# Supplemental Material

# for

# “Towards a Constitutive Relation for Yield stress fluids”

H. V. M. Kibbelaar,[1] A. Deblais,[1] G. Briand,[1] Y. Hendrix,[1]

A. Gaillard,[1] K. P. Velikov,[1,2] M. M. Denn,[3,4] and D. Bonn[1]

[1]*Van der Waals-Zeeman Institute, Institute of Physics,*

*University of Amsterdam, 1098 XH Amsterdam, The Netherlands.*

[2]*Unilever Innovation Centre Wageningen,*

*Bronland 14, 6708 WH Wageningen, The Netherlands.*

[3]*Benjamin Levich Institute and Department of Chemical Engineering,*

*CUNY City College of New York, New York 10031, USA*

[4]*Casali Institute of Applied Chemistry,*

*Hebrew University of Jerusalem, Jerusalem 9190401, Israel*

## Abstract

This document provides supporting figures to accompany the main text; it gives more details on the experimental method and set-up, the prefactor, the rescaling of the shear stress and normal stress difference data from Seth *et al.*, the interpretation of the pinch off experiments and the spatial profiles of the fluid necks from the pinch off experiments.

## I. Supplementary Note 1: Rheology measurements

A good heuristic for many polymers, which is the basis, for example, of the White-Metzner equation [**?** ], is that the square of the shear stress is proportional to the product of the first normal stress difference with a constant shear modulus:

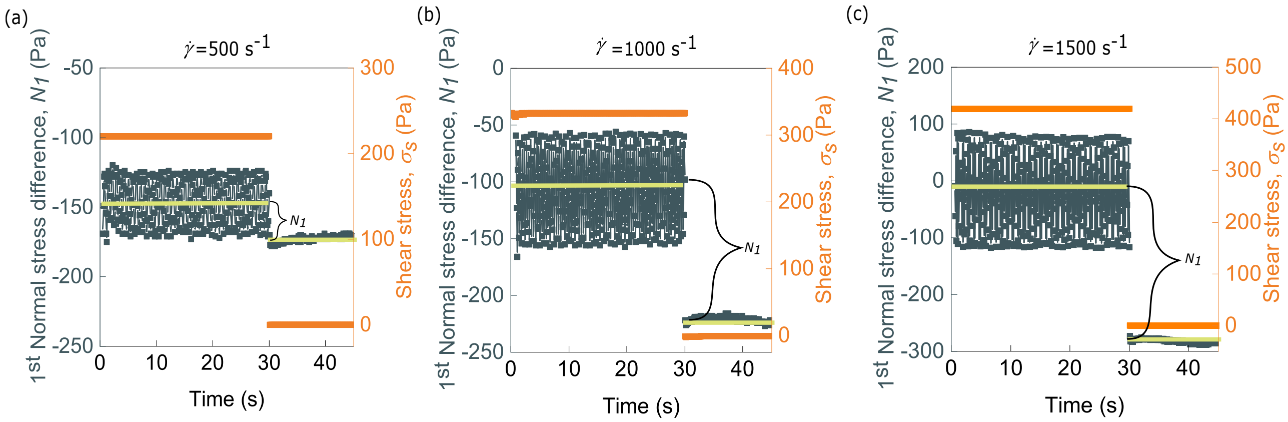
$$\sigma^2 = GN_1 \tag{1}$$

$G$ in turn can be written $G = \eta/\lambda$, where $\eta$ is the shear-dependent viscosity and $\lambda$ is the mean relaxation time, which thus has the same rate dependence as the viscosity. The data for emulsions with volume fractions of 0.70 and above show this quadratic dependence, with a coefficient that is independent of concentration and is in fact equal to the single-droplet pressure $\Sigma_{o/w}/\langle R\rangle/$; i.e., in this formalism $G = \alpha_1^{-1} = \Sigma_{o/w}/\langle R\rangle = 1250$ Pa.

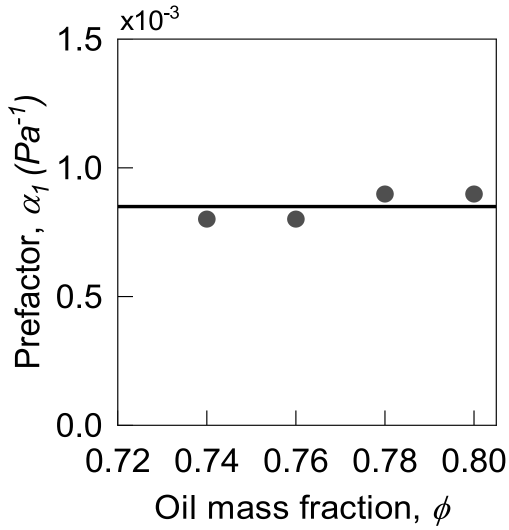
We are interested in computing the Deborah number for the extensional flow, which is the product of the relaxation time with the extension rate:

$$De = \lambda\dot{\varepsilon} = \eta\dot{\varepsilon}/G \tag{2}$$

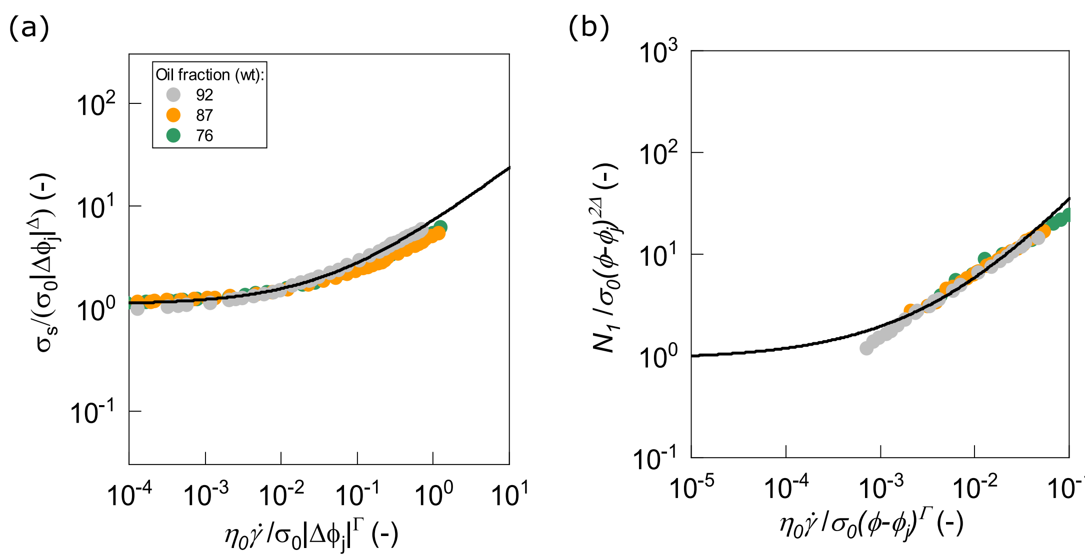
The viscosity here is evaluated at the extension rate. The product, $\eta\dot{\varepsilon}$, is close the to shear stress, so for the range of stresses studied here De $<<$ 1 and relaxation processes are unimportant.



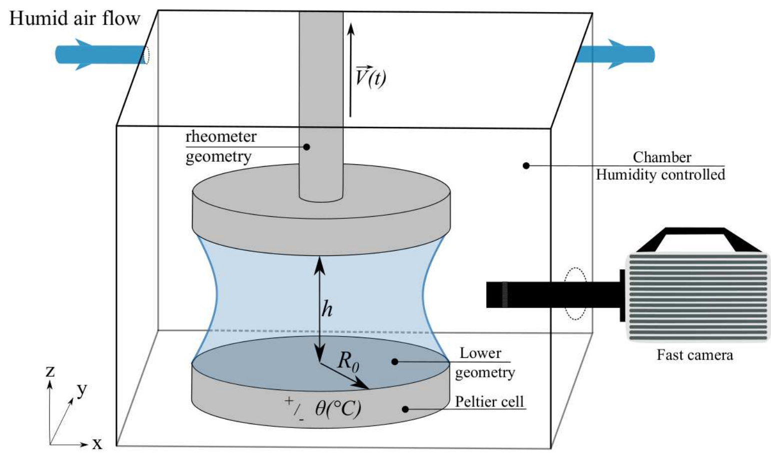

SUPPL. FIG. 1. The experimental protocol we designed consisted of imposing a flow sweep test in which the solution was sheared at different shear rates (from 50 to 3000 s$^{-1}$). After every shearing step a 15 second "rest" period is set during which no shearing was applied. This allows to reset the normal force in each step. The normal stress difference $N_1$ is consequently the difference between when a shear rate is applied and the "rest" period. As the normal stresses cannot be reset between the measurements, the shear rate is set to zero ("rest" period). The normal stress data should therefore be relatively interpreted (similarly done in the work of Casanellas *et al.*[**?** ]). The figures show, as an example of the measurements, the data obtained for 80 wt. % at three different shear rates (a) 500 s$^{-1}$, (b) 1000 s$^{-1}$, (c) 1500 s$^{-1}$. The shear stress, $\sigma_s$, and normal stress difference, $N_1$, are displayed in orange and green, respectively. The yellow line is the average normal stress difference $N_1$.



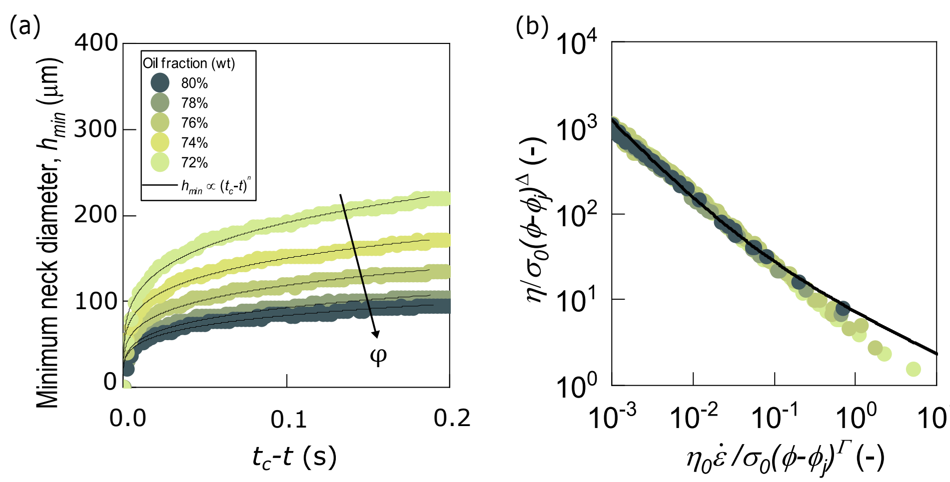

SUPPL. FIG. 2. The prefactor $\alpha_1$ as a function of the oil mass fraction. The prefactor is independent of the volume fraction. The value of $\alpha_1$ agrees well with the inverse of the Laplace pressure ($\sigma_0 =< r > /\Sigma$, with $\gamma$ being the interfacial tension) of our system, suggesting that the prefactor $\alpha_1$ is material dependent.



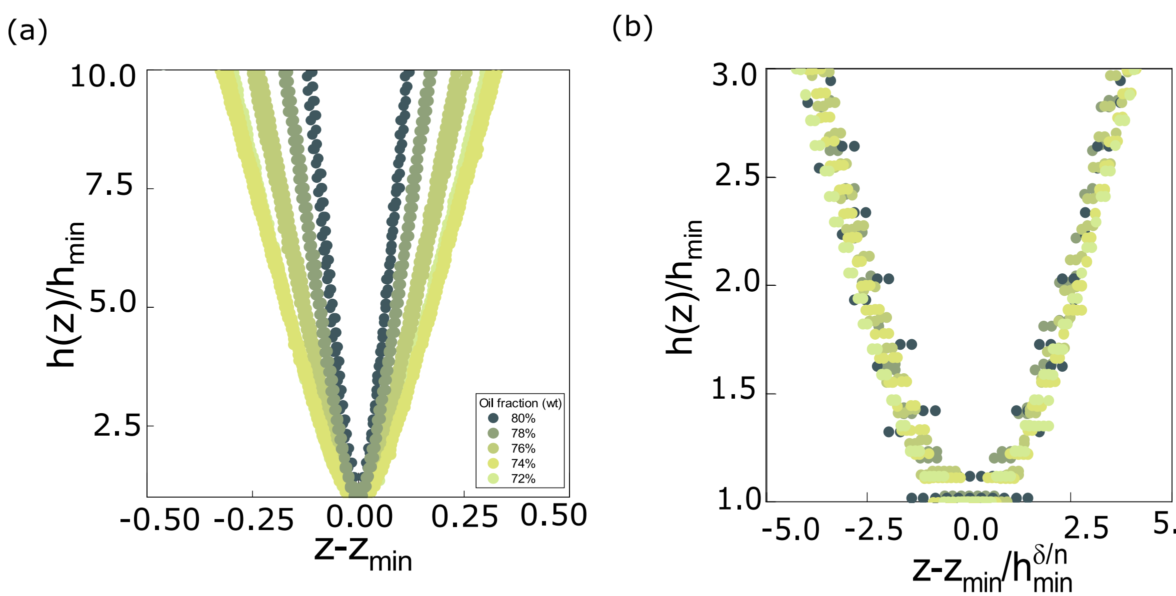

SUPPL. FIG. 3. Rescaling of the shear stress and normal stress difference data from Seth *et al.*[**?** ] applying only parameters determined from the shear rheology measurements. (a) Collapse of shear flow curves onto a master curve when plotted according to Eqs (2) and (3). The black line corresponds to a Herschel–Bulkley fit with $\Delta/\Gamma = 0.53$. (b) Collapse of the normal stress difference curves when plotted according to Eq.(6). The solid line is the prediction based on Herschel-Bulkley parameters.




SUPPL. FIG. 4. Sketch of experimental setup (not to scale) to create a purely extensional flow to study the extensional thinning and destabilization of HA filaments. A rheometer (Anton paar, MCR 302) was used as the building block of the device. A rheometer geometry plate with a diameter of 5 mm was used, the lower plate having the same diameter. The upper plate can be pulled vertically at a constant velocity until the capillary bridge breaks. The Peltier cell allows us to impose the temperature of the sample during the elongational process at a constant speed. The evolution of the liquid bridge is recorded with a fast camera (Phantom V7) allowing frame rates up to 10,000 frames per second. The camera is equipped with a microscope tube lens, with an objective up to 12x magnification (Navitar) and a spatial resolution of 3 $\mu$m per pixel. The whole setup is placed in a chamber and is continuously flushed with humid air (80% RH) to prevent evaporation during the measurement.




SUPPL. FIG. 5. (a) Evolution of the minimum neck diameter as a function of time to breakup for volume fractions from 72 to 80%. Continuous lines are fits to the power law shear-thinning regime $h_{min} = A(t_c - t)^n$, yielding $n = 0.2$. (b) Elongational flow curves collapse onto a master curve when plotted according to Eqs (2) and (3) with $\Delta = 2.1$ and $\Gamma = 4.1$. The black line corresponds to a Herschel–Bulkley fit with $\Delta/\Gamma = 0.55$.




SUPPL. FIG. 6. (a) Spatial profiles of the fluid bridge profiles for the different volume fractions. (b) For well-controlled and slow enough initial stretching rates, one should recover a self-similar profiles in the breakup of emulsions. A proper rescaling of $(h)_z$ and $z$ allows us to collapse the profiles for different volume fractions onto a universal curve independent of initial conditions.

[] F. Morrison, Understanding Rheology (Oxford University Press, Oxford, 2001).

[] L. Casanellas, M. A. Alves, R. J. Poole, S. Lerouge, and A. Lindner, Soft matter **12**, 6167 (2016).

[] J. R. Seth, L. Mohan, C. Locatelli-Champagne, M. Cloitre, and R. T. Bonnecaze, Nature materials **10**, 838 (2011).