

CHARACTERIZATION OF COMPLEX FLUIDS AT VERY LOW FREQUENCY: EXPERIMENTAL VERIFICATION OF THE STRAIN RATE-FREQUENCY SUPERPOSITION (SRFS) METHOD

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ABSTRACT:

Strain rate frequency superposition (SRFS) has been suggested as new method to extend the frequency range for assessment of the complex storage modulus G^* of soft glassy materials to lower frequencies. The basic idea is that relaxation processes in such fluids are accelerated by an external shear field, analogous to the effect of a temperature shift in polymer melts and solutions. Master curves for G' and G'' are constructed from the apparent modulus data determined from non-linear oscillatory shear experiments. Here we validate the SRFS principle for the first time by independent experiments and also demonstrate its limitations. We compare SRFS results to directly measured G' , G'' at frequencies down to 10^{-3} rad/s and creep experiments lasting up to 10^4 s for a variety of gel-like fluids, including polymeric thickener solutions, a highly concentrated w/o-emulsion, and worm-like micellar surfactant solutions, as well as a weakly viscoelastic non-Brownian suspension of glass beads. Good agreement between SRFS data and directly measured G' , G'' values for the thickener solutions, the emulsion as well as the suspension. Apparent viscosity data obtained from creep experiments and absolute values of the complex viscosity in the low frequency limit agree fairly well for these fluids. But the method fails for the worm-like micellar solutions and this could be due to non-uniform flow or due to flow-induced structural changes. Finally, we demonstrate that the combination of SRFS, rotational rheometry, and advanced high frequency rheology methods allows for a broad bandwidth characterization of complex fluids spanning an unprecedented frequency range of about eleven decades.

ZUSAMMENFASSUNG:

Die Scherraten-Frequenz-Superpositions Methode (SRFS) wurde zur Ausdehnung des experimentell zugänglichen Frequenzbereiches für elastische, gelartige Materialien speziell zu kleinen Frequenzen hin vorgestellt. Die Grundidee der SRFS besteht darin, dass die Relaxationsprozesse in solchen Materialien durch ein äußeres Scherfeld beeinflusst werden können, analog zum Einfluss einer Temperaturänderung auf die Relaxation von Polymerschmelzen und -lösungen. Masterkurven für die linearviskoelastischen Funktionen G' und G'' werden aus scheinbaren G' und G'' Daten konstruiert, die aus oszillatorischen Scherexperimenten im nicht-linearen Bereich ermittelt werden. Hier validieren wir erstmals das SRFS Prinzip durch unabhängige Experimente und demonstrieren ebenso die Grenzen. Die SRFS Ergebnisse von verschiedenen gelartigen Fluiden, darunter Verdickerlösungen, eine hochkonzentrierte w/o Emulsion, Lösungen wurmartiger, zylindrischer Tensid-Mizellen, und eine schwach viskoelastische, nicht-brownsche Suspension von Glaskugeln in Silikonöl, werden mit direkt messbaren G' und G'' im linear viskoelastischen Bereich bis zu Frequenzen von 10^{-3} rad/s, sowie mit Kriechversuchen (bis zu 10^4 s) direkt verglichen. Die SRFS Daten und die direkt ermittelten G' , G'' stimmen bei den Verdickerlösungen, der Emulsion sowie bei der Suspension gut überein. Die aus Kriechversuchen ermittelten scheinbaren Viskositätsdaten und die absoluten Werte der komplexen Viskosität im niedrigen Frequenzbereich stimmen recht gut überein. Allerdings versagt die SRFS Methode für die Tensidlösungen. Dies könnte auf einer inhomogenen Scherdeformation oder auf einer scherinduzierten Strukturänderung beruhen. Abschließend demonstrieren wir, dass die Kombination von SRFS, Rotationsrheometrie und Hochfrequenz-Rheologie Methoden eine Charakterisierung von komplexen Fluiden über einen bisher unerreichten Frequenzbereich von elf Dekaden ermöglicht.

RÉSUMÉ:

Le principe de superposition vitesse de déformation fréquence (SRFS) a été proposé comme nouvelle méthode pour déterminer le module complexe de cisaillement G^* des matériaux viscoélastiques élargi aux basses fréquences. Pour de tels fluides les processus de relaxation sont accélérés par un champ de cisaillement externe, comparable à l'effet de la température dans les fondus et solutions de polymères. Des courbes maîtresses pour G' et G'' sont déterminées à partir du module apparent obtenu par des mesures de cisaillement en oscillation non linéaires. Dans cette étude, nous validons pour la première fois le principe de SRFS par des expériences indépendantes et démontrons également ses limites. Nous comparons les données de SRFS aux valeurs de G' et G'' obtenues à des fréquences allant jusqu'à 10^{-3} rad/s et à des expériences de fluage allant jusqu'à 10^4 s pour une

série de fluides de type gel, comprenant des solutions épaississantes, une émulsion eau dans huile fortement concentrée, des solutions micellaires de type wormlike, et également une suspension non-Brownienne faiblement viscoélastique de billes de verre dans de l'huile de silicone. On observe aussi bien pour les solutions épaississantes, l'émulsion et la suspension, une bonne correspondance entre les données de SRFS et les valeurs de G' et G'' . Les valeurs de la viscosité apparente obtenues à partir des expériences de fluage et les valeurs absolues de la viscosité complexe obtenues dans la limite des basses fréquences concordent également. Néanmoins cette méthode échoue pour les solutions micellaires, dû peut être à la formation d'un écoulement non uniforme où à des changements structuraux survenant à de très grandes déformations. En conclusion, nous démontrons que la combinaison de la méthode de SRFS avec la rhéométrie en rotation classique et la rhéométrie à hautes fréquences permet une caractérisation de fluides complexes dans une gamme de fréquences jamais atteinte d'environ onze décades.

KEY WORDS: SRFS, complex fluids, high frequency rheology, creep experiments, non-linear viscoelasticity

1 INTRODUCTION

Rheological data like the frequency dependent storage G' and loss G'' moduli yield important information about the structure and dynamics of complex fluids like polymer melts and solutions or concentrated suspensions and emulsions. Often, a broad frequency range spanning ten decades or more has to be covered to catch the characteristic flow processes from the terminal flow at the low frequency end up to the glassy regime at high frequencies [2,3]. However, standard techniques like oscillatory shear experiments with conventional rotational rheometers are usually limited to frequencies between 10^{-3} and 100 rad/s. Time-temperature superposition, extensively used to expand the frequency range in the case of polymer melts and solutions often fails for multiphase fluids like suspensions and emulsions or surfactant solutions due to structures or physical properties of the solvent that are sensitive to temperature [3]. In other cases, especially for dilute solutions or in the case of disperse systems with low viscosity continuous phase the temperature dependent shift of relaxation times is too small to provide a significant expansion of the accessible frequency range. The upper limit in rotational rheometry is set by mechanical limitations and inertial effects in the gap loading limit. But special mechanical techniques like oscillatory squeeze flow and torsional resonance oscillation can be used to cover the frequency range up to 100 kHz [4, 5]. Nowadays, also optical microrheological techniques are available expanding the frequency range into the 100 kHz range [6, 7]. On the other hand, the low frequency range limit is set by the long-term stability of the experimental setup and often even more by the stability of the fluid, espe-

cially when volatile components are included or if the system is not in thermodynamic equilibrium, like e.g. emulsions.

Wyss et al. [1] suggested a new method – strain rate-frequency superposition (SRFS) – in order to expand the frequency range of measurements, especially to very low frequencies. The basic idea of SRFS is that relaxation processes in complex viscoelastic liquids are accelerated by an external shear field, analogous to the effect of a temperature increase in polymer melts and solutions. It is proposed that this shift in the characteristic relaxation time is determined solely by the applied strain rate amplitude. Master curves for the linear viscoelastic functions G' and G'' are constructed from the apparent G' and G'' data determined from non-linear oscillatory shear experiments. Data corresponding to a constant strain rate amplitude, $\dot{\gamma} = \omega \gamma_0$ are shifted along frequency and modulus axis with shift factors $a(\dot{\gamma}_0)$ and $b(\dot{\gamma}_0)$ only determined by strain rate amplitude.

Wyss et al. [1] have applied SRFS to various fluids including a highly concentrated emulsion (80 % silicon oil drops of $\approx 50 \mu\text{m}$ diam. in water, stabilized by 10 mM SDS), a commercial surfactant foam (Gillette Foamy), an aqueous microgel suspension and a hard-sphere colloidal suspension (PMMA in cycloheptylbromide/ decalin). These fluids exhibit typical, gel-like behavior ($G' > G''$, frequency independence) in the frequency range accessible for conventional rotational rheometry. SRFS has been applied to cover the frequency range down to 10^{-3} rad/s and the corresponding master curves reveal a crossover of G' and G'' and a terminal flow regime. These authors claim that SRFS extends the characteri-

zation of linear viscoelastic behavior to lower frequencies, but the limitation of this study is, that the results obtained from SRFS are not validated by an independent experimental approach. The SRFS principle has also been applied to a micelle-forming triblock copolymer system, namely Synperonic F-108 [8]. The characteristic relaxation time obtained from SRFS data as the inverse angular frequency at the maximum of G'' has been compared to corresponding values obtained from a fit of the Cole-Davidson model to conventional small amplitude oscillatory shear data [9, 10]. These two methods compare very well, but the SRFS approach is claimed more accurate [8]. This study supports the applicability of SRFS to soft glassy materials, but still the SRFS method has not been validated by independent measurements. In contrast, Erwin et al. [11] have pointed at discrepancies between SRFS data and directly measured G' and G'' values for a multiarm polybutadiene starpolymer suspension in squalene and a concentrated emulsion of silicon oil in a water-glycerol mixture.

In this paper we compare SRFS master curves directly to the linear viscoelastic response as determined from small amplitude oscillatory shear experiments at low frequencies and in addition we compare apparent shear viscosity values of converted frequency dependent SRFS data to long-term creep-compliance data. In order to check the validity of the SRFS concept, we use four rheologically well-characterized model systems: a suspension of glass spheres (diameter = 10 μm , particle volume fraction $\phi = 45\%$) [12, 13]; aqueous solutions of a commercial acrylic thickener (Sterocoll D) [14]; and two aqueous wormlike micellar solutions including cetylpyridinium chloride (CPyCl) and sodium salicylate (NaSal) with different salt surfactant ratio [15–17], and a water in oil emulsion with 75:25 phase volume water:oil [18].

For the glass bead suspension the terminal flow regime with $G' \sim \omega^2$ and $G'' \sim \omega$ is directly accessible from linear viscoelastic response and G^* data can be directly compared to SRFS results. The acrylic thickener, the water in oil emulsion and the surfactant solution exhibit gel-like, predominantly elastic behaviour with $G' \gg G''$ in a broad frequency range, but the crossover of G' and G'' , which characterizes the transition from the elastic plateau to the terminal flow regime is still accessible from small amplitude oscillatory shear

experiments and is used as a benchmark for the SRFS data. In standard shear experiments the thickener solutions as well as the w/o-emulsion exhibit an apparent yield stress σ_y and stress versus shear rate data are well described by the Hershel-Bulkey model [18]. The apparent yield stress values are on the order of several Pa and similar as for many other soft gel-like materials, this does not mean that these fluids do not flow at all below σ_y , but exhibit a very high low shear viscosity [19]. Therefore, we have performed long-term creep experiments in order to determine this low shear viscosity level and to compare with corresponding absolute values of the complex viscosity obtained from SRFS. The paper is organized as follows: First we describe the materials and the methods with special emphasis on the SRFS concept. Then we discuss the results for the thickener solutions, the w/o emulsion and the glass bead suspension confirming the applicability of SRFS for these kinds of materials. The results for the surfactant solutions highlight the limitations of the concept. Finally, we demonstrate for the commercial acrylic thickener, the SRFS principle in combination with classical rotational rheometry and advanced high frequency rheology methods like oscillatory squeeze flow [4] and torsional resonance oscillation [5] allow for a broad bandwidth characterization of complex fluids spanning a unprecedented frequency range of nearly twelve decades.

2 MATERIALS

2.1 THICKENER SOLUTIONS

Sterocoll D (BASF SE Ludwigshafen, Germany) is a commercial alkali-swellaable acrylic thickener. These acrylate esters are based on co-polymers with a typical composition of the main monomers methacrylic acid (50 %) and ethylacrylate (50 %) and a small amount of a crosslinking agent. This thickener is synthesized in an emulsion polymerization process and delivered as a milky liquid with a solids content of 25 % and $\text{pH} \approx 2.5 - 3$. Upon neutralization the weak methacrylic acid groups dissociate in aqueous environment, the polymer chains get soluble and the thickening properties are developed. For this study aqueous solutions of Sterocoll D with concentrations of 1–3 wt% were prepared. The solutions were stirred at room temperature for 48 h and adjusted to $\text{pH} = 8$ by slowly adding 1 N NaOH [14].

2.2 WATER IN OIL (W/O) EMULSION

We have used a commercial cosmetic water in oil (w/o) emulsion (Nivea Body Milk, Beiersdorf AG). Droplet size distribution was determined by static light scattering in the Fraunhofer diffraction limit. Droplet size distribution is narrow, the mean particle diameter is $d(0.5) = 0.91 \mu\text{m}$, the values at 10 and 90 % are $d(0.1) = 0.59 \mu\text{m}$ and $d(0.9) = 1.38 \mu\text{m}$, respectively. The phase volume, water:oil is 75:25. This means the emulsion is composed of a quasi-network of densely packed small water droplets in continuous oil phase. The latter essentially consists of a paraffin oil with viscosity of $\eta_s = 22 \text{ mPa}\cdot\text{s}$ (at $T = 20^\circ\text{C}$) [18].

2.3 GLASS BEAD SUSPENSION

A suspension of glass spheres ($\approx 10 \mu\text{m}$ diameter, $\phi = 45 \text{ vol}\%$) in silicon oil AK 10⁶ (Wacker Chemie AG, Munich, Germany) was prepared by twin screw compounding, for five minutes at a temperature of 25°C [12,13].

2.4 SURFACTANT SOLUTIONS

Two aqueous solutions of surfactant/counterion mixtures cetylpyridinium chloride/sodium salicylate (CPyCl/NaSal) (both obtained from C. Roth) with the same surfactant concentration $c_{surf} = 100 \text{ mM}$, but two different NaSal concentrations $c_{salt} = 55$ and 65 mM were prepared by gently stirring the surfactant and salt in deionized water. Solutions were stored for at least one day at 20°C prior to measurement [17].

3 METHODS

3.1 MECHANICAL RHEOLOGY MEASUREMENTS

Small amplitude oscillatory shear providing the linear viscoelastic moduli G' and G'' as well as nonlinear oscillatory shear experiments at constant strain rate amplitude necessary for the SRFS were performed at a temperature of 20°C using a Haake MARS II rheometer (Thermo Electron) equipped with cone-plate geometries (60 mm in diameter, 1° cone angle, and 35 mm in diameter, 4° cone angle). Creep experiments were performed using a Bohlin rheometer CS 10 also equipped with a cone-plate geometry (40 mm in diameter, 1° cone angle). Oscillatory squeeze flow experiments providing G' and G'' in the frequency range from 1 Hz to 7 kHz, were per-

formed using a piezo-driven axial vibrator [4, 20]. Two torsional resonators [5] have been used to get G' , G'' data at four distinct frequencies (8, 19, 31, and 58 kHz). Both instruments were customized at the Institute for Dynamic Material Testing (Ulm, Germany).

3.2 THE STRAIN RATE FREQUENCY SUPERPOSITION PRINCIPLE

SRFS aims at the characterization of the linear viscoelastic response of soft glassy materials at very low frequencies. Analogously to the well-known time-temperature superposition method for polymers [3] the concept of SRFS can be used to construct master curves for G' and G'' or other linear viscoelastic functions covering a broad frequency range. Slow relaxation processes control linear viscoelastic behavior of soft glassy materials, distinguished through a weak frequency dependence of storage G' and loss G'' moduli in the frequency range accessible by standard small amplitude oscillatory shear experiments. Wyss et al. [1] propose that the time scale $\tau(\dot{\gamma}_o)$ of the slow relaxation process that dominates the stress relaxation of the fluids they investigated depends on the applied strain rate amplitude $\dot{\gamma}_o$:

$$\frac{1}{\tau(\dot{\gamma})} \approx \frac{1}{\tau_o} + K\dot{\gamma}_o^\nu \quad (1)$$

with the material dependent positive exponent ν and constant K [21]. At very small constant strain rate amplitudes the relaxation time approaches its static value τ_o , while relaxation is accelerated as strain rate amplitudes increase. If the relaxation of the fluid is controlled by more than one process, one has to assume, analogously to the TTS principle, that all characteristic relaxation times τ_i exhibit the same dependence on $\dot{\gamma}_o$.

3.3 GENERAL EXPERIMENTAL APPROACH OF SRFS CONCEPT

■ Determination of apparent G' and G'' as a function of strain amplitude for various frequencies. From these classical amplitude sweeps we determine the linear response regime, which is needed to determine the true linear viscoelastic moduli as a function of frequency. The transition from linear to nonlin-

ear response is given by a critical strain amplitude $\gamma_{o,c}$ which is defined here as the strain at which $G^* = 0.9G^*|_{\gamma_o \rightarrow 0}$. Furthermore, these data yield the frequency dependent critical strain rate amplitude $\dot{\gamma}_{o,c} = \omega\gamma_{o,c}$.

- Determination of G' and G'' as a function of ω , from small amplitude oscillatory shear experiments performed at $\gamma_o < \gamma_{o,c}(\omega)$
- Measurement of apparent G' and G'' at various fixed strain rate amplitudes $\dot{\gamma}_o > \dot{\gamma}_{o,c}$
- Construction of the SRFS master curve by shifting the data sets obtained at constant $\dot{\gamma}_o$.

The shift procedure is started with the data corresponding to the lowest $\dot{\gamma}_o$. Shifting is done along the frequency and the modulus axis. The strain rate dependent scaling factors $a(\dot{\gamma}_o)$ and $b(\dot{\gamma}_o)$, which are defined analogous to the shift factors of TTS (The shift factors defined in this way are reciprocal to those used by Wyss et al. [1].) were determined for both horizontal and vertical:

$$a(\dot{\gamma}_o) = \frac{\omega_{ref}}{\omega} \quad (2)$$

$$b(\dot{\gamma}_o) = \frac{|G^*_{ref}|}{|G^*|} \quad (3)$$

- Finally, it has to be noted, that the strain amplitude γ_o decreases with increasing ω if measurements are performed at constant $\dot{\gamma}_o$. Therefore, the data obtained at high enough frequencies do not fulfil the condition $\dot{\gamma}_o > \dot{\gamma}_{o,c}$ and correspond to the linear response regime. Consequently, it is pointless to shift these data according to SRFS and the data points are rejected from the master curve. This was not done in the original approach of Wyss et al. and is most likely the reason for the scatter of their data at high frequencies.

4 RESULTS AND DISCUSSION

An aqueous solution of Sterocoll D with 3 wt% polymer concentration and pH = 8.43 is used to demonstrate the procedure of constructing master curves for G' and G'' using the SRFS principle. Frequency dependent storage G' (solid squares) and loss G'' (open squares) moduli determined in the linear response regime are shown in Fig. 1a.

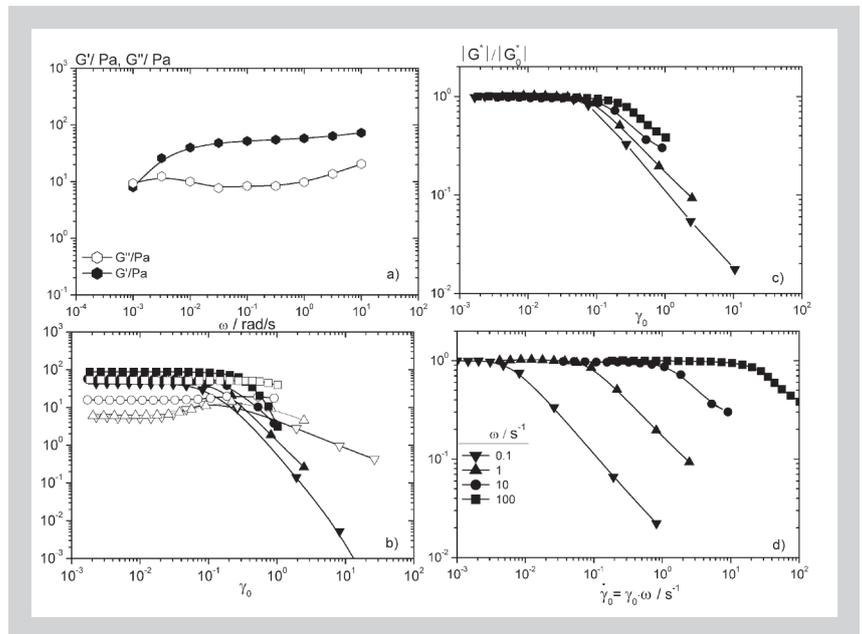


Figure 1 (above): Sterocoll D 3 wt%, pH = 8.43: (a) Frequency dependent storage $G'(\omega)$ (solid hexagons) and loss modulus $G''(\omega)$ (open hexagons), measured in linear oscillatory shear experiments. (b) Strain dependent storage G' (solid symbols) and loss G'' (open symbols) moduli and scaled complex shear modulus versus strain (c) and strain rate (d) are shown for four different frequencies. Different symbols correspond to different frequencies as shown in Figure 1d.

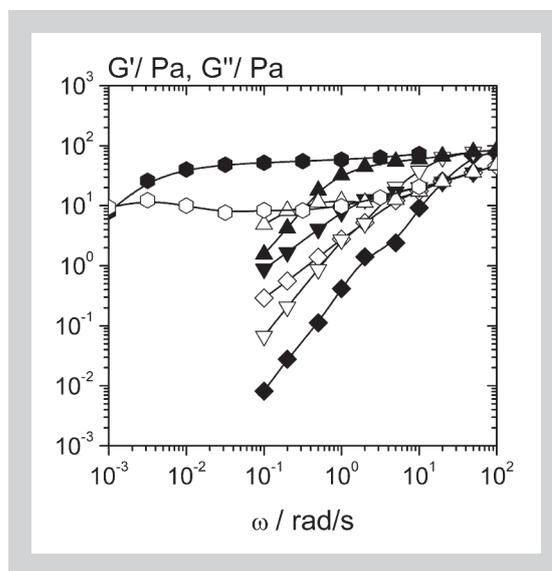


Figure 2: Sterocoll D 3 wt%, pH = 8.43: Frequency dependent storage $G'(\omega)$ (solid symbols) and loss modulus $G''(\omega)$ (open symbols), measured in linear response oscillatory shear experiments (hexagons) and at different constant strain rate amplitudes ($\dot{\gamma}_o = 0.1 \text{ s}^{-1}$ (triangles), 1 s^{-1} (turned triangles), 5 s^{-1} (diamonds)).

In the displayed frequency range ($\omega = 10^{-3}$ - 10^1 rad/s) the linear viscoelastic response shows typical gel-like behavior ($G' > G''$, independent of frequency), but the crossover of G' and G'' and the onset of the terminal flow regime are clearly visible. In the high frequency range the onset of Rouse/Zimm modes [3] manifests itself in the upturn of the G'' -curve. Figure 1b shows the apparent G' and G'' data as a function of strain amplitude covering the deformation range $\gamma_o = 10^{-3}$ - 10^2 at four different frequencies ($\omega = 0.1, 1, 10, \text{ and } 100$ rad/s). The results agree with the frequency response data. This thickener solution shows an elastic, gel-like behavior ($G' > G''$) at low strain $\gamma_o < 10^{-1}$ and transition to viscous character ($G'' > G'$) at large strain $\gamma_o > 10^{-1}$. Also in agreement with the data shown in Figure 1a: the ratio G' and G'' decreases as ω increases. The strain dependent scaled complex modulus $|G^*|/|G^*_0|$ shown in Figure 1c is used to determine the critical strain amplitude $\gamma_{o,c}$. The limiting critical strain ampli-

Figure 3 (left): Sterocoll D 3 wt%, pH = 8.43: Shift of constant strain rate amplitude measurements onto a master curve leads to frequency dependent storage $G'(\omega)$ (solid symbols) and loss $G''(\omega)$ (open symbols) moduli covering almost seven decades in the frequency domain. Insert: Vertical shift factor b (triangles) and horizontal shift factor a (diamonds) as a function of strain rate amplitude.

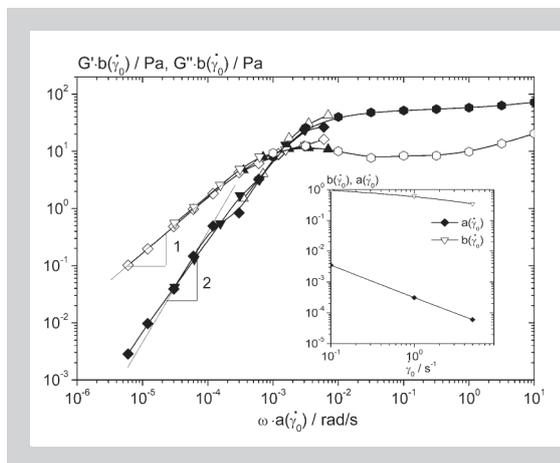
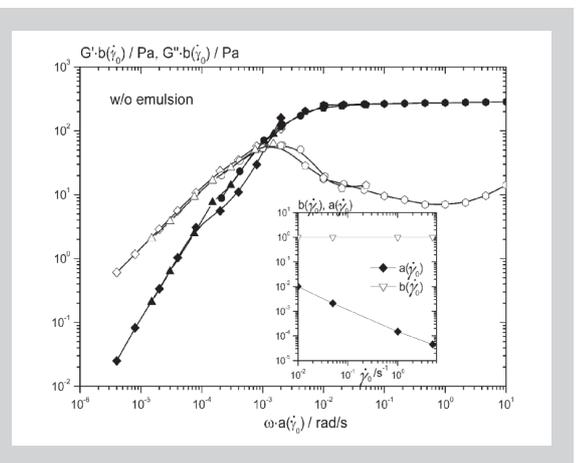


Figure 4: w/o emulsion: frequency dependent moduli after shifting onto master curve.



tude $\gamma_{o,c}$ increases weakly with ω . The normalized strain rate dependent $|G^*|/|G_o^*|$ data are shown in Figure 1d. This representation of the data animates that the shape of $|G^*|$ versus $\dot{\gamma}_o$ curves is similar for all frequencies. However, a displacement to higher strain rate amplitudes appears with increasing frequency. This representation of the data is needed in order to distinguish between data points in the linear and nonlinear response regime in subsequent measurements at constant strain rate amplitudes. Only amplitudes for which $|G^*|/|G_o^*| < 0.9$ are used for the construction of the master curve.

Figure 2 shows the true linear viscoelastic moduli (hexagons) together with the apparent G' (solid symbols) and G'' data measured in nonlinear oscillatory shear experiments at different constant strain rate amplitudes (open symbols) as a function of frequency. (Strain rate amplitude $\dot{\gamma}_o$ has been varied between 0.1 and 5 s⁻¹). Non-linear response data are presented in the frequency range $\omega = 10^{-1} - 10^2$ rad/s. At the constant strain rate amplitude $\dot{\gamma}_o = \omega\gamma_o$ and constant frequency, the strain γ_o increases with increasing $\dot{\gamma}_o$. So, the absolute values of G' and G'' decrease and the ratio of G' and G'' reverts as $\dot{\gamma}_o$ increases. At large $\dot{\gamma}_o$ and low frequencies the apparent G' and G'' data resemble the terminal flow regime of a viscoelastic liquid. At the highest frequencies, the G' and G'' data obtained at different $\dot{\gamma}_o$ essential coincide as expected, since the strain amplitude γ_o decreases with increasing ω and the linear viscoelastic regime is approached.

In the next step the apparent G' and G'' data sets obtained at different $\dot{\gamma}_o$ are shifted mainly along the frequency axis but also slightly along the moduli axis in order to construct a SRFS master curve. This curve, which is displayed in Figure 3, extends the accessible frequency range by three decades towards lower frequencies and allows to obtain the terminal flow regime with the characteristic slopes of one and two for G'' and G' , respectively. Good agreement is achieved between different data sets in the respective overlap regions. It should be noted, that in par-

ticular, the characteristic crossover frequency ω_c (at which $G' = G''$) from the SRFS master curve agrees very well with the corresponding value from experiments in the linear response regime. The data points shown in Figure 2 at the high frequencies have been removed since it is pointless to shift those data which already correspond to the linear response regime. The shift factors $a(\dot{\gamma}_o)$ and $b(\dot{\gamma}_o)$ are shown as an insert in Figure 3. Data are shifted by orders of magnitude on the frequency axis and according to Equation 1 a scaling exponent $\nu = -1$ is found for $a(\dot{\gamma}_o)$, which is close to the values reported in [1, 11]. In contrast, the shift factors $b(\dot{\gamma}_o)$ deviate from unity by not more than a factor of two.

For the w/o-emulsion a master curve for G' and G'' was constructed in a similar manner, results are shown in Figure 4. In this case ω_c is not directly accessible from linear viscoelastic measurements, but the curvature of the G' and G'' curves at low frequencies indicate, that a crossover should occur at a frequency slightly lower than 10⁻³ rad/s. Good agreement is found between different data sets including the G' and G'' data directly measured in the linear response regime and again the scaling exponent $\nu = -1$ is obtained for $a(\dot{\gamma}_o)$. Moreover, the SRFS data suggest the existence of a terminal flow regime with the characteristic slopes of one and two for G'' and G' , respectively.

In order to compare SRFS data to long-term creep experiments the frequency dependent modulus data of the SRFS master curve were converted into a time dependent relaxation modulus $G(t)$ and creep compliance $J(t)$ using the IRIS Rheo Hub 3 software and an apparent time dependent viscosity $\eta(t) = t/J(t)$ was calculated. As shown in Figure 5 converted SRFS approach a constant viscosity value at times between 5·10³ and 10⁴ s corresponding to the zero-shear viscosity η_o for the thickener solution as well as for the w/o-emulsion. For the thickener solution creep experiments at different stresses below the apparent yield stress also reveal the existence of a stress independent steady shear viscosity, i.e. a

c [wt%]	1	2	3
$\omega_{C,Ref}$ [rad/s]	$2.6 \cdot 10^{-3}$	$1.1 \cdot 10^{-3}$	$1.2 \cdot 10^{-3}$
$\omega_{C,SRFS}$ [rad/s]	$1.9 \cdot 10^{-3}$	$1.1 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$
$\eta_{0,SRFS}$ [Pa·s]	$1.9 \cdot 10^3$	$1.0 \cdot 10^4$	$2.9 \cdot 10^4$
$\eta_{0,creep}$ [Pa·s]	$1.7 \cdot 10^3$	$1.5 \cdot 10^4$	$5.6 \cdot 10^4$

low shear Newtonian plateau. The viscosity data from SRFS and creep tests agree within a factor of two and taking into account all experimental uncertainties we consider this reasonable agreement. SRFS and creep experiments have also been performed on thickener solutions with 1% and 2% polymer concentration, characteristic parameters ω_c from SRFS and linear oscillatory shear measurements as well as η_0 values from SRFS and creep experiments are compared in Table 1. Good agreement between independently determined ω_c and η_0 is found and this further confirms the applicability of the SRFS principle to this class of fluids.

In the case of the emulsions, the situation is more complicated. The creep experiments even at the lowest stresses do not show a constant viscosity value. Even after 10^4 s no steady state is reached similar as reported earlier [19]. Moreover, this emulsion is extremely sensitive to the applied stress as can be seen from a comparison of the creep test results for shear stresses of 1 and 2 Pa. In contrast to SRFS the creep experiments do not reveal a Newtonian low shear viscosity plateau. Nevertheless, the apparent viscosity from SRFS lies in the same range as the results from long-term creep experiments and thus SRFS seems to provide a fast and reasonable estimate of the low shear viscosity of such fluids.

We have also applied the SRFS method to a non-Brownian suspension of glass beads ($\approx 10.4 \mu\text{m}$ diameter, $\phi = 45 \text{ vol}\%$) in silicone oil AK 10⁶ ($\eta_0 = 10^3 \text{ Pa}\cdot\text{s}$, $T = 25^\circ\text{C}$). The linear viscoelastic moduli directly obtained from small amplitude oscillatory shear are shown in Figure 6a. In contrast to all previously investigated materials this suspension is not predominantly elastic in the accessible frequency range. The crossover frequency $\omega_c = 40 \text{ rad/s}$ is orders of magnitude larger than for the thickener solutions and the emulsion discussed above as well as all the systems discussed by Wyss et al. [1] and Mohan and Bandyopadhyay [8]. G'' is proportional to ω and dominates over G' at frequencies below ω_c as expected for a viscoelastic fluid in the terminal flow regime. But it should be noted, that deviations from the expected $G' \sim \omega^2$ are observed at low frequencies, which are presumably due to a non-uniform distribution of particles in that highly viscous oil.

The apparent moduli obtained at various constant strain rate amplitudes are shown in Fig-

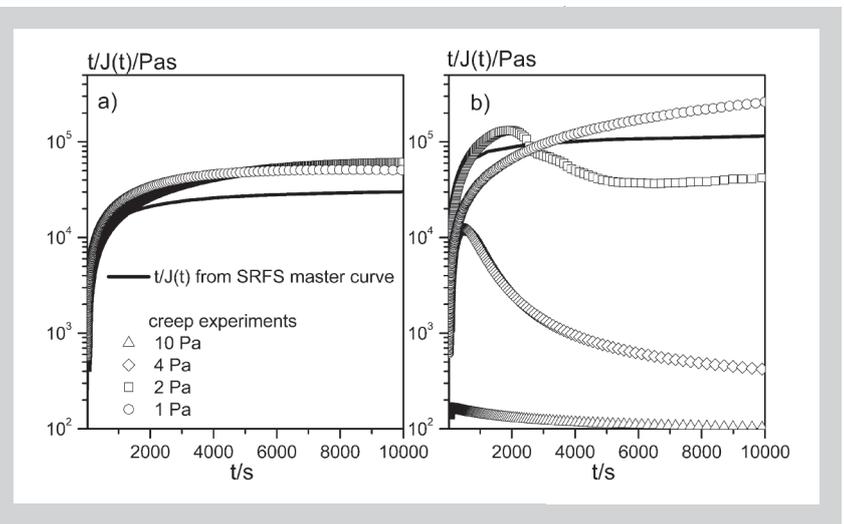


Figure 5 (above): Time dependent apparent viscosity converted of SRFS data (IRIS) and long-term creep experiments for (a) thickener solution and (b) water in oil emulsion.

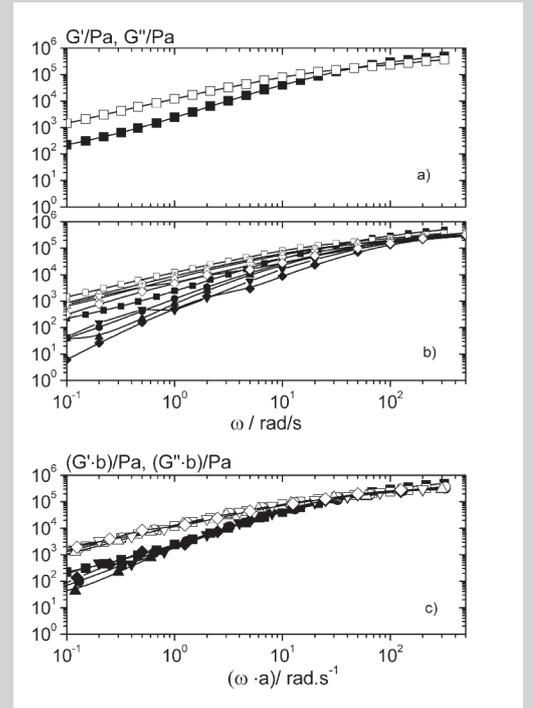


Figure 6: Suspension of glass spheres ($\approx 10 \mu\text{m}$ diameter, $\phi = 45 \text{ vol}\%$) in silicon oil: (a) Frequency dependent storage $G'(\omega)$ (solid squares) and loss modulus $G''(\omega)$ (open squares), measured in linear oscillatory measurement, (b) Different nonlinear response strain rate amplitudes ($\dot{\gamma}_0 = 0.01 \text{ s}^{-1}$ (circles), 0.1 s^{-1} (triangles), 1 s^{-1} (turned triangles), 5 s^{-1} (diamonds)), (c) SRFS master curve.

Table 1: Summary of concentration dependent characteristically rheological parameters of commercial acrylic thickener solutions, Sterocoll D.

ure 6b and the SRFS master curve is shown in Figure 6c. Obviously, there is good agreement between the true linear viscoelastic moduli G' , G'' and those values obtained by SRFS over the whole frequency range. In particular, the values for ω_c and η_0 agree very well. At the low frequency end where deviations from the expected $G' \sim \omega^2$ behavior occur there is some scatter in the shifted G' data, but the results obtained from large amplitude oscillatory shear seem to be closer to the ideal $G' \sim \omega^2$ curve, maybe due to a re-arrangement of particles induced by the large strain applied in these experiments. Again the shift factors $b(\dot{\gamma}_0)$ are almost unity, but in contrast to the Sterocoll D case the shift factors $a(\dot{\gamma}_0)$ are also small, for the highest $\dot{\gamma}_0 = 5 \text{ s}^{-1}$ we find a $(5 \text{ s}^{-1}) = 0.2$. At this point, it should be noted, that the SRFS method is not applicable to the pure silicone oil, since this fluid has an extended linear response range and the strain rate amplitudes accessible

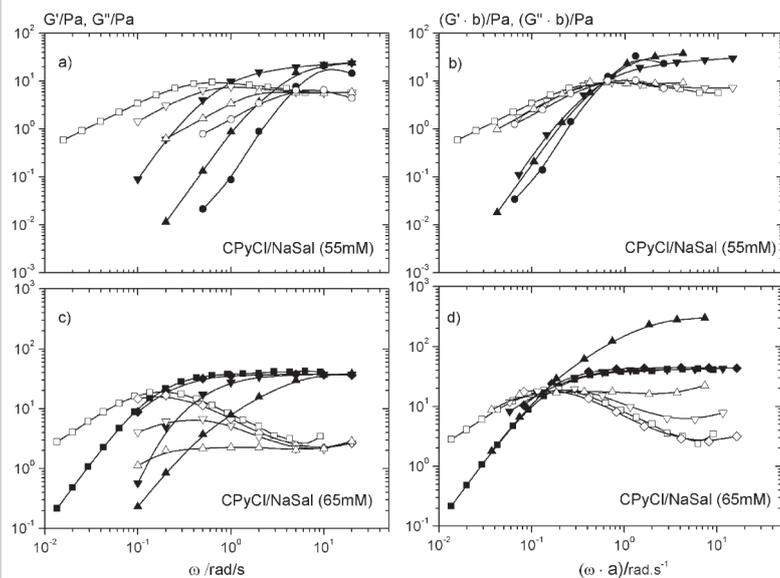


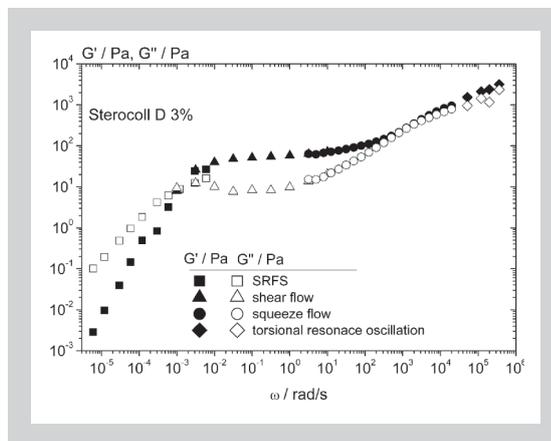
Figure 7 (left): Frequency dependent storage $G'(\omega)$ (solid symbols) and loss modulus $G''(\omega)$ (open symbols), measured in linear oscillatory shear measurement (squares) and at different constant strain rate amplitudes ($\dot{\gamma}_0 = 0.1 \text{ s}^{-1}$ (diamonds), 1 s^{-1} (turned triangles), 5 s^{-1} (triangles), 10 s^{-1} (circles)).

Figure 8: Sterocoll D 3 wt%, pH = 8.43: Frequency dependent storage $G'(\omega)$ and loss $G''(\omega)$ modulus in a frequency range of about eleven decades. By application of SRFS (squares), linear oscillatory shear measurements (triangles), oscillatory squeeze flow (circles) and torsional resonance oscillation (diamonds).

with our rheometer setup are not sufficient to achieve a significant shift of G' , G'' data.

The fourth model system investigated here is a pair of aqueous solutions of the surfactant CPyCl with the same surfactant concentration $c_{surf} = 100 \text{ mM}$ but two different NaSal concentrations $c_{salt} = 55$ and 65 mM . It is well-known, that these salt/surfactant mixtures self-assemble into flexible (wormlike) cylindrical micelles, which give rise to a pronounced viscoelasticity of the respective solutions and their rheological properties have been characterized thoroughly [15–17]. The linear viscoelastic moduli G' and G'' for both solutions are shown in Figure 6. The solution with 65 mM NaSal exhibits ideal Maxwell-type relaxation behaviour in a broad frequency range from $\omega \approx 10^{-2} \text{ rad/s}$ up to $\omega \approx 5 \text{ rad/s}$, with $\omega_c = 0.15 \text{ rad/s}$ and $\eta_0 = 210 \text{ Pa}\cdot\text{s}$. For the solution with 55 mM salt concentration the transition from predominantly viscous to elastic behaviour is smoother than for the sample with higher salt content. The linear viscoelastic behavior of this solution is characterized by a broad distribution of relaxation times (so-called stretched exponential behavior) [15, 16] and we find $\omega_c \approx 0.55 \text{ rad/s}$ and $\eta_0 = 36.6 \text{ Pa}\cdot\text{s}$.

Figures 7a and c show the linear viscoelastic moduli G' and G'' together with the apparent moduli from SRFS as a function of angular frequency for various strain rate amplitudes. Similar as for the thickener solution and the emulsion the apparent moduli decrease with increasing strain rate amplitude at fixed frequency as long as the response is non-linear. In the high frequency range the data obtained at different $\dot{\gamma}_0$ coincide, since the fluids responds linearly. Moreover, ω_c shifts to higher frequencies as $\dot{\gamma}_0$ increases. The attempt to construct SRFS master curves from



these data obviously fails as documented in Figures 7b and d. Shifting was done here using ω_c as a reference point, this approach is not unique but other attempts to construct master curves from the data shown in Figures 7a and c failed as well. We assume, that this is either due to shear-induced structural changes or due to non-uniform deformation (shear banding) within the gap occurring in the non-linear deformation regimes. So far, there is no direct experimental evidence for that, but such wormlike micellar solutions are well known for a variety of such phenomena occurring at large deformations [22–24].

Finally, we recall that, verification of the SRFS concept is satisfying for the commercial thickener solutions, the w/o-emulsion and the suspension of glass spheres. Therefore, the combination of the SRFS concept with advanced high frequency rheology methods like oscillatory squeeze flow and torsional resonance oscillation offers an unprecedented frequency range of about eleven decades accessible for the characterization of certain classes of complex, multiphase fluids. The aqueous thickener solution with 3 wt% polymer concentration and pH = 8.43 is used here to demonstrate the capability of broad bandwidth characterization of linear viscoelastic behavior (Figure 8).

5 CONCLUSIONS

The basic idea of SRFS is that relaxation processes in complex viscoelastic liquids like soft glassy or gel-like materials are accelerated by an external shear field, analogous to the effect of a temperature shift in polymer melts and solutions. It is proposed that this shift in the characteristic relaxation time is determined solely by the applied strain rate. Master curves for the linear viscoelastic functions G' and G'' are constructed from the apparent G' and G'' data determined from non-linear oscillatory shear experiments. Data corresponding to a constant strain rate amplitude, $\dot{\gamma}_0$ are shifted along frequency and modulus axis with shift factors $a(\dot{\gamma}_0)$ and $b(\dot{\gamma}_0)$ only determined by strain rate amplitude.

In this study we have applied the SRFS concept to a variety of strongly viscoelastic complex fluids including a set of polymeric thickener solutions, a highly concentrated emulsion and worm-like micellar surfactant solutions, but also a weakly viscoelastic non-Brownian suspension of glass beads in silicon oil. Similar as in the previous work of Wyss et al. [1], Mohan and Bandyopadhyay [8], and Erwin et al. [11] SRFS reveals a terminal flow regime for the thickener solutions and the emulsion. But in contrast to the fluids used in previous work, the thickener solutions used here have been chosen such that the onset of the terminal regime, in particular the crossover frequency ω_c is directly accessible with small amplitude oscillatory shear experiments at frequencies close to 10^{-3} rad/s. Good agreement is found between SRFS data and G' , G'' values directly measured in the linear response regime and in particular the ω_c values coincide very well. It should be noted that the high frequency data obtained in the linear response regime have to be removed carefully from the frequency sweep measurements at constant strain rate amplitude in order to avoid scatter in the master curves as reported earlier [1]. Furthermore, the existence of a terminal flow regime has been confirmed by independent long-term creep experiments revealing that a steady state viscosity is reached within about 10^4 s and that this viscosity is essentially independent of the applied stress. These values for the zero shear viscosities agree with the low frequency limiting absolute values of the complex viscosity within a factor of two. Taking into account the experimental uncertainties, we consider this fair agreement and SRFS is a fast and reliable tool to characterize the terminal flow behavior of such solutions.

In the case of the highly concentrated w/o-emulsion, SRFS again reveals a terminal flow regime. In this case ω_c is not directly accessible by small amplitude oscillatory shear experiments, but SRFS data agree very well with directly determined G' , G'' values in the frequency range down to 10^{-3} rad/s. Furthermore, the limiting low frequency absolute value of the complex viscosity lies in the same range as the apparent viscosities obtained in creep tests. But it has to be kept in mind that a true constant viscosity value is not yet reached even within 10^4 s and that the emulsion's response is extremely sensitive to the applied stress, so that a Newtonian plateau

seems not to be accessible. Nevertheless, the SRFS concept provides a reasonable estimate of the low shear flow behavior of such an emulsion. For the weakly viscoelastic suspension of glass beads in silicon oil again good agreement is found between SRFS data and G' , G'' data directly obtained in the linear response regime. In this case the terminal flow behavior is already accessed by small amplitude oscillatory shear measurements and due to the weak non-linearities SRFS does not offer a substantial extension of the accessible frequency range.

For the surfactant solution the SRFS concept obviously fails completely and this is presumably either due to non-uniform flow or structural changes, which may appear at large shear deformations. The occurrence of these phenomena is well-documented in the literature [22–24]. Finally, we have combined the SRFS concept with classical small amplitude oscillatory shear experiments and advanced high frequency rheometry techniques like oscillatory squeeze flow and torsional resonance oscillation. For an acrylic thickener solution we have demonstrated that this combination allows for a characterization of the linear viscoelastic behavior of such complex fluids over an unprecedented frequency range of about eleven decades spanning from $5 \cdot 10^{-6}$ to $3.6 \cdot 10^5$ rad/s.

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