Different experimental methods in stress and strain control to characterize non-linear behaviour

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Abstract
The non-linear behaviour of complex fluids has been investigated by various experimental methods using different control modes. The results illustrate that such samples show a different response whether a periodic stress or a periodic strain is applied outside the linear visco-elastic region. A rheometer based on an air bearing supported electrically commutated synchronous motor with integrated torque measurement is shown to perform all tests in stress and strain control.

Various techniques have been proposed to characterize the cross over from linear to non-linear behaviour and the behaviour in the non-linear regime. A widely used method is the so-called Fourier Transform rheology in which not just the base wave but also the higher harmonics are measured in oscillatory testing. The rising of higher harmonics is associated with the onset of non-linear behaviour. However, no clear physical meaning can be attributed to the higher harmonics itself. A new theoretical framework as proposed recently by Ewoldt et al. [1] provides a quantitative analyzes of Lissajous figures during Large Amplitude Oscillatory Shear (LAOS). Their approach is based on the work of Cho et al. [2] in which a method is proposed to decompose the nonlinear response in LAOS conditions into elastic and viscous parts. Intra- and intercycle nonlinearities, strain-stiffening and -softening, and shear-thinning and -thickening are described and can be distinguished. The approach of Ewoldt et al. as most other published work on LAOS, both theoretical and experimental, is based on the assumption of a sinusoidal strain input $\gamma(t) = \gamma_0 \sin(\omega t)$. Experimental investigations following this assumption obviously require a rheometer, which is able to generate such an input function. Historically rheometers are used in which the strain input is applied to one side of the sample by a motor and the resulting stress is measured on the other side of the sample with a separate torque transducer.

With the paper from Ewoldt et al. as a starting point the following questions arise:
- Can the same formalism be used for a sinusoidal stress input as well?
- Can a rheometer with an EC-Motor and integrated torque measurement, i.e. without a separate transducer where the torque is a measure of the motor current, give the same results?
- Are the results the same for a sinusoidal strain and a sinusoidal stress input?
- Can the results be confirmed by data from other non-sinusoidal periodic functions?

In the linear regime an applied sinusoidal stress or a sinusoidal strain input reveal the same result and the same formalism can be used to calculate the relevant rheological properties. In the SAOS regime the elliptically shaped Lissajous diagrams have a strong symmetry, which is lost outside the linear visco-elastic range. The Lissajous diagrams for the LAOS regime still show point symmetry around the origin but the reflective or mirror symmetry is lost. This implies that in the LAOS regime it is not possible to calculate the properties for a sinusoidal
stress input form the results of a sinusoidal strain input and vice versa. An extension of the existing framework to include sinusoidal stress input has been described in detail [3]. In the case of a sinusoidal strain input, Ewoldt et al. define minimum strain and maximum strain moduli and minimum rate and maximum rate viscosities. All four properties can be either calculated from the Fourier coefficients via Chebyshev polynomials or obtained as slopes in the respective Lissajous Figures. The ratio of the two newly defined strain moduli represents the intracycle strain stiffening ratio, whereas the ratio of the two viscosities is the intracycle shear thickening ratio. Similarly, small strain and large strain compliances as well as small rate and large rate fluidities are defined in the case of a sinusoidal stress input. The respective ratios are the intracycle stress softening and the intracycle shear thinning ratio [3].

In order to investigate the response of a complex fluid to either a sinusoidal strain or a sinusoidal stress input it is crucial that these input conditions are met. Otherwise the non-linearities are in both the stress and the strain and the outlined formalism is not applicable. It is therefore crucial to understand the working principle of modern rheometer.

The main components of a rotational rheometer are the motor with its supporting bearing system and the force measurement. Historically there are two principles used for research grade rotational drag flow rheometers [4]. In one a displacement or speed (strain or strain rate) is applied to the sample by the motor and the resulting torque (stress) is measured separately by an additional force sensor. In this type of instrument, which is commonly referred to as CR (controlled strain or controlled strain rate) rheometer or separate motor transducer system the electrical current used to generate the displacement or speed of the motor is not used as a measure of the electrical torque. With the other type of instruments, often called CS (controlled stress) rheometer or combined motor transducer system, a certain electrical current is applied onto the motor assembly. The current builds up a magnetic field which produces an electrical torque resulting in a rotation of the drive shaft. In such a design there is no separate torque sensor needed, since the torque signal is directly calculated from the motor current. The movement of the motor shaft is measured by an angular displacement sensor, which in most types of CS rheometers is an optical encoder. Most CS rheometers are based on the so-called drag cup motor, which was already used in the first CS instrument, the Deer Rheometer build in 1968 [5].

In 1995 a rheometer based on a different motor system, an electrically commuted (EC) motor, sometimes also referred to as brushless DC-motor, was introduced [6]. In 2010 the fourth generation of rheometers employing this motor technology is now in use. From the principle of torque determination from the motor current this new rheometer resembles a classical control stress, or combined motor transducer system, but instead of a drag-cup motor it employs a fast and dynamic motor with a similar principle as is used in a classical strain or separate motor transducer system.

For a better understanding the motor principle is described in more detail.

An EC-motor is a direct current (DC) motor. In the EC-motor the rotor rotates synchronously with the rotating field on the stator, thus the name synchronous motor is often used to designate servo motors of this design. In the EC-motor the current is commutated electronically and there are no brushes or other mechanical contacts to excite the motor. Therefore, an EC motor is sometimes also called brushless DC-motor. The motor is excited by special permanent magnets with a high flux density located on the rotor. The permanent magnet poles on the rotor are attracted to the rotating poles of the stator by their opposite magnetic polarity. The magnetic poles of the stator are produced by an electric current flowing through a coil system located on the stator. The flux of the current carrying windings of the coil system rotates with respect to the stator. Like the DC motor, the current carrying flux remains in position with respect to the field flux rotating with the rotor. The major
difference is that the synchronous EC motor maintains position by an electrical commutation, rather than mechanical commutation. The torque is proportional to the strength of the permanent magnetic field and to the field created by the current carrying coils. The magnetic field in the stator rotates at a speed proportional to the frequency of the applied voltage. This is called a synchronous motor since the rotor rotates at the same speed, i.e. synchronously, with the stator field. The rotor field is produced by high energy permanent magnets, each one is mounted at a fixed position on the rotor disc. Since the positions, shapes and strengths of these permanent magnets are known, also the rotor field is well-known. The EC control makes use of this knowledge of the rotor field. Therefore, it is possible to adjust the electro-magnetical torque in such a way that it is linear to the total amount of the stator current, i.e. $M \sim I_s$. In this case a change of the stator current will be followed by a change of the torque almost instantaneously. The strain or shear rate can be adjusted in a very fast way and without any overshoots. In combination with a high resolution optical encoder real strain and strain rate control is possible.

In a traditional strain rheometer a similar motor concept is used. In distinction to a traditional controlled strain rheometer no separate torque transducer is needed but the electrical current of the motor, $I_s$, is used as a measure of the torque. Like for CS rheometers both presetting and measuring of the corresponding properties are done from the same side of the rheometer. The described motor setup basically combines the advantage of both the traditional controlled strain rheometer with a fast motor control and the traditional controlled stress instrument with the ability to take the motor current as a measure of the torque. In the case of a traditional CR-rheometer where the torque is measured separately from the motor the torque value is not influenced by the torque needed to accelerate the motor. In a setup which uses the motor current as a measure of the torque, the effect of accelerating the motor needs to be accounted for. The moment of inertia of a given mechanical system should be constant. However, effects like resonance, electro-magnetic couplings between stator and rotor, thermal expansion etc. can change the value of the moment of inertia. Using an EC-motor and its constant magnetic field on the rotor, the moment of inertia can be determined quite accurately for a given configuration. The actual value of the moment of inertia is considered by the electronics in the control mechanism. The set stresses in controlled stress mode or the measured stresses in controlled strain mode are the sample stresses and not like in a traditional controlled stress instrument the stresses calculated based on the total electrical torque the instrument applies. Using the actual moment of inertia value during the control mechanism also eliminates the resonance peak which often limits the frequency range of traditional controlled stress rheometers toward high frequencies. This was always integrated in the calculation of the rheological data points, i.e. for the full oscillation cycle information. However, it was not possible to access the real sample stress wave form but only the wave form of the total stress based on the electrical torque the rheometer applies. The capability of the rheometer has now been extended to provide the real sample stress wave form, which offers the possibility to do real intracycle LAOS investigations in strain and stress control. Historically, CS rheometers are controlling the amplitude of the oscillation. In a controlled stress mode an instrument applies a sine wave with torque amplitude. However, when a strain controlled mode is used the instrument still applies a torque or stress sine wave.

Generally, a strain controlled oscillatory test in a CS rheometer consists of the following steps: applying one full oscillation cycle with an arbitrary stress amplitude, measuring the strain amplitude, adjusting the stress in the next oscillation cycle, and repeating this routine until the desired strain amplitude is reached. This method can be referred to as amplitude control. It has been shown earlier that rheometers with EC-motors are able to perform not just this traditional amplitude control, but they are able to carry out strain oscillation also with a real position or true strain control (Läuger et al. 2002). This oscillation technique was called Direct Strain Oscillation (DSO). DSO does not require a full (or even part of an) oscillation
cycle but uses a real-time position control and adjusts to the desired strain directly on the sine wave. Therefore, the actual movement of the measuring system follows directly the required change in strain during each individual oscillation cycle. Since then the term DSO sometimes has been used also for the strain amplitude control methods. In this paper we use the expression DSO, as it was introduced, exclusively for the strain position control method. Including DSO there are three different ways to perform an oscillatory test:

1. Stress control by applying a sinusoidal stress input and controlling the stress amplitude (controlled shear stress or CSS).
2. Strain control by applying a sinusoidal stress input and controlling the strain amplitude (controlled shear deformation or CSD)
3. Strain control by controlling the strain position during an oscillation cycle (direct strain oscillation or DSO) and therefore applying a sinusoidal strain input. In the following we will only consider the DSO (sinusoidal strain) and CSD (sinusoidal stress) methods.

A gel like 4% Xanthan gum solution has been used as a sample. Various MCR301 and MCR501 rheometers from Anton Paar with Peltier temperature control at 25°C and cone-and-plate geometries with 50mm diameter and a 1° cone angle has been employed.

Figure 1. Top: Amplitude sweeps with DSO (closed symbols) and CSD (open symbols). Bottom: Strain and stress wave forms for DSO (left) and CSD (right) for the data point at 40% strain indicated by the arrow in the amplitude sweep diagram.

In Figure 1 amplitude sweeps with the DSO (sinusoidal strain) and the CSD (sinusoidal stress) methods are presented. In the linear region the results are for both methods the same. After leaving the linear region indicated by a decrease in G' a small but reproducible difference in the G' values can be observed. In the bottom of Figure 1 the wave forms of the strain and the stress at a strain of 40% are shown for the two oscillation methods. As can be
seen the DSO method produces a perfect sinusoidal strain input wave and all non-linearities are in the stress response, whereas in the CSD method the input wave is a sinusoidal stress and the non-linearities are in the strain. Figure 1 therefore proves that the conditions of a perfect sinusoidal input functions in stress and strain are given.

The results also show that the response looks rather different when a sinusoidal stress or a sinusoidal strain is applied. In so-called Lissajous plots in which the stress is plotted versus the strain or versus the strain rate this finding can be further highlighted. In Figure 2 these plots are shown for both the DSO and the CSD method at a strain value of 40%. The plots for the two different input functions have significantly different shapes indicating a different response to a sinusoidal strain or a sinusoidal stress input.

![Figure 2. Lissajous-diagrams with stress versus strain (left) and stress versus strain rate (right) for DSO (filled symbols) and CSD (open symbols) methods at 40% strain.]

The intra-cycle behaviour at various strains can be investigated by looking at Lissajous-plots with stress versus strain and stress versus strain rate as depicted in Figure 3. The data are normalized onto the base wave, i.e. the first harmonic. At small strains the sample behaves like a visco-elastic solid. The area within the ellipse of the stress/strain plot is small, i.e. the dissipated energy is small, whereas the area within the ellipse of the stress/strain rate plot is large, i.e. the stored energy is large. With increasing strain the area gets larger in the stress/strain plot (increasing dissipated energy) and the area in the stress/strain rate plots decreases (decreasing stored energy). With increasing strain the shape changes from an elliptical to a non-elliptical form indicating the cross-over from linear to non-linear behaviour. In the measurement with a sinusoidal strain input an extra peak occurs in the Lissajous presentation of stress versus strain for larger strains. This peak starts to evolve just after G” reached its maximum at a strain of about 20%. The peak increases up to a strain of about 40%. The size of the peak is reduced at larger strains but still visible at strains up to 1000%. At strains for which the peak in the stress/strain plot is at or close to its maximum a kind of bow or loop is formed at the end of the elliptical figure in the stress/strain rate presentation. Both of these features the peak and the bow are not occurring in the measurements with a sinusoidal stress input.
Figure 3. Normalized Lissajous-diagrams with stress versus strain (left) and stress versus strain rate (right). Sinusoidal strain (top) and sinusoidal stress (bottom) at 1, 10, 20, 40, 100, and 1000% strain. The arrows indicate the direction of increasing strain.

As already discussed in Figure 1 the waveforms are also significantly different. In the sinusoidal stress input the stress shows a nice sinusoidal shape. All non-linearity is in the strain wave. The strain waveform is not sinusoidal but has a shoulder. On the other hand with a sinusoidal strain input, the non-linearity is in the stress response. The stress wave form shows the peak, which obviously is also present in the Lissajous figures. An interesting point now is that this peak is occurring with a sinusoidal strain input but not with a sinusoidal stress input. That means the structure forming (or structure destroying) process differs significantly depending whether a strain or stress input function is used.

In addition a quantitative analysis according to the formalisms for strain [1] and for stress [3] input reveals that at larger strain amplitudes the following intracycle behaviour occurs: strain stiffening and shear thickening for a sinusoidal strain input; also stress stiffening but shear thinning for a sinusoidal stress input.

This means that there are not just small quantitative differences, but the response of the sample to a sinusoidal strain input is qualitatively different compared to the response of a sinusoidal stress input. An possible explanation could be that in a situation with a strain input the sample has to follow exactly the commanded strain whereas in a stress input the sample can adapt its strain response to the stress by some sort of relaxation processes.

To further validate this finding and to be sure that the occurrence of this peak is not an artifact in the data treatment of the rheometer firmware during oscillatory measurements so-called cyclic loading tests with strain and stress input have been performed. The idea of the cyclic loading technique is to apply a periodic triangle function in strain or stress. Compared to the sinusoidal input functions, which are executed in the oscillatory mode of the rheometer, the triangle functions are programmed in the rotational mode. This means a strain (or stress)
profile is applied and the responding stress (or strain) signal is recorded. There is no special analysis and in particular no Fourier transformation required to collect the data. Such cyclic loading tests in strain and stress confirm the results of the oscillatory tests for both the strain and the stress input, which means that the sample behaves differently whether a periodic strain or a periodic stress input function is applied.

**Conclusions**

The new LAOS framework from Ewoldt and coworkers has been extended to a sinusoidal stress input. The comparison of the samples response to stress and strain input functions shows significant differences. For a Xanthan sample the results differ significantly depending on the use of a sinusoidal stress or strain input. For a sinusoidal strain input the sample shows intracycle shear thickening, whereas a sinusoidal stress input leads to intracycle shear thinning. For both sinusoidal inputs the results have been verified by cyclic stress and strain loading tests. This implies that complex fluids can behave differently whether periodic stress or periodic strain input functions outside the linear visco-elastic range are applied. For a strain input the sample has to follow the deformation control, whereas it can adapt its movement to a force input for a stress input. This will result in stronger nonlinearities for a strain input compared to a stress input.

A rheometer based on an air bearing supported electrically commutated (EC) synchronous motor offers true controlled strain and controlled stress in rotational and oscillatory testing. This is needed to quantitatively measure the different response of complex fluids to periodic strain and periodic stress inputs.

**References**

3. Läuger J, Stettin H; Rheo Acta (2010) to be published