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Laukkanen, Olli-Ville

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Small-diameter parallel plate rheometry: a simple technique for measuring rheological properties of glass-forming liquids in shear

Olli-Ville Laukkanen

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003, United States & Department of Chemical and Metallurgical Engineering, School of Chemical Technology, Aalto University, P.O. Box 16100, 00076 Aalto, Finland

Abstract The rheological characterization of glass-forming liquids is challenging due to their extreme temperature dependence and high stiffness at low temperatures. This study focuses on the special precautions that need to be taken to accommodate high sample stiffness and torsional instrument compliance in shear rheological experiments. The measurement errors due to the instrument compliance can be avoided by employing small-diameter parallel plate (SDPP) rheometry in combination of numerical instrument compliance corrections. Measurements of that type demonstrate that accurate and reliable rheological data can be obtained by SDPP rheometry despite unusually small diameter-to-gap (d/h) ratios. Specimen preparation for SDPP requires special attention, but then experiments show excellent repeatability. Advantages and some current applications of SDPP rheometry are briefly reviewed. SDPP rheometry is seen as a simple and versatile way to measure rheological properties of glass-forming liquids especially near their glass transition temperature.

Keywords: rheometry; glass-forming liquids; instrument compliance; measurement repeatability

Introduction

Glass-forming liquids are amorphous materials that exhibit solid-like mechanical properties at low temperatures, but become liquid upon heating. When going from the liquid into the glassy state, the values of several rheological parameters, such as the characteristic relaxation time τ and the viscosity η , increase by over 15 orders of magnitude in the experimentally measurable temperature range. This extreme range in the material properties poses a major challenge to rheological characterization: how to accurately measure viscoelastic properties of glass-forming liquids in their highly variable mechanical states, i.e. in the glass and in the liquid? This paper focusses on the rheological characterization near and within the glassy state, which has turned out to be especially challenging.

It is the sample's high mechanical stiffness near the glass transition which causes major problems, resulting in significant torsional distortion of the instrument as compared to the torsional deformation experienced by the sample (Hutcheson and McKenna 2008; Schröter et al. 2006). Torsional instrument compliance, or just instrument compliance in short, results from the fact that the mechanical components of the rheometer configuration – i.e. the shaft of the motor, the (upper) measurement fixture and the temperature control unit – are not perfectly stiff (Franck 2006; Gottlieb and Macosko 1982; Liu et al. 2011). Only a part of the angular deflection measured at the optical encoder reaches the sample, while the remaining part results

in the deflection of the compliant rheometer components. Instrument compliance may cause artifacts when the sample stiffness is comparable to the instrument stiffness.

The effect of instrument compliance can be demonstrated, for example, by measuring rheological properties of a glassy material with parallel plate geometries having different plate diameter. An example of this type of experiment is shown in Fig. 1 that depicts dynamic moduli data for glycerol as reported by Schröter et al. (2006). The measured data are geometry-dependent with moduli values increasing when reducing plate diameter. As stated by Schröter et al. (2006), this result demonstrates how instrument compliance effects can be reduced and more reliable data can be obtained with parallel plates of smaller diameter. However, it should be noted that even the G' data measured with a tiny 2-mm diameter parallel plate geometry fail to reach the glassy modulus value of $G_g = 3.5$ GPa reported in the literature for glycerol (Schröter and Donth 2000). Consequently, as will be discussed in the next section, instrument compliance needs to be numerically corrected in order to obtain accurate rheological data in the glassy state (i.e. at high sample stiffness).

Fig. 1. Effect of plate diameter on the measured dynamic moduli data of glycerol at $T = -81$ °C. The dashed line corresponds to the glassy modulus value of $G_g = 3.5$ GPa reported in the literature for glycerol. Adapted from Schröter et al. (2006).

Since Schröter et al. (2006) published their results, several researchers have adopted the use of the small-diameter parallel plate technique – referred to as the “small-diameter parallel plate (SDPP) rheometry” in this paper – in the measurement of the rheological properties of various types of glass-forming liquids (Inoue et al. 2013; Laukkanen 2015; Laukkanen et al. 2015; Laukkanen et al. 2016a; Laukkanen et al. 2016b; Laukkanen et al. 2017; Lu et al. 2016; Maeda et al. 2013; Möbius et al. 2010; Sui et al. 2010; Sui et al. 2011). However, although this technique has become increasingly popular during recent years, the current literature lacks a detailed description of the SDPP rheometry. In fact, other than instrument compliance corrections (Schröter et al. 2006), the experimental details or limitations of this technique have not been discussed in the literature. Hence, the purpose of this paper is to explore the

fundamentals of the SDPP rheometry technique, both from theoretical and experimental perspectives.

First, the theory and correction of torsional instrument compliance are revisited. This is followed by the analysis of the effect of using unorthodoxically small diameter-to-gap ratios in SDPP experiments. In addition, the paper discusses specimen preparation and test repeatability as these are particularly critical to successful SDPP rheometry. Advantages of SDPP rheometry over some more traditional measurement techniques are presented. SDPP rheometry is further discussed in the context of current applications.

Torsional instrument compliance and its correction

Instrument compliance due to the finite torsional stiffness of the rheometer setup can lead to significant errors in the measured rheological data. Macosko and Davis (1974) were probably the first researchers to discuss the effect and correction of instrument compliance in rheological measurements in a systematic fashion. However, their investigations focused on a different type of rheological measurement geometry, eccentric rotating disks (ERD), for which instrument compliance effects are different from the parallel plate geometry. Gottlieb and Macosko (1982) also discussed instrument compliance effects in parallel plate experiments (called “forced oscillation experiments” in their paper). Liu et al. (2011) pointed out, though, that their approximation underestimates the magnitude of instrument compliance errors.

As far as the author knows, Marin (1988) was the first to give the correct mathematical expressions for the instrument compliance in a parallel plate geometry. Later, identical analytical expressions have been derived by many other researchers (Farrar et al. 2015; Franck 2006; Lauser 2010; Rides and Olusanya 1996; Sui et al. 2010). The mathematical treatment of the instrument compliance is presented in Appendix A. The resulting instrument compliance correction equations for the storage modulus, loss modulus, and loss tangent

$$G'_s = \frac{G'_m \left(1 - \frac{J_i}{k_g} G'_m\right) - \frac{J_i}{k_g} G''_m{}^2}{\left(1 - \frac{J_i}{k_g} G'_m\right)^2 + \left(\frac{J_i}{k_g} G''_m\right)^2} \quad (1)$$

$$G''_s = \frac{G''_m}{\left(1 - \frac{J_i}{k_g} G'_m\right)^2 + \left(\frac{J_i}{k_g} G''_m\right)^2} \quad (2)$$

$$\tan \delta_s = \frac{G''_s}{G'_s} = \frac{G''_m}{G'_m \left(1 - \frac{J_i}{k_g} G'_m\right) - \frac{J_i}{k_g} G''_m{}^2} \quad (3)$$

are ready to use. For the storage modulus, loss modulus and loss tangent of the sample, G'_s , G''_s , and $\tan \delta_s$, subscript “s” denotes the true values after applying the correction. G'_m and G''_m are the measured storage modulus and loss modulus values, J_i is the instrument compliance, and k_g is the geometry conversion factor (for the parallel plate geometry, $k_g = 2h / \pi R^4$ where h is the gap between the plates of radius R).

It is noted that the instrument compliance J_i represents the total torsional compliance of the rheometer setup. Therefore, it equals to the sum of the torsional compliances of the three different components of the rheometer configuration:

$$J_i = J_{sm} + J_{mf} + J_{tcu} \quad (4)$$

where J_{sm} , J_{mf} and J_{tcu} are the torsional compliances of the shaft of the motor, the (upper) measurement fixture and the temperature control unit, respectively. Consequently, it should be kept in mind that the value of J_i is always unique to the specific rheometer setup, including both the rheometer and its accessories. In other words, J_i varies on a case-by-case basis depending on the mechanical design of the rheometer and its accessories. It is therefore important to remember that a different value of J_i needs to be used in the instrument compliance corrections whenever the measurement fixture or the temperature control unit is changed.

By looking at Eqs. (1)-(3), it is obvious that the torsional instrument compliance J_i is the only parameter that needs to be determined experimentally in order to correct dynamic rheological data for instrument compliance.¹ The principle of measuring this parameter value is very simple: an experiment is performed to determine how much the rheometer setup deflects under different levels of torque (by definition, $J = \theta/M$). To measure the deflection of the rheometer setup alone, the upper and lower fixture of the rheometer need to be fastened together. As far as the author knows, three different methods have been used to attach the upper and lower part of the parallel plate fixture rigidly together: the “gluing method” (Farrar et al. 2015; Lauser 2010; Laukkanen 2015; Pogodina et al. 2011), the “freezing method” (Pogodina et al. 2011) and the “solid rod method” (Farrar et al. 2015; Schroter et al. 2006). Often, the gluing method is preferred because it is easy to perform and it has proven to yield a reliable estimation of J_i (Farrar et al. 2015).

In the gluing method, the upper and lower plate are fixed together with a very thin layer of superglue (cyanoacrylate). It is recommended to use a glue layer thickness of less than 20 μm so that the torsional stiffness of the “glue sample” can be assumed to be much larger compared to any real sample measured at significantly larger gaps (typically between 0.5 and 2 mm) (Lauser 2010). After the superglue has cured, an oscillatory torque sweep is performed and the resulting deflection angles are measured. When the deflection angles are plotted against the applied torque, as shown in Fig. 2, the instrument compliance J_i can be determined as the slope of the linear relationship. In the case of Fig. 2, we find $J_i = 0.01925 \text{ rad/Nm}$. This instrument compliance value was measured for a single-head, stress-controlled Anton Paar MCR 301 rheometer equipped with a CTD 450 convection oven and a 4-mm parallel plate fixture. However, it should be noted that in this case default values (provided by the rheometer manufacturer) were used for the torsional compliances of the shaft of the rheometer motor (J_{sm}) and of the CTD 450 oven (including its lower shaft) (J_{tcu}). Therefore, the specific compliance value J_i actually represents only the torsional compliance of the 4-mm parallel plate fixture (J_{mf}).²

¹ It is also possible to estimate the value of J_i by performing theoretical calculations. However, experience has shown that these calculations are rather complicated and do not always provide a reliable estimate of J_i . Therefore, it is often recommended to determine J_i experimentally.

² As of writing, it is often recommended that the default compliance values for the motor shaft and the temperature control unit (provided by the rheometer manufacturer) should not be modified by the rheometer user. In case there are any inaccuracies in these default compliance values, those are taken into account in the measured compliance value for the measurement fixture.

Fig. 2. Example of the determination of the torsional instrument compliance. Two torque sweeps were performed to ensure data consistency. In this case, $J_i = 0.01925$ rad/Nm represents the torsional compliance of the 4-mm parallel plate fixture alone.

Two examples of the effect of instrument compliance corrections on dynamic rheological data are given in Fig. 3. Fig. 3(a) shows uncorrected and corrected dynamic data for a petroleum oil, measured close to its glass transition temperature. This data set was measured with the 4-mm diameter parallel plate setup whose torsional compliance $J_i = 0.01925$ rad/Nm is determined in Fig. 2. In this case, the instrument compliance corrections are notable only at high frequencies where $|G^*| > 10^8$ Pa. It is generally true that the corrections on G'' data are relatively larger than those on G' data. A more extreme case of instrument compliance corrections is shown in Fig. 3(b) that presents uncorrected and corrected ($J_i = 0.008102$ rad/Nm) dynamic data for glycerol, measured again close to the nominal glass transition temperature. In this case, the corrections are significantly larger than in Fig. 3(a) because of the higher stiffness of glycerol in the glassy state and because of the larger (8-mm diameter) parallel plate geometry used. For example, the apparent G_g of glycerol shifts from ~ 0.5 GPa to ~ 3.5 GPa as a result of the instrument compliance corrections. The compliance corrected value of $G_g \approx 3.5$ GPa is consistent with ultrasonic data (Harrison 1976; Piccirelli and Litovitz 1957) and light scattering results (Scarponi et al. 2004) from the literature, therefore providing confidence that the compliance-corrected data from SDPP rheometry is accurate. In addition, the compliance-corrected data in Figs. 3(a) and 3(b) satisfy the Kramers-Kronig relation (Winter 1997), providing further evidence of the correctness of this data.

Fig. 3. The effect of instrument compliance corrections, Eqs. (1)-(3), on dynamic rheological data. (a) Frequency sweep data for a petroleum oil ($T_g = -74$ °C) measured at -75 °C. This data set was measured with a 4-mm diameter parallel plate geometry at a gap of about 1.22 mm, the torsional compliance of the measurement setup being $J_i = 0.01925$ rad/Nm. (b) Frequency sweep data for glycerol ($T_g = -82$ °C) measured at -81 °C. This data set was measured with a 8-mm diameter parallel plate geometry at a gap of about 2 mm, the torsional compliance of the measurement setup being $J_i = 0.008102$ rad/Nm.

Although instrument compliance corrections can be seemingly easily performed, and they are often carried out automatically by the rheometer software, it should be kept in mind that there are some practical limitations to these corrections. In case very large compliance corrections are applied, even small inaccuracies in the instrument compliance value J_i may cause significant errors in the compliance corrected rheological data. Because of this, it is generally recommended that the plate diameter and measurement gap should be selected in such a way that the ratio between the angular displacement due to instrument compliance and the angular displacement due to sample deformation is less than 10 (i.e. more than 10 % of the angular displacement applied at the optical encoder of the rheometer reaches the sample) (Nill 2014).

Analysis of small diameter-to-gap ratio

As described by Schröter et al. (2006), instrument compliance effects can be reduced by decreasing the plate diameter and/or by increasing the measurement gap. It is important to note, however, that by doing this, the diameter-to-gap (d/h) ratio of the measurement geometry is also decreased. For example, when using a 4-mm parallel plate geometry with typical gap heights of 0.5 to 2 mm, the d/h ratio is in the range of 2 to 8. This is in contradiction with the recommendation of ISO 6721-10 standard which says that the d/h ratio of a parallel plate geometry should be preferably in the range of 10 to 50 for this geometry to be considered as an absolute measuring system.

As the d/h ratios employed in SDPP experiments are unusually small, it is necessary to examine carefully whether the rheological data obtained with this measurement technique is accurate and reliable. Most typically, the use of a parallel plate geometry with a too small d/h ratio leads

in inertia and secondary flow effects at high frequencies (Ewoldt et al. 2015; Lauser and Stettin 2016). However, these experimental artifacts are usually present only when measuring rheological properties of low-viscosity liquids and are therefore not relevant for liquids that are characterized near and within the glassy state. Numerical calculations demonstrating that instrument and fluid inertia effects are typically not an issue in SDPP experiments are presented in Appendix B.

A more practical way to test whether a small d/h ratio has any influence on the measured rheological properties is to perform experiments at different gap heights. Figure 4 shows frequency sweep data for a soft bitumen grade (penetration (EN 1426): 145 dmm, Ring-and-Ball softening point (EN 1427): 39.8 C) measured with a 4-mm diameter parallel plate fixture at gaps ranging from 0.5 to 2.5 mm, corresponding to d/h ratios of 1.6 to 8. It is observed that the data measured at -20 C do not exhibit systematic gap dependence, the minor variability in the measurement data is due to the test repeatability (discussed more in detail later in this paper). However, at a higher temperature of 10 C, the data measured at 2.5 mm gap ($d/h = 1.6$) deviates considerably from the data measured at gap heights of 2.0 mm and less ($d/h \geq 2$). This demonstrates the fact that the use of extremely large gaps / small d/h ratios becomes increasingly critical when material becomes softer. Based on the limited results presented here, the use of gap heights of 2 mm or less and d/h ratios of 2 or more is recommended when measuring in the temperature range where dynamic moduli values are higher than 10^5 Pa.

Fig. 4. Gap or d/h ratio dependence of the measured dynamic moduli of bitumen at (a) -20 C and (b) 10 C.

It is also notable that the free surface area-to-volume ratio increases with decreasing plate diameter ($A_{free\ surface}/V \sim 1/d$). Because of this, there are a couple of practical points that should be emphasized here. Firstly, this means that a high portion of the test specimen is exposed to the surrounding gas, and therefore it should be carefully ensured that the specimen is chemically inert to this gas. For example, it is critical to prevent moisture uptake in hygroscopic glass formers as their rheological properties may be highly sensitive to water content (see the data of Shi et al. (2005) for sucrose benzoate as an example). Dry nitrogen gas is typically used

for this purpose. Secondly, the large free surface area-to-volume ratio sets a high standard for the temperature control of the rheometer as the temperature of the surrounding gas needs to be very carefully controlled in order to avoid temperature gradients within the test specimen. This is a particularly important issue since the rheological properties of glass-forming liquids are typically extremely temperature sensitive. Furthermore, it is noted that the thermal contact to surrounding gas becomes relatively more important with decreasing d/h ratio as the ratio between the area exposed to the gas and that in contact with the plates becomes larger ($A_{free\ surface}/A_{plate\ contact} \sim h/d$). Any issues related to the chemical instability of the test specimen or to the rheometer's temperature control would manifest themselves as gap-dependent rheological data in an analysis similar to that shown in Fig. 4.

Specimen preparation and dimensional errors

Depending on the properties of a glass-forming liquid, two alternative procedures can be used to prepare a test specimen for SDPP testing. If the material of interest is a low-viscosity liquid at room temperature (like glycerol or lubricant oils), it is preferable to apply a sufficient amount of material on the lower plate of the rheometer, and then to lower the gap until it is completely filled with the material. On the other hand, if the investigated material exhibits high viscosity and/or solid-like behavior at room temperature (like bitumen), it is easier to apply sufficient amount of material on the lower plate of the rheometer, lower the gap to a predefined height, and finally trim the specimen with a spatula. An example of a properly trimmed bitumen specimen in a 4-mm diameter parallel plate geometry is shown in Fig. 5.

Fig. 5. Trimmed bitumen specimen in a 4-mm diameter parallel plate geometry, gap = 1.87 mm. Note that also the nub of the lower plate is covered with bitumen; the lower edge of the test specimen is indicated by a dashed curved line.

Whichever of the two afore described methods is used to prepare a test specimen, a great care should be taken to ensure the correct specimen shape and dimensions. This is because the torsional stiffness of a disk-shaped material specimen is proportional to the fourth power of the plate radius (see Eq. (11) in Appendix A). Consequently, in the case of a parallel plate

geometry, the errors in the apparent measured values of various stiffness parameters, such as G' and G'' , scale with the fourth power of the error in the specimen radius. Therefore, when using parallel plates of small diameter, even a small error in the specimen radius can lead in significant errors in the measured rheological properties. For example, a tiny 50- μm wide cavity at the periphery of a 4-mm diameter specimen would theoretically result in $\sim 10\%$ underestimation of the dynamic moduli values. It is therefore highly recommended to use magnifying glasses to carefully inspect the correct shape and dimensions of the specimens prepared for SDPP testing.

It is also important to ensure that the shape of the test specimen remains unaltered during rheological measurements. Especially, the significant thermal contraction of glass-forming liquids upon cooling needs to be considered when performing SDPP experiments. To adjust the measurement gap for the decreasing volume of the test specimen, it is recommended to use the normal force control option in a rheometer. This helps to avoid the build-up of negative normal stresses in the test specimen while maintaining good adhesion between the plates and the specimen. It is also a good idea to examine the test specimen after the completion of a rheological experiment to ensure the intactness of the specimen shape.

Measurement repeatability

Considering the high sensitivity of measured rheological properties on the exact specimen dimensions, it is important to establish the repeatability of SDPP measurements. In this study, repeatability tests were performed on bitumen modified with 10 wt% of styrene-butadiene-styrene (SBS) triblock copolymer (penetration (EN 1426): 50 dmm, Ring-and-Ball softening point (EN 1427): 112.5 °C). Blends of bitumen and SBS are known to be partially miscible and exhibit a microstructure that is strongly dependent on their thermal history and conditioning time (Soenen et al. 2008; Xia et al. 2016; Zhu et al. 2016a; Zhu et al. 2016b). Consequently, the rheological properties of SBS-modified bitumens are highly sensitive to the temperature profile and loading conditions during specimen preparation (Lu et al. 2011), and therefore these materials can be used as sensitive indicators of possible repeatability issues. Frequency sweep data on three replicate samples of the SBS-modified bitumen are shown in Fig. 6. The test specimens were carefully trimmed at 120 °C, where $\eta \approx 10^2\text{-}10^3$ Pa.s; the author has found experimentally that specimens can be most easily trimmed when their viscosity is in this range. An excellent repeatability is observed; the single-operator standard deviation of the dynamic moduli values being estimated as less than 5 %. We can hence conclude that, as long as specimen preparation is carried out carefully and in a systematic way, there does not appear to be any repeatability issues associated with SDPP rheometry.

Fig. 6. Repeatability of 4-mm diameter parallel plate experiments demonstrated with frequency sweep data of SBS-modified bitumen.

Advantages over other existing measurement techniques

As indicated by the title of this article, SDPP rheometry is a particularly suitable technique for measuring rheological properties of glass-forming liquids, i.e. highly viscous liquids, in shear. On the other hand, dynamic mechanical measurements in torsion, tension or bending are more commonly used to characterize rheological behavior of viscoelastic solids, using either a dynamic mechanical analyzer (DMA) or a torsion bar fixture on a rotational rheometer (Dessi et al. 2016). However, some high-viscosity fluids, like bitumen, may in principle be tested by any of the aforementioned techniques. In the following, some arguments are presented in favor of using SDPP rheometry in the characterization of these type of materials:

- Preparation of test specimens is more straightforward for SDPP testing than for torsional, tension or bending experiments. If a high-viscosity liquid was to be characterized in torsion, tension or bending, a bar-shaped test specimen would need to be prepared by molding and transferred to the rheometer or DMA at a low temperature. This is a considerably more complicated procedure than preparing a test specimen directly into a parallel plate geometry as described in Section ‘Specimen preparation and dimensional errors’.
- Less material is needed for SDPP testing than for torsional, tension or bending testing. For example, if a 4-mm diameter parallel plate geometry is used at a typical gap of 1.75 mm, the volume of the test specimen is only about 0.022 cm³.
- In SDPP rheometry the test specimen does not need to be clamped or glued to the measurement fixture, as is the case with bar-shaped test specimens used in torsional or tension testing. Any issues related to the specimen clamping and to the resulting stress concentrations are therefore avoided in SDPP rheometry.
- In addition to the capability of measuring rheological properties in the glassy state, SDPP rheometry can also be used to measure rheological properties well above the glass transition temperature, i.e. when the sample is softer and more liquid-like. Further

analysis and experimental data demonstrating the wide measurement range of this technique is presented in Appendix B.

It is also worth mentioning that small-diameter parallel plate geometries, in particular 4-mm diameter parallel plate geometries, are commercially available and can be purchased from any major rheometer manufacturer.

In addition to the aforementioned measurement techniques, there are also some other, less common methods for measuring rheological properties of glass-forming liquids. For example, a piezoelectric shear modulus gauge (PSG) is used by the DNRF Centre 'Glass and Time' at Roskilde University for this purpose (Christensen and Olsen 1995). This technique allows the measurement of the dynamic shear modulus in the range between 0.1 MPa and 10 GPa over a wide frequency range (10^{-3} - 10^4 Hz). However, this method is not commercially available or widely used, and therefore it is not further discussed here.

Current applications of SDPP rheometry

At the time of writing, the most popular application area of SDPP rheometry is probably in the field of asphalt research. As first demonstrated by Sui et al. (2010), 4-mm diameter parallel plate geometry is particularly suitable for measuring rheological properties of bituminous binders at low temperatures. In this application, the main advantage of SDPP rheometry – also known as the “4-mm DSR” technique in the asphalt community – is that it requires only very small amounts of material (~ 25 mg) as compared to the more traditionally used bending beam rheometer (BBR) test method (~ 15 g). Based on the 4-mm parallel plate technique, a new low-temperature performance-grading method has been proposed for bituminous binders (Sui et al. 2011). From a more scientific standpoint, the data obtained by SDPP rheometry has recently led to the description of bitumen as a complex glass-forming liquid (Laukkanen et al. 2016b; Laukkanen et al. 2017).

SDPP rheometry has also been employed to study glassy dynamics of various simple, small-molecule glass-forming liquids. Among the most well-established studies in this field are the ones carried out by McKenna and coworkers (Hutcheson and McKenna 2008; Schröter et al. 2006).³ In these investigations, the importance of instrument compliance corrections has been highlighted, and it has been shown that the stress relaxation in simple glass-forming liquids generally follows the Kohlrausch-Williams-Watts (KWW) stretched exponential function (Kohlrausch 1854; Williams and Watts 1970). More recently, Möbius et al. (2010) employed SDPP rheometry to study the effect of solidification and slush formation on the rheological properties of supercooled glycerol during physical aging.

³ The rheological studies of McKenna et al. and Pogodina et al. were performed mainly with 8-mm diameter parallel plate geometries that are not ideal for the measurement of rheological properties at very high stiffness levels (parallel plates with an even smaller diameter are typically preferred). However, they carefully corrected their measurement data for instrument compliance and therefore obtained reliable rheological data even when $|G^*| > 1$ GPa.

Furthermore, SDPP rheometry has been successfully used to probe glassy dynamics of ionic liquid based materials. Pogodina et al. (2011) were the first ones to study the low-temperature molecular dynamics of ionic liquids by rheology.³ In their investigation, they found that room-temperature ionic liquids show a broad relaxation time spectrum with distinct contributions both from the motion of single ions and from the cooperative motion of a group of ions. Inoue and coworkers (Inoue et al. 2013; Maeda et al. 2013) recently combined SDPP measurements with birefringence experiments in an investigation of the structural and dynamic properties of polymerized ionic liquids and ionic liquid based solutions.

Conclusions

The rheological characterization of glass-forming liquids poses significant technical challenges due to their extreme temperature dependence and high stiffness at low temperatures. Recently, small-diameter parallel plate (SDPP) rheometry has been developed to overcome these experimental difficulties. In this article, it has been shown that SDPP rheometry is a relatively simple measurement technique that can be used to obtain accurate rheological data at shear modulus levels up to several gigapascals. Yet, special attention needs to be paid to experimental details such as instrument compliance corrections and specimen preparation to ensure data reliability.

SDPP rheometry can be used to rheologically characterize virtually any type of glass-forming liquid. Therefore, it can be employed in a wide variety of applications such as performance grading of bituminous binders and ionic liquid research. Furthermore, rheological data produced by this technique appears to be useful in advancing the fundamental understanding of glass dynamics. Due to the commercial availability of parallel plate fixtures of small diameter, the variety of applications is expected to further increase in the future.

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Appendix A. Derivation of the instrument compliance correction equations

The angular displacement measured at the optical encoder (θ_m) is composed of the sample angular displacement (θ_s) and the instrument angular displacement (θ_i).

$$\theta_m = \theta_s + \theta_i \quad (5)$$

The torsional stiffness (K) is defined as the ratio of the angular displacement (θ) and the torque (M):

$$K = \frac{M}{\theta} \quad (6)$$

By combining Eqs. (5) and (6), the relationship between the measured torsional stiffness (K_m) and the torsional stiffness of the sample (K_s) and of the instrument (K_i) can be written as follows:

$$\frac{1}{K_m} = \frac{1}{K_s} + \frac{1}{K_i} \quad (7)$$

where the torsional stiffness of the instrument is the inverse of the instrument compliance:

$$J_i = \frac{1}{K_i} \quad (8)$$

By rearranging Equation (7), the torsional sample stiffness can be obtained as:

$$K_s = \frac{K_i K_m}{K_i - K_m} \quad (9)$$

The torsional stiffness (K) can be converted into the shear modulus (G) by introducing the geometry conversion factor (k_g):

$$K = \frac{G}{k_g} \quad (10)$$

For a parallel plate geometry with the plate radius R and the gap between the plates h the geometry conversion factor is calculated as follows:

$$k_g = \frac{2h}{\pi R^4} \quad (11)$$

Due to the viscoelastic nature of samples, the measured and sample stiffness and moduli are written in the complex form hereafter. On the other hand, the instrument stiffness and modulus are scalars since the rheometer setup can be assumed to be purely elastic.⁴ The substitution of Eqs. (8) and (10) into Eq. (9) yields:

$$G_s^* = \frac{G_m^*}{1 - \frac{J_i}{k_g} G_m^*} \quad (12)$$

which can also be written in terms of the storage (G') and loss (G'') moduli:

$$G_s' + iG_s'' = \frac{G_m' + iG_m''}{1 - \frac{J_i}{k_g} (G_m' + iG_m'')} \quad (13)$$

⁴ To be accurate, this is strictly true only for single-head rheometers, in which the effect of the instrument compliance is instantaneous and fully recoverable (Läuger 2010). In the case of dual-head rheometers, on the other hand, the control routines for the torque transducer will lead to an additional viscous compliance contribution. It has been experimentally shown that the inelastic compliance contribution may result in a notable frequency dependence of instrument compliance (Farrar et al. 2015). However, the more complicated instrument compliance analysis of dual-head rheometers is omitted here due to the fact that the vast majority of modern rotational rheometers are single-head rheometers (however, an interested reader is referred to Franck (2006)).

Finally, the storage and loss moduli of the sample can be solved from Eq. (13):

$$G'_s = \frac{G'_m \left(1 - \frac{J_i}{k_g} G'_m\right) - \frac{J_i}{k_g} G''^2_m}{\left(1 - \frac{J_i}{k_g} G'_m\right)^2 + \left(\frac{J_i}{k_g} G''_m\right)^2} \quad (1)$$

$$G''_s = \frac{G''_m}{\left(1 - \frac{J_i}{k_g} G'_m\right)^2 + \left(\frac{J_i}{k_g} G''_m\right)^2} \quad (2)$$

and the loss tangent of the sample becomes:

$$\tan \delta_s = \frac{G''_s}{G'_s} = \frac{G''_m}{G'_m \left(1 - \frac{J_i}{k_g} G'_m\right) - \frac{J_i}{k_g} G''^2_m} \quad (3)$$

Appendix B. Analysis of the effective measurement range of SDPP rheometry

The effective measurement range of SDPP rheometry is limited at low modulus values by the minimum torque of the rheometer. According to Ewoldt et al. (2015), the minimum measurable viscoelastic moduli G_{min} in oscillatory experiments is defined by the following expression:

$$G_{min} = \frac{F_\sigma T_{min}}{\gamma_0} \quad (14)$$

where F_σ is a geometry factor that correlates the applied torque T to the shear stress σ , T_{min} is the minimum torque of the rheometer in oscillation, and γ_0 is the strain amplitude. G_{min} refers to either G' or G'' , whichever is smaller. For the parallel plate geometry:

$$F_\sigma = \frac{\sigma}{T} = \frac{2}{\pi R^3} \quad (15)$$

where R is the plate radius. Fig. 7 shows dynamic oscillatory data for a petroleum oil, measured with 4-mm diameter parallel plate geometry. This data set was measured with a stress-controlled Anton Paar MCR 301 rheometer, having a minimum torque limit $T_{min} = 0.01 \mu\text{Nm}$ in oscillation. The strain amplitude was varied in the range of 0.01 to 0.05 %, being 0.05 % at the highest measurement temperatures (corresponding to the lowest moduli values). Therefore, using Eqs. (14) and (15), the minimum measurable moduli can be calculated to be $G_{min} = 1.59 \text{ kPa}$ in this case. The dynamic moduli master curves of Fig. 7(a) demonstrate the good quality of the 4-mm diameter parallel plate data down to this G_{min} value, the terminal slopes of G' and G'' being close to 2 and 1, respectively. However, it should be kept in mind that the value of G_{min} varies on a case-by-case basis, depending on T_{min} and γ_0 . The low-torque sensitivity limit can be lowered, when possible, by using a more sensitive rheometer (lower T_{min} limit) and/or by increasing γ_0 . Eventually, larger parallel plate geometries need to be used if glass-forming liquids are to be characterized in a low-viscosity liquid state (below G_{min} limit).

The upper stiffness limit of the effective measurement range of SDPP rheometry is practically determined by the recommendation that the ratio between the angular displacement due to instrument compliance and the angular displacement due to sample deformation should be less than 10. If we assume typical values of $J_i = 0.01925 \text{ rad/Nm}$, $R = 2 \text{ mm}$, and $h = 1.5 \text{ mm}$ in Eq. (12), the critical $|G^*|$ value at which the aforementioned ratio becomes equal to 10 is 27.9 GPa.

This value is much higher than the glassy modulus of any known glass-forming liquid. Therefore, in most cases, there is no practical upper stiffness limit for using SDPP rheometry. Fig. 7(b) shows this same data set plotted in the van Gorp-Palmen plot of phase angle versus $\log|G^*|$. The purpose of this plot is to demonstrate that even very liquid-like samples can be characterized by SDPP rheometry, i.e. phase angle values close to 90° can be reliably measured. Therefore, it can be concluded that this technique is applicable for the rheological characterization of glass-forming liquids even well above the glass transition temperature, which is not possible by using torsion bar or DMA techniques.

Fig. 7. (a) Dynamic moduli master curves and (b) the Booij-Palmen plot for a petroleum oil. The data were measured with 4-mm diameter parallel plate geometry. In part (a), the dashed line indicates the low-torque limit, $G_{min} = 1.59$ kPa, from Eq. (14) ($T_{min} = 0.01$ μNm , $R = 2$ mm, $\gamma_0 = 0.05$ %), and the dotted line corresponds to the upper stiffness limit due to the instrument compliance correction limitations, $|G^*|_{max} = 27.9$ GPa ($J_i = 0.01925$ rad/Nm, $R = 2$ mm, $h = 1.5$ mm).

Another factor limiting the effective measurement range of oscillatory rheological experiments is instrument inertia (Läuger and Stettin 2016). In the case of SDPP rheometry, the effect of instrument inertia is magnified due to the small plate diameter and large gap. Although all modern rheometer models correct measurement data for instrument inertia, inertial errors may still exist due to the inaccuracies in the instrument inertia determination. The effect of imperfect instrument inertia corrections on the effective measurement range can be assessed from the following equation (Ewoldt et al. 2015):

$$G_{iner,inst} = \varepsilon \frac{F_\sigma I}{F_\gamma} \omega^2 \quad (16)$$

where $G_{iner,inst}$ is artificial inertial moduli, ε is the error in the instrument inertia value used for the corrections, F_γ is a geometry factor that correlates the applied angular deformation θ to the shear strain γ , I is the combined moment of inertia of the rotating parts of the rheometer (motor, air bearing, optical encoder, motor axis with geometry coupling, and measuring geometry), and ω is the angular frequency. In the case of the parallel plate geometry:

$$F_\gamma = \frac{\gamma}{\theta} = \frac{R}{h} \quad (17)$$

Since $G_{iner,inst} \sim \omega^2$, the instrument inertia effects are most pronounced at high frequencies. For example, if there is a 1-% error in the instrument inertia corrections ($\varepsilon = 0.01$) and we assume typical values of $I = 13.4 \mu\text{Nm.s}^2$, $R = 2 \text{ mm}$, and $h = 1.5 \text{ mm}$, the artificial inertial moduli obtain a value of $G_{iner,inst} = 79.8 \text{ kPa}$ at $\omega = 100 \text{ rad/s}$. For any practical purposes, this modulus contribution can be considered negligible as compared to the true material moduli (typically, at this frequency, G' and G'' values are in excess to 1 MPa for materials that are to be characterized by SDPP rheometry). However, it should be noted that instrument inertia values can vary significantly depending on the rheometer model, and therefore the inertia limits for the effective measurement range should be evaluated on a case-by-case basis.

Lastly, the effective measurement range of oscillatory experiments may be affected by fluid (sample) inertia (Läuger and Stettin 2016). In order to be sure that fluid inertia does not influence rheological measurement data, the wavelength λ_s of a propagating shear wave should be much larger than the geometry gap h . The wavelength of a linear viscoelastic shear wave between a moving boundary and a fixed reflecting boundary can be calculated as follows (Ewoldt et al. 2015):

$$\lambda_s = \frac{1}{\cos(\delta/2)} \left(\frac{|G^*|}{\rho} \right)^{1/2} \frac{2\pi}{\omega} \quad (18)$$

where ρ is the density of the sample. Linear viscoelastic wave propagation has been analyzed in detail by Schrag (1977) who suggested the criterion $\lambda_s/h \geq 40$ for high-precision measurements in which errors must be less than 1 % in $|G^*|$ and 1° in phase angle. By substituting the Schrag criterion into Eq. (18) and by rearranging it we obtain:

$$|G^*_{iner,fluid}| > \left(\frac{40}{2\pi} \right)^2 \cos^2(\delta/2) \rho \omega^2 h^2 \quad (19)$$

As the critical value for $|G^*_{iner,fluid}|$ scales with ω^2 , the fluid inertia effects are most pronounced at high frequencies. If we assume typical values of $\delta = 89^\circ$, $\rho = 1000 \text{ kg/m}^3$ and $h = 1.5 \text{ mm}$, the criterion for having fluid inertia-free measurement data becomes $|G^*_{iner,fluid}| > 464 \text{ Pa}$ at $\omega = 100 \text{ rad/s}$. Again, this modulus limit is significantly lower than the $|G^*|$ values typically measured by SDPP rheometry at $\omega = 100 \text{ rad/s}$. Therefore, the fluid inertia effects can be considered negligible in SDPP experiments.

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