is one of the main reasons for understanding the effect of process structuring and its parameters on the functional properties. Rheological measurements have been done to characterize different forms of cellulose (CNF, CNC suspensions) during past few decades. Rheological measurements help investigate the dispersion microstructure or phase transition (liquid crystalline, liquid crystalline structure, gel-like structure). Investigations from previous work showed dependency of characteristics of CNCs (e.g. surface charge), applied ultrasound energy, temperature on rheological behavior of CNC suspensions, among others.[10,11,13] However, studies to investigate data on microstructure-rheology relationship are limited. Therefore, it is highly relevant to implement proper and precise analyzing methods sufficiently sensitive to detect changes in the microstructure. Nonlinear oscillatory shear analysis via Fourier-Transform Rheology (FT-Rheology) and Large Amplitude Oscillatory Shear (LAOS) allows to investigate the relevance of nonlinear material rheological parameters on flow-field-CNC interactions. In linear viscoelastic oscillatory shear tests, a sinusoidal strain input, $\gamma(t) = \gamma_0 \sin(\omega t)$, where γ_0 is imposed strain amplitude and ω is imposed angular frequency, results in a sinusoidal shear stress output $\sigma_{12} = \sigma_0 \sin(\omega t + \delta)$, shifted with the phase angle δ, where σ_0 results in a stress amplitude. Therefore, shear rate can be represented as $\dot{\gamma}(t) = \gamma_0 \omega \cos(\omega t)$. Consequently, the Fourier spectrum of the shear stress $\Sigma(\omega)$ contains entirely the contribution, $I_1(\omega_i)$, of the imposed excitation, whereω_i is the angular frequency of the excitation. However, in the case of a nonlinear viscoelastic shear stress, the output is non-sinusoidal which will lead to higher harmonics in the corresponding Fourier spectra in addition to fundamental intensity I_1. The principle is detailed elsewhere, e.g.[2,4,9,16] The higher harmonics can be used to quantify the nonlinear material response. Higher harmonics are typically detected also in the small amplitude oscillatory shear (SAOS), however, they are the result of instrumentation noise.[2] With increasing strain amplitude, nonlinearities are detectable at higher shear strain amplitude and increase in medium amplitude oscillatory shear (MAOS) region at $I_{3/1} \propto \gamma_0^2$ or above that region at large amplitude oscillatory shear (LAOS). Consequent, a nonlinear coefficient from Fourier-Transform Rheology can be defined as (intrinsic nonlinearity).[5]

$$Q \equiv \frac{I_{3/1}}{\gamma_0^2}. \quad (1)$$

The zero-strain limit of the Q-parameter therefore is

$$Q_0 = \lim_{\gamma \to 0} Q(\gamma) \quad (2)$$

The magnitude of this intrinsic nonlinearity can be evaluated for any complex fluids.[6,8] A visual inspection of the nonlinear response can be performed using elastic and viscous Lissajous-Bowditch diagrams. A linear viscoelastic response is represented by elliptic shaped diagrams. A nonlinear viscoelastic response due to distorted signal (non-sinusoidal) results in distorted (non-elliptic) signatures.[8]

EXPERIMENTAL

Aqueous suspensions of juvenile CNC were obtained by the acid hydrolysis H_2SO_4 of microcrystalline cellulose using a procedure outlined by Hasani et al.[3] Deionized water (Milipore Milli-Q Purification System) was used to obtain following concentrations: 1 wt%, 1.5 wt%, 2 wt%, 3 wt%, 4 wt% and 5 wt%. The suspensions were stirred by sonicator to ensure homogeneity. Directly before measurements, suspensions were treated in ultrasonic bath for 15 min. Rheological behavior of CNC suspensions depends on pretreatment (e.g. applied ultrasound energy, standing time).[11,14] Thus, the same procedure was performed before each measurement.

Nonlinear oscillatory shear tests were performed on an Anton Paar MCR 702 TwinDrive rheometer (Graz, Austria) in strain controlled mode (separate mode-transducer) using a parallel plate geometry of ($2R =$) 50 mm in diameter, with 1 mm gap. The frequency sweep tests were performed in counter oscillation. All experiments were performed at 23 °C. Relaxation time was 300 s. In this presented study, elastic ($\sigma(t)/\sigma_{max}$ vs. $\gamma(t)/\gamma_0$) and viscous ($\sigma(t)/\sigma_{max}$ vs. $\dot{\gamma}(t)/\dot{\gamma}_0$) Lissajous-Bowditch diagrams were used for visual inspection of the nonlinearities, whereas the quantitative data analysis was performed in the framework of Fourier-transform rheology analysis.[15] Strain sweep measurements were performed within a strain range from 0.01 to 1500 % at following frequencies: 0.6 Hz, 1 Hz, 2 Hz and 4 Hz for each suspension. Frequency sweep measurements were

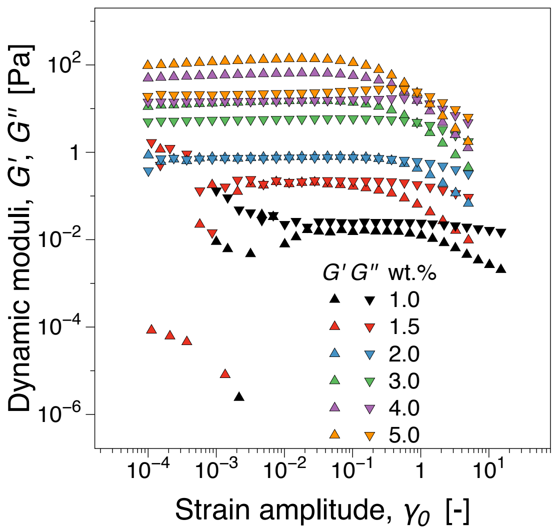

Figure 1. Dynamic Storage (G') and Loss modulus (G") for different concentrations of CNC suspensions from strain sweep tests, $\omega = 2$ rad/s.

carried out over an angular frequency range from 600 to 0.001 rad/s, with constant strain 0.3 %. The nonlinear analysis of the shear stress output signal was performed in the framework of Fourier-Transform analysis.

RESULTS AND DISCUSSION

Dynamic strain sweep measurements with constant frequency $\omega = 2$ rad/s and increasing strain amplitude were performed to determine storage and loss modulus (G', G'') of unmodified CNC suspensions (Fig. 1). From the linear viscoelastic data, the 1 wt% suspension exhibited rheological liquid crystal fluid behavior ($G'' > G'$). At 1.5 wt% concentration appears gel-point which is more clear detectable at 2 wt%, where storage and loss modulus are equal ($G' \cong G''$). The suspensions above 2 wt% (3-5 wt%) showed a cross-over after which the $G' > G''$. They are confirmed as a rheological gels. A similar qualitative concentration dependence applies to the complex viscosity (Fig. 2). It is observed a significant increase of the complex viscosity $|\eta^*|$ above 2 wt% unmodified CNC suspension, meaning above the gel-point. This is quite important, because $|\eta^*|$ increases above the gel point whereas Q_0 increases at the

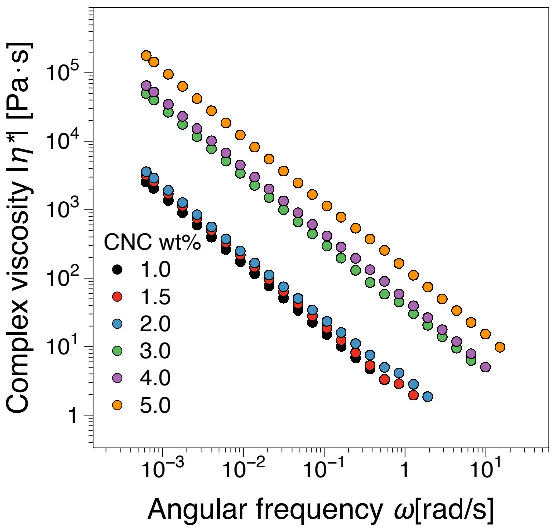

Figure 2. Complex viscosity functions, $|\eta^*|$ (ω, ϕ) from linear viscoelastic frequency sweep measurements.

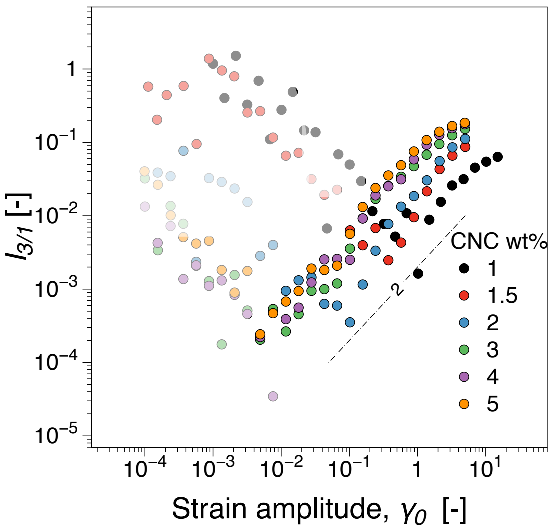

Figure 3. Third relative higher harmonic, $I_{3/1}$, from dynamic strain sweeps for different concentrations of CNC suspensions, $\omega = 2$ rad/s.

gel point.

The nonlinear material response expressed by the third relative higher harmonic, $I_{3/1}$ is presented in Fig. 3. SAOS region is characterized by instrumentation noise (semi-transparent data points) and LAOS is region beyond. The quadratic scaling of $I_{3/1}$ in the MAOS region can be distinguished for all samples, with differences in the magnitude of the nonlinearities with concentration. Local distortions in the quadratic scaling could however be inferred with constituency for all samples above 1.5 wt% CNC. The distortions include the possibility of successive quadratic scaling regions. However, these have not been considered in the subsequent analysis, and their origin and significance needs to be further investigated.

The elastic and viscous Lissajous-Bowditch (LB) diagrams, for selected ω, γ_0 for chosen concentrations are shown in Fig. 4. The material signatures are represented by a Pipkin diagrams. The diagrams reveal significant qualitative changes especially when comparing CNC concentrations below and above gel-point in both, elastic and viscous components. The spe-

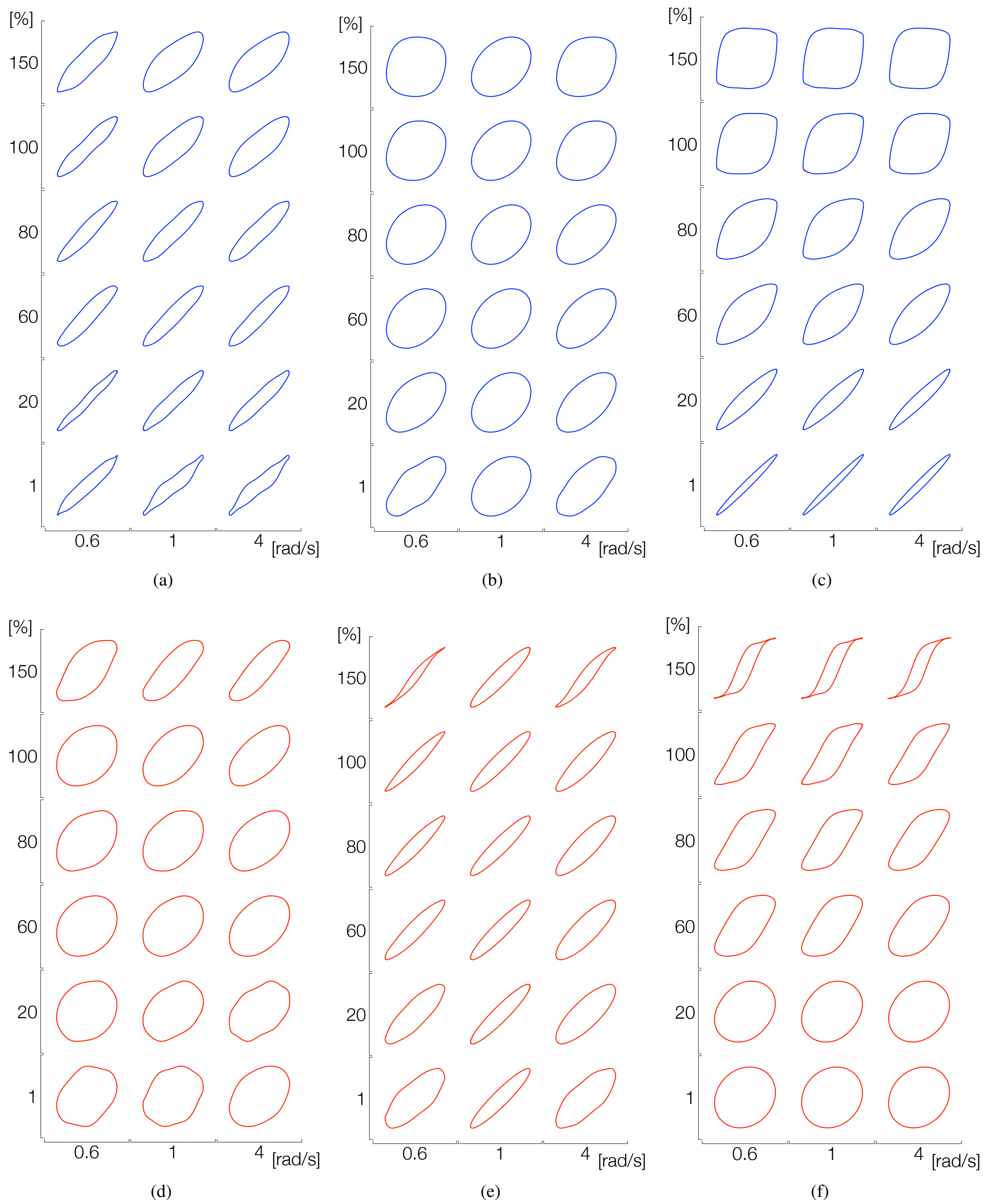

Figure 4. Lissajous-Bowditch diagrams for unmodified CNC suspensions for selected ω=0.6, 1, 4 rad/s for (a,d)1 wt% (below gel-point), (b,e) 1.5 wt% (gel-point), (c,f) 5 wt% (above gel-point) compiled in Pipkin diagrams. Top row, (a)-(c) represent the Elastic Lissajous-Bowditch diagrams and bottom one, (d)-(f), represent viscous Lissajous-Bowditch diagrams.

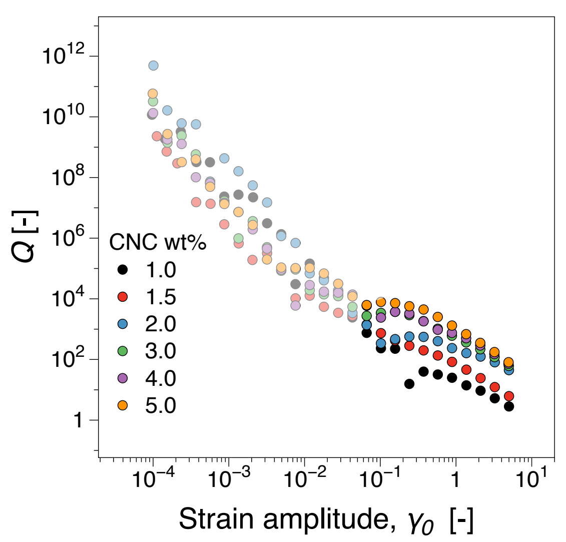

Figure 5. Q-parameter, variation with strain amplitude, see Eq. 1, $\omega = 2$ rad/s. Semi-transparent points represent instrumentation noise.

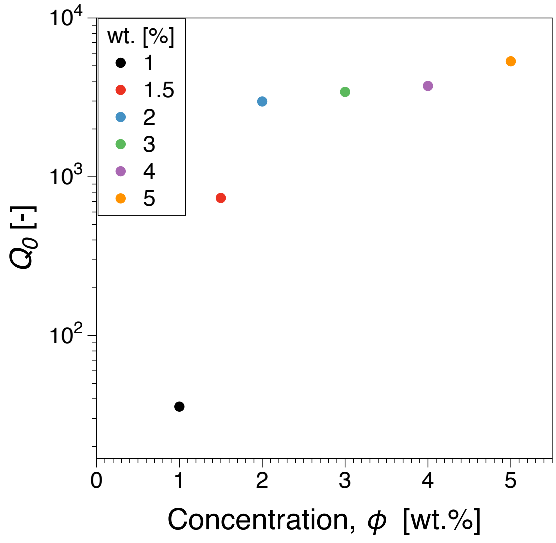

Figure 6. Zero-strain Q-parameter, Q_0 see Eq. 2, depending on wt% of CNC, $\omega = 2$ rad/s.

cific features of the nonlinear signatures require further analysis and are not discussed in this publication.

Using the Q-parameter, changes in nonlinear $I_{3/1}$ magnitude can be clearer detected and read. Q-parameter variation with strain amplitude at $\omega = 2$ rad/s for all concentrations is shown in Fig. 5. Therefrom, the zero-strain Q-parameter can be extrapolated, according to Lim et al. (2013).[12] The Q_0 parameter is presented in Fig. 6. The relative linear increase in Q_0 with increasing concentration is observed.

We note a significant gradient across the gel transition concentrations, whereafter the zero-shear intrinsic nonlinearity stabilizes (concentrations above 1.5 wt%). Thus, it can be inferred that the magnitude of the nonlinear response mirrors the gelation in the aqueous CNC suspensions analyzed, similarly to the analysis of percolation in filled polymer systems.[15] We note that a comparative advantage is the simplicity of the matrix whereas a disadvantage is the obtaining of data towards a reference due to the low viscosities involved.

SUMMARY AND CONCLUSIONS

Rheology is an essential tool for characterization of suspension flow dynamics. In particular, nonlinear viscoelastic analysis from oscillatory shear tests have the potential to provide novel insights into the flow-field - CNC interactions, particularly in the framework of surface modification of CNC and their self-organization. In this pre-study, several concentrations of aqueous CNC dispersions were examined mainly using Fourier-transform rheology. Dynamic strain sweep measurements showed dependence of the suspension concentration on its form and transition around the gel-point. Correspondingly, the magnitude of the nonlinear shear stress distortions as quantified by the zero-strain nonlinearity, Q_0, exhibited a steep increase around the gel point. Furthermore, a visual examination of elastic and viscous Lisssajous-Bowditch diagrams reveal significant qualitative changes between CNC concentrations below and above gel-point. Further work will focus on surface treated CNC suspensions and further insights into the nonlinear behavior of the dispersions will be sought by expanding the scope of the nonlinear analysis.

ACKNOWLEDGEMENTS
The project is funded through a grant from the Wallenberg Wood Science Centre (WWSC).

REFERENCES

1. Krässig, H. A. (1993), "Cellulose : structure, accessibility, and reactivity.", Gordon and Breach Science.

2. Wilhelm, M., Maring, D. and Spiess, H.-W. (1998), "Fourier-transform rheology", *Rheologica Acta*, **37**, 399–405.

3. Hasani, M., Cranston, E. D., Westman, G. and Gray, D. G. (2008), "Cationic surface functionalization of cellulose nanocrystals", *Soft Matter*, **4**, 2238-2244.

4. Ewoldt, R., Hosoi, A. and McKinley, G. (2008), "New measures for characterizing nonlinear viscoelasticity in large amplitude oscillatory shear", *Journal of Rheology*, **52**, 1427-1458.

5. Hyun, K. and Wilhelm, M. (2009), "Establishing a New Mechanical Nonlinear Coefficient Q from FT-Rheology: First Investigation of Entangled Linear and Comb Polymer Model Systems", *Macromolecules*, **42**, 411-422.

6. Wagner, M. H., Rolón-Garrido, V. H., Hyun, K. and Wilhelm, M. (2011), "Analysis of medium amplitude oscillatory shear data of entangled linear and model comb polymers", *Journal of Rheology*, **55**, 495-516.

7. Klemm, D., Kramer, F., Moritz, S., Lindström, T., Ankerfors, M., Gray, D. and Dorris, A. (2011), "Nanocelluloses: A New Family of Nature-Based Materials", *Angewandte Chemie (International ed. in English)*, **50**, 5438-66.

8. Hyun, K. and Kim, W. (2011), "A new nonlinear parameter Q from FT-Rheology under nonlinear dynamic oscillatory shear for polymer melts system", *Korea Australia Rheology Journal*, **23**, 227-235.

9. Hyun, K., Wilhelm, M., Klein, C. O., Cho, K. S., Nam, J. G., Ahn, K. H., Lee, S. J. et al. (2011), "A review of nonlinear oscillatory shear tests: Analysis and application of large amplitude oscillatory shear (LAOS)", *Progress in Polymer Science*, **36**, 1697 - 1753.

10. Shafiei-Sabet, S., Hamad, W. Y. and Hatzikiriakos, S. G. (2012), "Rheology of Nanocrystalline Cellulose Aqueous Suspensions", *Langmuir*, **28**, 17124-17133.

11. Shafeiei-Sabet, S., Hamad, W. and Hatzikiriakos, S. (2013), "Influence of degree of sulfation on the rheology of cellulose nanocrystal suspensions", *Rheologica Acta*, **52**, 741-751.

12. Lim, H. T., Ahn, K. H., Hong, J. S. and Hyun, K. (2013), "Nonlinear viscoelasticity of polymer nanocomposites under large amplitude oscillatory shear flow", *Journal of Rheology*, **57**, 767-789.

13. Wu, Q., Meng, Y., Wang, S., Li, Y., Fu, S., Ma, L. and Harper, D. (2014), "Rheological behavior of cellulose nanocrystal suspension: Influence of concentration and aspect ratio", *Journal of Applied Polymer Science*, **131**, 40525.

14. Li, M.-C., Wu, Q., Song, K., Lee, S., Qing, Y. and Wu, Y. (2015), "Cellulose Nanoparticles: Structure–Morphology–Rheology Relationships", *ACS Sustainable Chemistry & Engineering*, **3**, 821-832.

15. Gaska, K., Kádár, R., Rybak, A., Siwek, A. and Gubanski, S. (2017), "Gas barrier, thermal, mechanical and rheological properties of highly aligned graphene-LDPE nanocomposites", *Polymers*, **9**, 294.

16. Naue, I. F. C., Kádár, R. and Wilhelm, M. (2018), "High sensitivity measurements of normal force under large amplitude oscillatory shear", *Rheologica Acta*, **57**, 757–770.