High-frequency rheology of nonlinear silicone fluids

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1. Introduction

Rheological properties and modeling of high viscosity silicone oils (polydimethylsiloxane, PDMS) are important because these nonlinear viscoelastic fluids have multiple applications ranging from fundamental research to industry [1]. Certain application areas and processing steps require a reliable rheological model. Our aim is to create a lumped parameter model which describes the viscoelastic properties of the silicone fluid in shear flow.

2. Linear viscoelastic model based on TTS

Small amplitude oscillatory shear (SAOS) measurements of the samples (Wacker) were performed with a conventional rotational rheometer (Anton Paar) up to 100 Hz and in a broad temperature range. We demonstrate in Fig. 1. that these silicon fluids obey the time-temperature superposition (TTS) principle, forming a master curve up to ca. 300 Hz, which can be accurately modeled with a 5-element Maxwell-model that is valid in the linear regime [2], see Fig. 2.

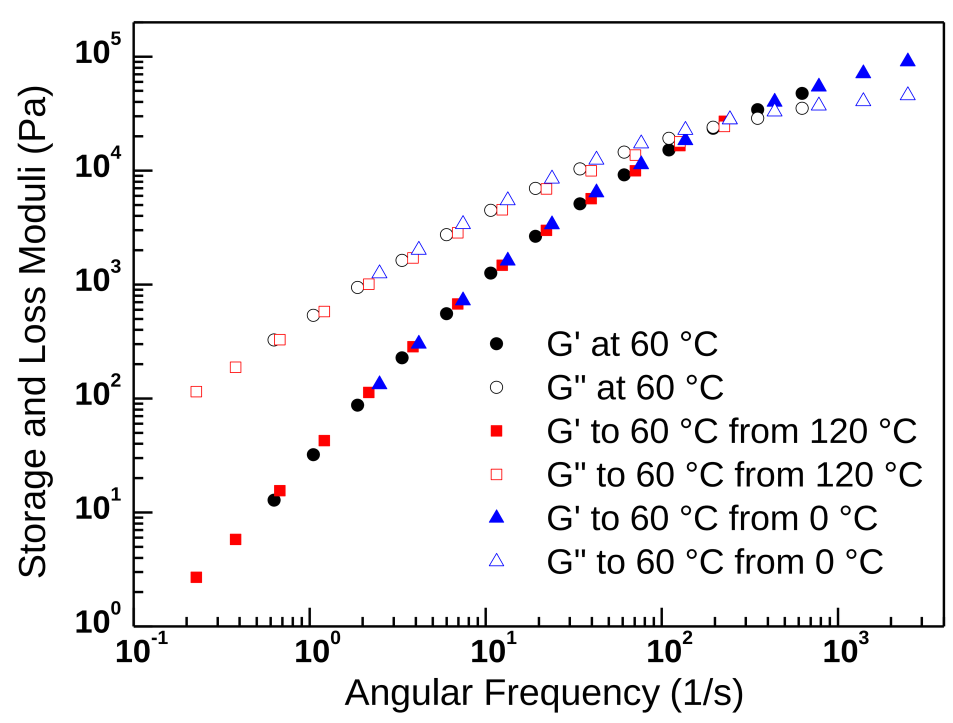

Figure 1: SAOS curves measured at different temperatures can be well shifted to form a master curve according to TTS

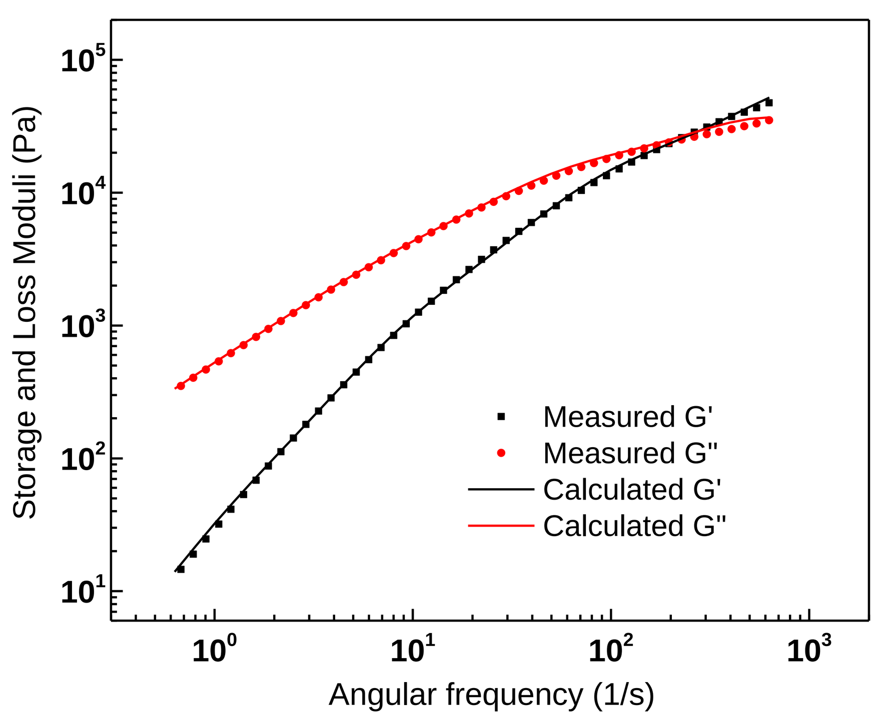

Figure 2: A 5-element Maxwell-model accurately models the SAOS master curve of Fig. 1.

3. High-frequency rheology from DWS

Diffusing Wave Spectroscopy (DWS, Fig. 3, [5]) was applied in order to characterize the rheological behavior of the fluids in a much wider frequency range, up to an angular frequency of 100000/s. Titanium dioxide particles were successfully dispersed in the silicone oil as tracers to perform DWS micro-rheology. The storage and the loss modulus that were derived from the DWS signal, agree very well with the rotational rheometry data in the overlapping frequency range, as shown in Fig. 4.

Moreover, the silicone oils show a pronounced transition from a strongly dominant viscous modulus at low frequencies to a strongly dominant elastic modulus at high frequencies, which is almost temperature-independent, see Fig 5.

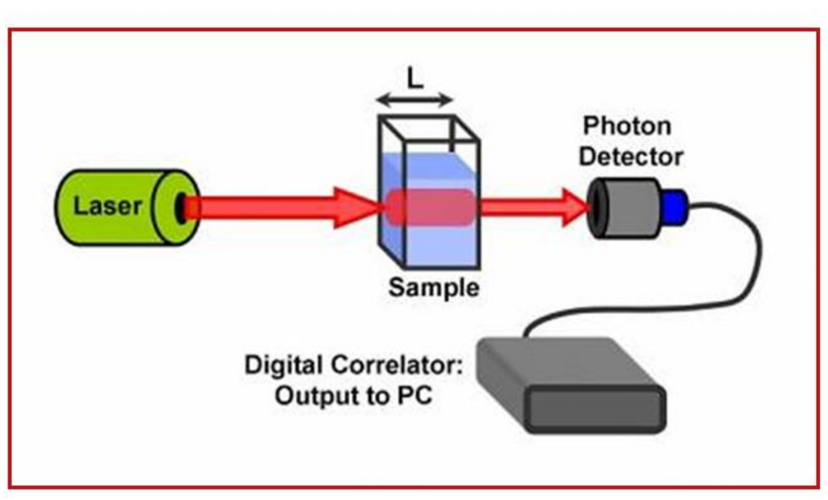

Figure 3: DWS setup

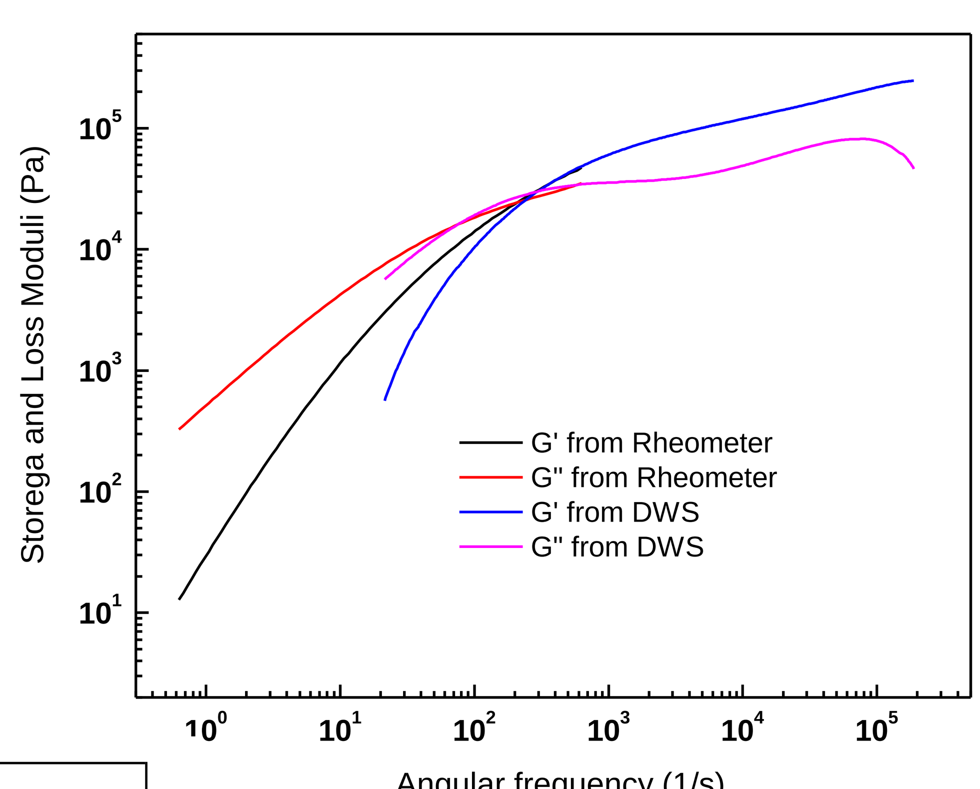

Figure 4: DWS data extend the frequency range of the rheometry with a smooth transition in the overlapping frequency range.

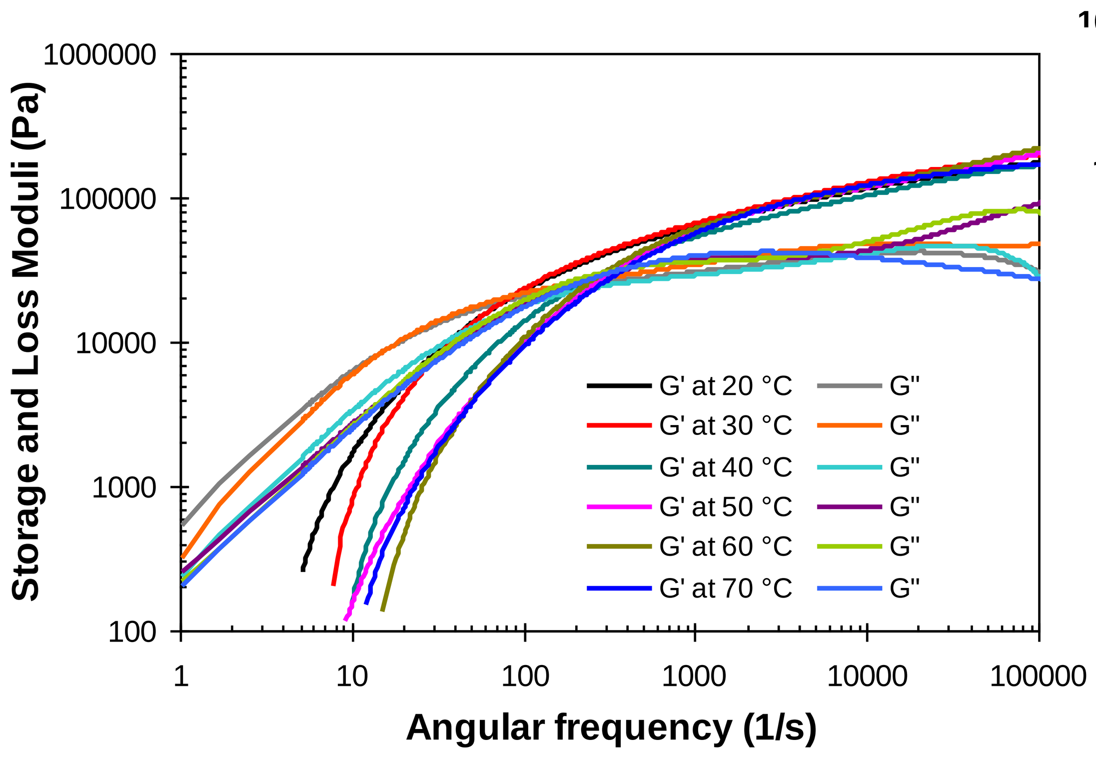

Figure 5: DWS data at different temperatures show a strongly dominant elastic behavior at high frequencies

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3. Nonlinearity

Measurements of shear flow curves with a rotational rheometer, limited by the Weissenberg effect to ca. 20/s, show that the samples are shear-thinning and obey the Cox-Merz rule, i.e. the complex viscosity curve matches the shear flow viscosity curve very well [3]. Capillary viscometry measurements up to a shear rate of 76100/s were done in order to check the DWS data and the Cox-Merz rule in the high frequency range. The capillary shear flow viscosity data are in excellent agreement with the complex viscosity calculated from DWS data, see Fig. 6. The results from these rather different rheological techniques thus show that these silicone oils obey the Cox-Merz rule over an extended frequency range, spanning six orders of magnitude.

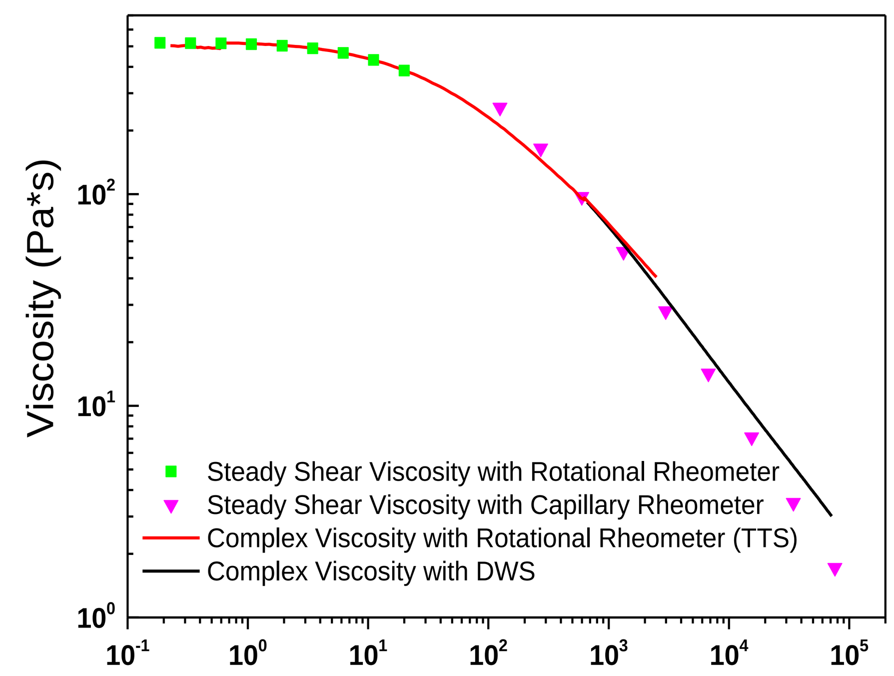

Figure 6: DWS and Capillary data show that the Cox-Merz rule is fulfilled even at very high frequencies

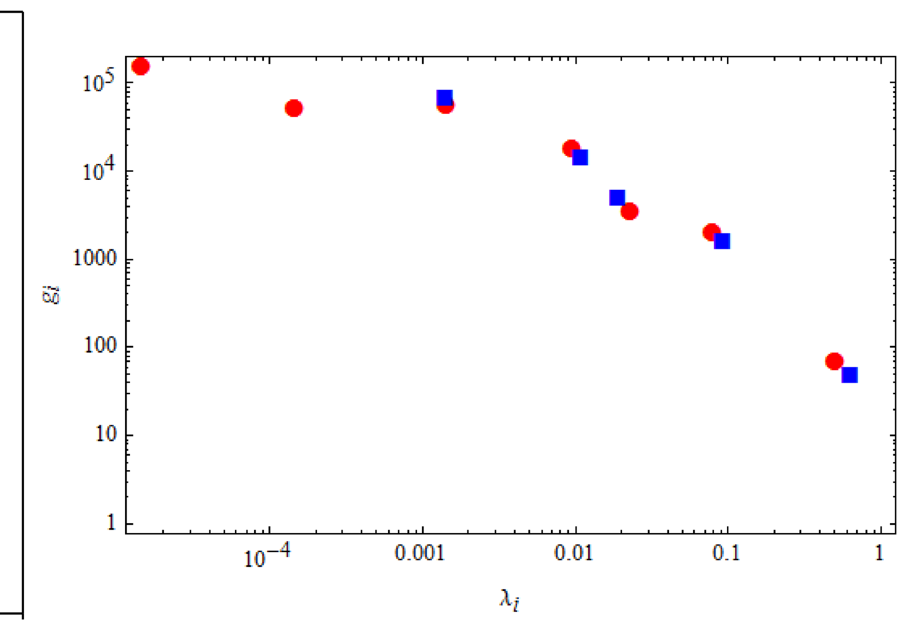

Figure 7: Parameters of the 7 nonlinear Maxwell elements underlying the White-Metzner model (red), in comparison with the parameters of the Maxwell model fitting the SAOS curves of Fig.2 (blue)

4. White-Metzner model

The experimental data suggest the following White-Metzner type model, which consists of 7 nonlinear Maxwell-elements with shear-rate dependent viscosities:

$$\tau_i(t) + \frac{\eta_i(\dot{\gamma})}{g_i}\dot{\tau}_i(t) = -\eta_i(\dot{\gamma})\cdot\dot{\gamma}(t), \qquad \eta_i(\dot{\gamma}) = \sqrt{\left(\frac{\eta_i}{1+(\lambda_i\dot{\gamma})^2}\right)^2 + \left(\frac{\eta_i\lambda_i\dot{\gamma}}{1+(\lambda_i\dot{\gamma})^2}\right)^2}$$

$$\tau(t) = \sum_i \tau_i(t),$$

The 7 g_i and $\lambda_i = \eta_i / g_i$ parameters are shown in Fig. 7, in comparison with the 5 Maxwell parameters that fit the SAOS curves of Fig. 2. This 7-element White-Metzner model accurately describes the nonlinear viscous properties: large amplitude oscillatory shear (LAOS) data are in a very good agreement with computed values based on this White-Metzner model, see Figs. 8 and 9.

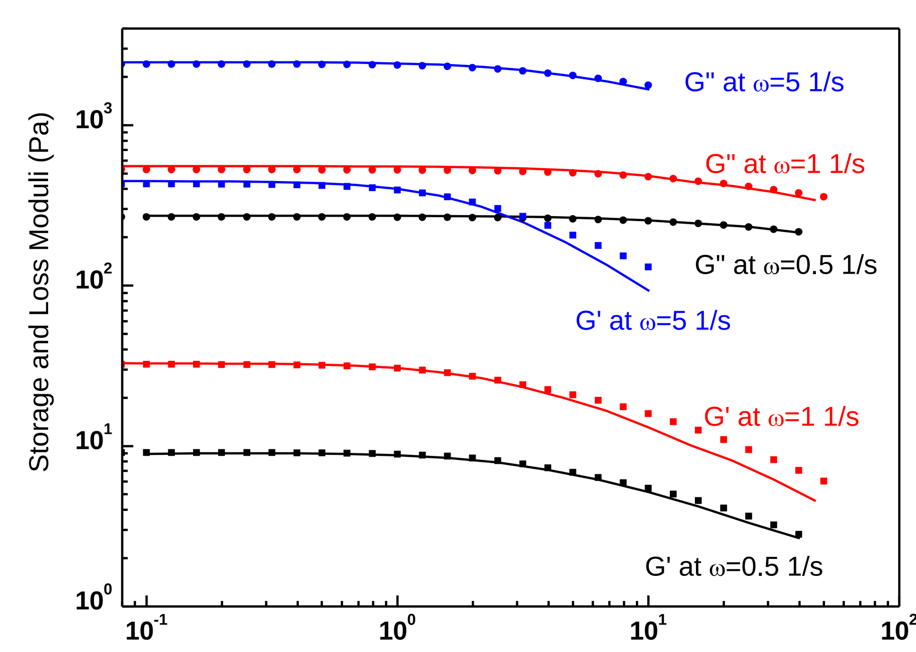

Figure 8: Measured LAOS data and their simulations with White-Metzner model at lower frequencies

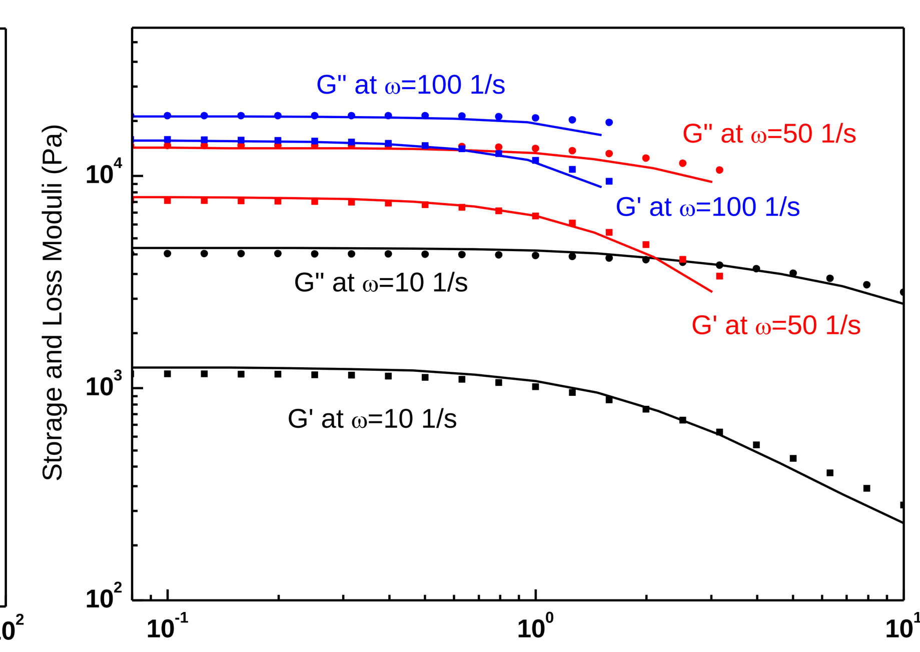

Figure 9: Measured LAOS data and their simulations with White-Metzner model at higher frequencies

We welcome your comments or questions!
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