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1 **Small-diameter parallel plate rheometry: a simple technique for measuring** 2 **rheological properties of glass-forming liquids in shear**

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7
8 **Abstract** The rheological characterization of glass-forming liquids is challenging due to their
9 extreme temperature dependence and high stiffness at low temperatures. This study focuses on
10 the special precautions that need to be taken to accommodate high sample stiffness and
11 torsional instrument compliance in shear rheological experiments. The measurement errors due
12 to the instrument compliance can be avoided by employing small-diameter parallel plate
13 (SDPP) rheometry in combination of numerical instrument compliance corrections.
14 Measurements of that type demonstrate that accurate and reliable rheological data can be
15 obtained by SDPP rheometry despite unusually small diameter-to-gap (d/h) ratios. Specimen
16 preparation for SDPP requires special attention, but then experiments show excellent
17 repeatability. Advantages and some current applications of SDPP rheometry are briefly
18 reviewed. SDPP rheometry is seen as a simple and versatile way to measure rheological
19 properties of glass-forming liquids especially near their glass transition temperature.

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

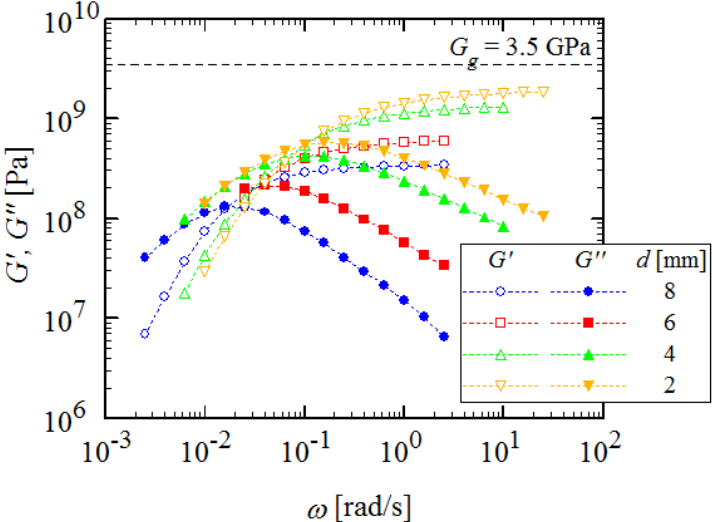
22 23 **Introduction**

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

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

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

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



15
 16 **Fig. 1.** Effect of plate diameter on the measured dynamic moduli data of glycerol at $T = -81$
 17 $^{\circ}\text{C}$. The dashed line corresponds to the glassy modulus value of $G_g = 3.5$ GPa reported in the
 18 literature for glycerol. Adapted from Schröter et al. (2006).

19
 20 Since Schröter et al. (2006) published their results, several researchers have adopted the use of
 21 the small-diameter parallel plate technique – referred to as the “small-diameter parallel plate
 22 (SDPP) rheometry” in this paper – in the measurement of the rheological properties of various
 23 types of glass-forming liquids (Inoue et al. 2013; Laukkanen 2015; Laukkanen et al. 2015;
 24 Laukkanen et al. 2016a; Laukkanen et al. 2016b; Laukkanen et al. 2017; Lu et al. 2016; Maeda
 25 et al. 2013; Möbius et al. 2010; Sui et al. 2010; Sui et al. 2011). However, although this
 26 technique has become increasingly popular during recent years, the current literature lacks a
 27 detailed description of the SDPP rheometry. In fact, other than instrument compliance
 28 corrections (Schröter et al. 2006), the experimental details or limitations of this technique have
 29 not been discussed in the literature. Hence, the purpose of this paper is to explore the

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

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

9

10 **Torsional instrument compliance and its correction**

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

20 As far as the author knows, Marin (1988) was the first to give the correct mathematical
21 expressions for the instrument compliance in a parallel plate geometry. Later, identical
22 analytical expressions have been derived by many other researchers (Farrar et al. 2015; Franck
23 2006; Lauger 2010; Rides and Olusanya 1996; Sui et al. 2010). The mathematical treatment of
24 the instrument compliance is presented in Appendix A. The resulting instrument compliance
25 correction equations for the storage modulus, loss modulus, and loss tangent

$$26 \quad G'_s = \frac{G'_m \left(1 - \frac{J_i}{k_g} G'_m\right) - \frac{J_i}{k_g} G_m''^2}{\left(1 - \frac{J_i}{k_g} G'_m\right)^2 + \left(\frac{J_i}{k_g} G_m''\right)^2} \quad (1)$$

$$27 \quad G''_s = \frac{G_m''}{\left(1 - \frac{J_i}{k_g} G'_m\right)^2 + \left(\frac{J_i}{k_g} G_m''\right)^2} \quad (2)$$

$$28 \quad \tan \delta_s = \frac{G''_s}{G'_s} = \frac{G_m''}{G'_m \left(1 - \frac{J_i}{k_g} G'_m\right) - \frac{J_i}{k_g} G_m''^2} \quad (3)$$

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

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

1 $J_i = J_{sm} + J_{mf} + J_{tcu}$ (4)

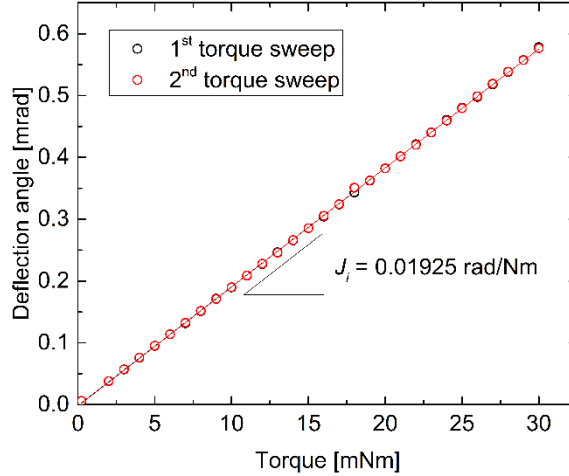
2 where J_{sm} , J_{mf} and J_{tcu} are the torsional compliances of the shaft of the motor, the (upper)
3 measurement fixture and the temperature control unit, respectively. Consequently, it should be
4 kept in mind that the value of J_i is always unique to the specific rheometer setup, including
5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

9 By looking at Eqs. (1)-(3), it is obvious that the torsional instrument compliance J_i is the only
10 parameter that needs to be determined experimentally in order to correct dynamic rheological
11 data for instrument compliance.¹ The principle of measuring this parameter value is very
12 simple: an experiment is performed to determine how much the rheometer setup deflects under
13 different levels of torque (by definition, $J = \theta/M$). To measure the deflection of the rheometer
14 setup alone, the upper and lower fixture of the rheometer need to be fastened together. As far
15 as the author knows, three different methods have been used to attach the upper and lower part
16 of the parallel plate fixture rigidly together: the “gluing method” (Farrar et al. 2015; Lauger
17 2010; Laukkanen 2015; Pogodina et al. 2011), the “freezing method” (Pogodina et al. 2011)
18 and the “solid rod method” (Farrar et al. 2015; Schroter et al. 2006). Often, the gluing method
19 is preferred because it is easy to perform and it has proven to yield a reliable estimation of J_i
20 (Farrar et al. 2015).

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

36 ¹ It is also possible to estimate the value of J_i by performing theoretical calculations. However,
37 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.



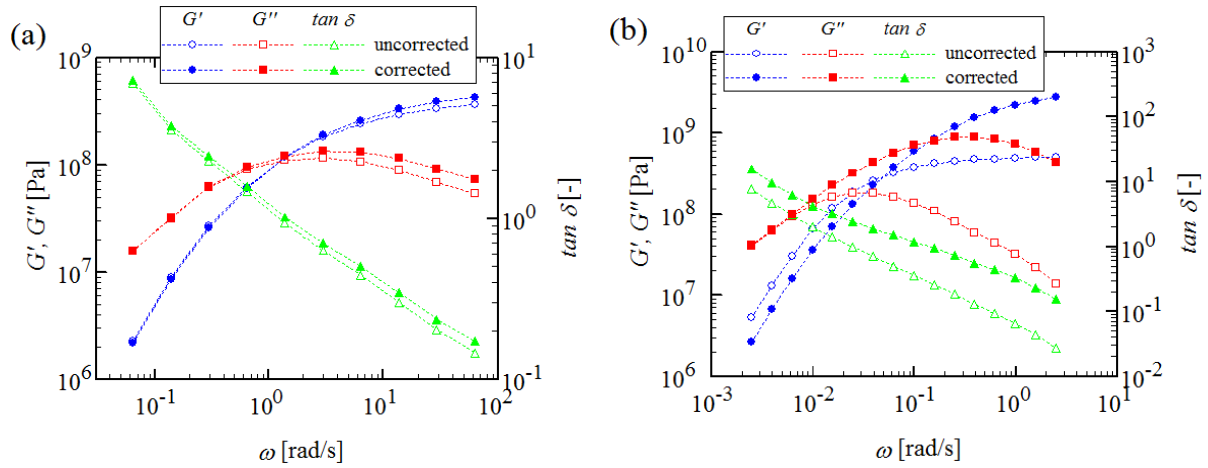
1

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

5

6 Two examples of the effect of instrument compliance corrections on dynamic rheological data
 7 are given in Fig. 3. Fig. 3(a) shows uncorrected and corrected dynamic data for a petroleum
 8 oil, measured close to its glass transition temperature. This data set was measured with the 4-
 9 mm diameter parallel plate setup whose torsional compliance $J_i = 0.01925$ rad/Nm is
 10 determined in Fig. 2. In this case, the instrument compliance corrections are notable only at
 11 high frequencies where $|G^*| > 10^8$ Pa. It is generally true that the corrections on G'' data are
 12 relatively larger than those on G' data. A more extreme case of instrument compliance
 13 corrections is shown in Fig. 3(b) that presents uncorrected and corrected ($J_i = 0.008102$
 14 rad/Nm) dynamic data for glycerol, measured again close to the nominal glass transition
 15 temperature. In this case, the corrections are significantly larger than in Fig. 3(a) because of
 16 the higher stiffness of glycerol in the glassy state and because of the larger (8-mm diameter)
 17 parallel plate geometry used. For example, the apparent G_g of glycerol shifts from ~ 0.5 GPa
 18 to ~ 3.5 GPa as a result of the instrument compliance corrections. The compliance corrected
 19 value of $G_g \approx 3.5$ GPa is consistent with ultrasonic data (Harrison 1976; Piccirelli and Litovitz
 20 1957) and light scattering results (Scarponi et al. 2004) from the literature, therefore providing
 21 confidence that the compliance-corrected data from SDPP rheometry is accurate. In addition,
 22 the compliance-corrected data in Figs. 3(a) and 3(b) satisfy the Kramers-Kronig relation
 23 (Winter 1997), providing further evidence of the correctness of this data.

24



1
2 **Fig. 3.** The effect of instrument compliance corrections, Eqs. (1)-(3), on dynamic rheological
3 data. (a) Frequency sweep data for a petroleum oil ($T_g = -74$ °C) measured at -75 °C. This data
4 set was measured with a 4-mm diameter parallel plate geometry at a gap of about 1.22 mm, the
5 torsional compliance of the measurement setup being $J_i = 0.01925$ rad/Nm. (b) Frequency
6 sweep data for glycerol ($T_g = -82$ °C) measured at -81 °C. This data set was measured with a
7 8-mm diameter parallel plate geometry at a gap of about 2 mm, the torsional compliance of the
8 measurement setup being $J_i = 0.008102$ rad/Nm.

9
10 Although instrument compliance corrections can be seemingly easily performed, and they are
11 often carried out automatically by the rheometer software, it should be kept in mind that there
12 are some practical limitations to these corrections. In case very large compliance corrections
13 are applied, even small inaccuracies in the instrument compliance value J_i may cause
14 significant errors in the compliance corrected rheological data. Because of this, it is generally
15 recommended that the plate diameter and measurement gap should be selected in such a way
16 that the ratio between the angular displacement due to instrument compliance and the angular
17 displacement due to sample deformation is less than 10 (i.e. more than 10 % of the angular
18 displacement applied at the optical encoder of the rheometer reaches the sample) (Nill 2014).

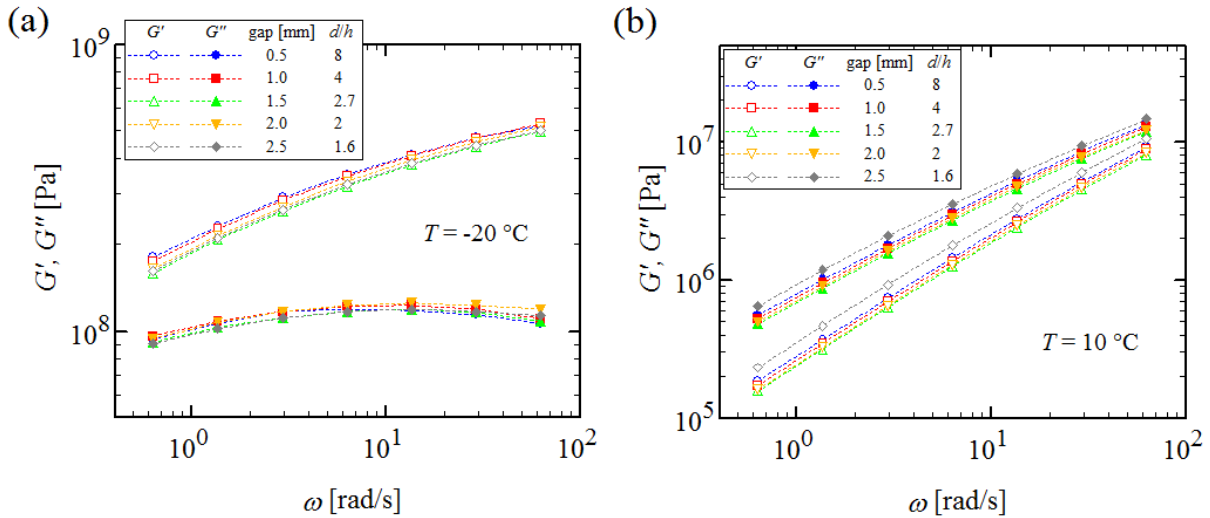
20 **Analysis of small diameter-to-gap ratio**

21 As described by Schröter et al. (2006), instrument compliance effects can be reduced by
22 decreasing the plate diameter and/or by increasing the measurement gap. It is important to note,
23 however, that by doing this, the diameter-to-gap (d/h) ratio of the measurement geometry is
24 also decreased. For example, when using a 4-mm parallel plate geometry with typical gap
25 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
26 recommendation of ISO 6721-10 standard which says that the d/h ratio of a parallel plate
27 geometry should be preferably in the range of 10 to 50 for this geometry to be considered as
28 an absolute measuring system.

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

1 in inertia and secondary flow effects at high frequencies (Ewoldt et al. 2015; Lauger and Stettin
 2 2016). However, these experimental artifacts are usually present only when measuring
 3 rheological properties of low-viscosity liquids and are therefore not relevant for liquids that are
 4 characterized near and within the glassy state. Numerical calculations demonstrating that
 5 instrument and fluid inertia effects are typically not an issue in SDPP experiments are presented
 6 in Appendix B.

7 A more practical way to test whether a small d/h ratio has any influence on the measured
 8 rheological properties is to perform experiments at different gap heights. Figure 4 shows
 9 frequency sweep data for a soft bitumen grade (penetration (EN 1426): 145 dmm, Ring-and-
 10 Ball softening point (EN 1427): 39.8  C) measured with a 4-mm diameter parallel plate fixture
 11 at gaps ranging from 0.5 to 2.5 mm, corresponding to d/h ratios of 1.6 to 8. It is observed that
 12 the data measured at -20  C do not exhibit systematic gap dependence, the minor variability in
 13 the measurement data is due to the test repeatability (discussed more in detail later in this
 14 paper). However, at a higher temperature of 10  C, the data measured at 2.5 mm gap ($d/h =$
 15 1.6) deviates considerably from the data measured at gap heights of 2.0 mm and less ($d/h \geq 2$).
 16 This demonstrates the fact that the use of extremely large gaps / small d/h ratios becomes
 17 increasingly critical when material becomes softer. Based on the limited results presented here,
 18 the use of gap heights of 2 mm or less and d/h ratios of 2 or more is recommended when
 19 measuring in the temperature range where dynamic moduli values are higher than 10^5 Pa.



20
 21 **Fig. 4.** Gap or d/h ratio dependence of the measured dynamic moduli of bitumen at (a) -20  C
 22 and (b) 10  C.
 23

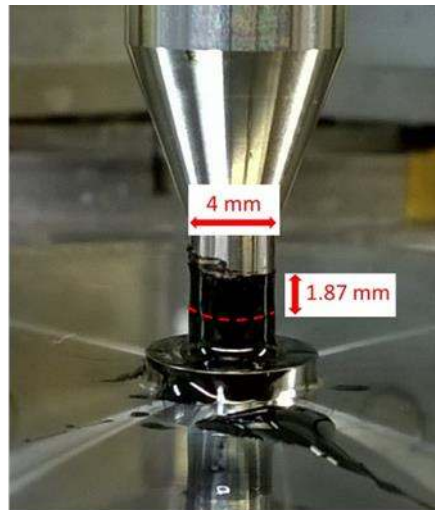
24 It is also notable that the free surface area-to-volume ratio increases with decreasing plate
 25 diameter ($A_{free\ surface}/V \sim 1/d$). Because of this, there are a couple of practical points that should
 26 be emphasized here. Firstly, this means that a high portion of the test specimen is exposed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

1 for this purpose. Secondly, the large free surface area-to-volume ratio sets a high standard for
2 the temperature control of the rheometer as the temperature of the surrounding gas needs to be
3 very carefully controlled in order to avoid temperature gradients within the test specimen. This
4 is a particularly important issue since the rheological properties of glass-forming liquids are
5 typically extremely temperature sensitive. Furthermore, it is noted that the thermal contact to
6 surrounding gas becomes relatively more important with decreasing d/h ratio as the ratio
7 between the area exposed to the gas and that in contact with the plates becomes larger (A_{free}
8 $surface/A_{plate\ contact} \sim h/d$). Any issues related to the chemical instability of the test specimen or to
9 the rheometer's temperature control would manifest themselves as gap-dependent rheological
10 data in an analysis similar to that shown in Fig. 4.

11

12 Specimen preparation and dimensional errors

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



22

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

26

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

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

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

17

18 **Measurement repeatability**

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

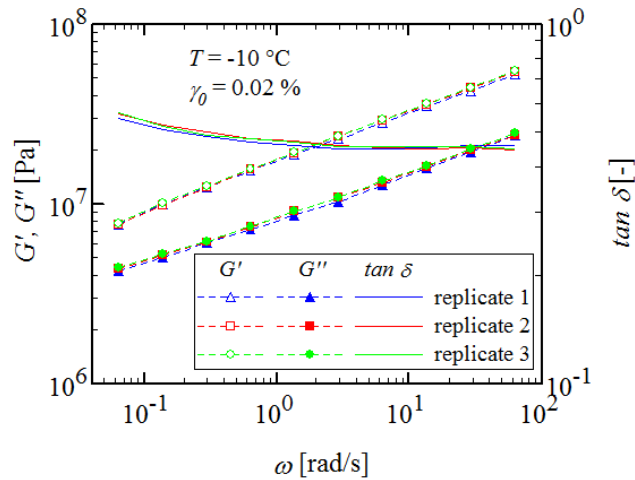


Fig. 6. Repeatability of 4-mm diameter parallel plate experiments demonstrated with frequency sweep data of SBS-modified bitumen.

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

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

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

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

14 **Current applications of SDPP rheometry**

15 At the time of writing, the most popular application area of SDPP rheometry is probably in the
16 field of asphalt research. As first demonstrated by Sui et al. (2010), 4-mm diameter parallel
17 plate geometry is particularly suitable for measuring rheological properties of bituminous
18 binders at low temperatures. In this application, the main advantage of SDPP rheometry – also
19 known as the “4-mm DSR” technique in the asphalt community – is that it requires only very
20 small amounts of material (~ 25 mg) as compared to the more traditionally used bending beam
21 rheometer (BBR) test method (~ 15 g). Based on the 4-mm parallel plate technique, a new low-
22 temperature performance-grading method has been proposed for bituminous binders (Sui et al.
23 2011). From a more scientific standpoint, the data obtained by SDPP rheometry has recently
24 led to the description of bitumen as a complex glass-forming liquid (Laukkanen et al. 2016b;
25 Laukkanen et al. 2017).

26 SDPP rheometry has also been employed to study glassy dynamics of various simple, small-
27 molecule glass-forming liquids. Among the most well-established studies in this field are the
28 ones carried out by McKenna and coworkers (Hutcheson and McKenna 2008; Schröter et al.
29 2006).³ In these investigations, the importance of instrument compliance corrections has been
30 highlighted, and it has been shown that the stress relaxation in simple glass-forming liquids
31 generally follows the Kohlrausch-Williams-Watts (KWW) stretched exponential function
32 (Kohlrausch 1854; Williams and Watts 1970). More recently, Möbius et al. (2010) employed
33 SDPP rheometry to study the effect of solidification and slush formation on the rheological
34 properties of supercooled glycerol during physical aging.

³The 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.

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

10 **Conclusions**

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

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

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33 **Appendix A. Derivation of the instrument compliance correction equations**

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

$$36 \theta_m = \theta_s + \theta_i \quad (5)$$

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

1 $K = \frac{M}{\theta}$ (6)

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

5 $\frac{1}{K_m} = \frac{1}{K_s} + \frac{1}{K_i}$ (7)

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

7 $J_i = \frac{1}{K_i}$ (8)

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

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

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

12 $K = \frac{G}{k_g}$ (10)

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

15 $k_g = \frac{2h}{\pi R^4}$ (11)

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

20 $G_s^* = \frac{G_m^*}{1 - \frac{J_i}{k_g} G_m^*}$ (12)

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

22 $G_s' + iG_s'' = \frac{G_m' + iG_m''}{1 - \frac{J_i}{k_g}(G_m' + iG_m'')}$ (13)

23

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)).

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

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

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

4 and the loss tangent of the sample becomes:

$$5 \quad \tan \delta_s = \frac{G''_s}{G'_s} = \frac{G''_m}{G'_m \left(1 - \frac{J_i}{k_g} G'_m\right) - \frac{J_i}{k_g} G''^2} \quad (3)$$

6

7 **Appendix B. Analysis of the effective measurement range of SDPP** 8 **rheometry**

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

$$12 \quad G_{min} = \frac{F_\sigma T_{min}}{\gamma_0} \quad (14)$$

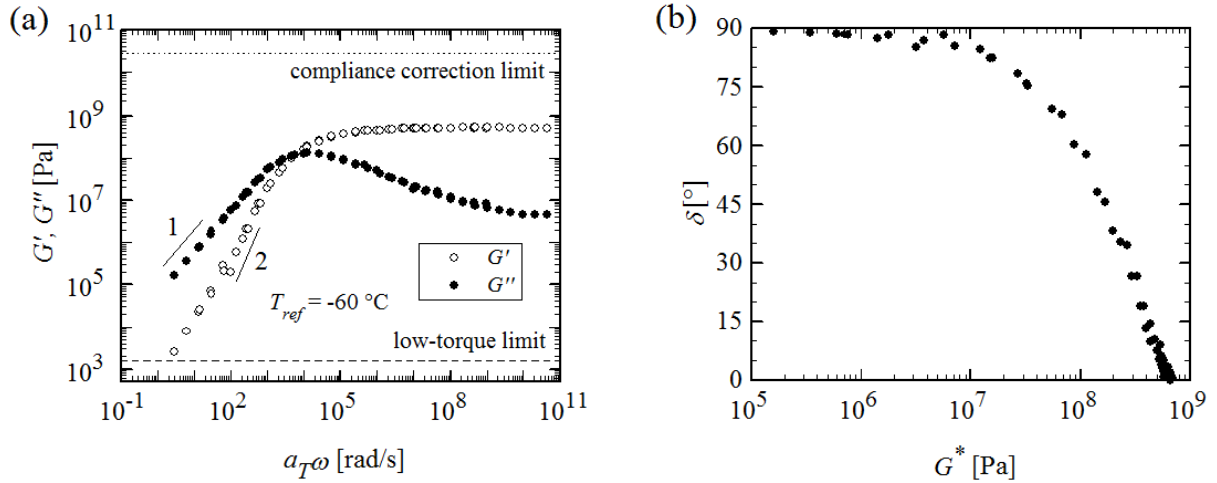
13 where F_σ is a geometry factor that correlates the applied torque T to the shear stress σ , T_{min} is
14 the minimum torque of the rheometer in oscillation, and γ_0 is the strain amplitude. G_{min} refers
15 to either G' or G'' , whichever is smaller. For the parallel plate geometry:

$$16 \quad F_\sigma = \frac{\sigma}{T} = \frac{2}{\pi R^3} \quad (15)$$

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

30 The upper stiffness limit of the effective measurement range of SDPP rheometry is practically
31 determined by the recommendation that the ratio between the angular displacement due to
32 instrument compliance and the angular displacement due to sample deformation should be less
33 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.
34 (12), the critical $|G^*|$ value at which the aforementioned ratio becomes equal to 10 is 27.9 GPa.

1 This value is much higher than the glassy modulus of any known glass-forming liquid.
 2 Therefore, in most cases, there is no practical upper stiffness limit for using SDPP rheometry.
 3 Fig. 7(b) shows this same data set plotted in the van Gorp-Palmen plot of phase angle versus
 4 $\log|G^*|$. The purpose of this plot is to demonstrate that even very liquid-like samples can be
 5 characterized by SDPP rheometry, i.e. phase angle values close to 90° can be reliably
 6 measured. Therefore, it can be concluded that this technique is applicable for the rheological
 7 characterization of glass-forming liquids even well above the glass transition temperature,
 8 which is not possible by using torsion bar or DMA techniques.



9

10 **Fig. 7.** (a) Dynamic moduli master curves and (b) the Booy-Palmen plot for a petroleum oil.
 11 The data were measured with 4-mm diameter parallel plate geometry. In part (a), the dashed
 12 line indicates the low-torque limit, $G_{min} = 1.59$ kPa, from Eq. (14) ($T_{min} = 0.01$ μNm , $R = 2$ mm,
 13 $\gamma_0 = 0.05$ %), and the dotted line corresponds to the upper stiffness limit due to the instrument
 14 compliance correction limitations, $|G^*|_{max} = 27.9$ GPa ($J_i = 0.01925$ rad/Nm, $R = 2$ mm, $h = 1.5$
 15 mm).

16

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

$$24 \quad G_{iner,inst} = \varepsilon \frac{F_\sigma I}{F_\gamma} \omega^2 \quad (16)$$

25 where $G_{iner,inst}$ is artificial inertial moduli, ε is the error in the instrument inertia value used for
 26 the corrections, F_γ is a geometry factor that correlates the applied angular deformation θ to the
 27 shear strain γ , I is the combined moment of inertia of the rotating parts of the rheometer (motor,
 28 air bearing, optical encoder, motor axis with geometry coupling, and measuring geometry), and
 29 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 $I = 13.4 \mu\text{Nm}\cdot\text{s}^2$, $R = 2 \text{ mm}$, 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.

29

30 **References**

- 31 Christensen T, Olsen NB (1995) A Rheometer for the Measurement of a High Shear Modulus
 32 Covering More than Seven Decades of Frequency Below 50 kHz. Rev Sci Instrum
 33 66(10):5019-5031
- 34 Dessi C, Tsibidis GD, Vlassopoulos D, De Corato M, Trofa M, D'Avino G, Maffettone PL,
 35 Coppola S (2016) Analysis of Dynamic Mechanical Response in Torsion. J Rheol 60(2):275-
 36 287

- 1 Ewoldt RH, Johnston MT, Caretta LM (2015) Experimental Challenges of Shear Rheology:
2 How to Avoid Bad Data. In: Spagnolie SE (ed) *Complex Fluids in Biological Systems*,
3 Springer, pp. 207-241
- 4 Farrar M, Sui C, Salmans S, Qin Q (2015) Determining the Low Temperature Rheological
5 Properties of Asphalt Binder using a Dynamic Shear Rheometer (DSR). Technical White
6 Paper FP08 Prepared by Western Research Institute for the Federal Highway Administration,
7 Contract no. DTFH61-07-D-00005, *Fundamental Properties of Asphalts and Modified*
8 *Asphalts, III*.
- 9 Franck A (2006) Understanding Instrument Compliance Correction in Oscillation. TA
10 Instruments Product Note APN 013
- 11 Gottlieb M, Macosko C (1982) The Effect of Instrument Compliance on Dynamic
12 Rheological Measurements. *Rheol Acta* 21(1):90-94
- 13 Harrison G (1976) *The Dynamic Properties of Supercooled Liquids*, Academic Press, London
14 and New York, p. 112
- 15 Hutcheson S, McKenna G (2008) The Measurement of Mechanical Properties of Glycerol,
16 M-Toluidine, and Sucrose Benzoate Under Consideration of Corrected Rheometer
17 Compliance: An in-Depth Study and Review. *J Chem Phys* 129(7):074502
- 18 Inoue T, Matsumoto A, Nakamura K (2013) Dynamic Viscoelasticity and Birefringence of
19 Poly (Ionic Liquids) in the Vicinity of Glass Transition Zone. *Macromolecules* 46(15):6104-
20 6109
- 21 Kohlrausch R (1854) Theorie Des Elektrischen Rückstandes in Der Leidener Flasche.
22 *Annalen Der Physik* 167(2):179-214
- 23 Läger J, Stettin H (2016) Effects of Instrument and Fluid Inertia in Oscillatory Shear in
24 Rotational Rheometers. *J Rheol* 60(3):393-406
- 25 Läger J (2010) Radial Compliance in Oscillatory Measurements. Technical Note, Anton
26 Paar Rheometers
- 27 Laukkanen O, Winter HH, Soenen H, Seppälä J (2017) From Simple to Complex Glass-
28 Forming Liquids: Broadening of the Glass Transition as Studied by Shear Rheology. *Annu*
29 *Trans Nord Rheol Soc* , 25:157-161
- 30 Laukkanen O, Winter HH, Soenen H, Seppälä J (2016a) Rheological Characterization of
31 Styrene-Butadiene-Styrene Block Copolymer Modified Bitumens. *Annu Trans Nord Rheol*
32 *Soc* 24:53-57
- 33 Laukkanen O, Winter HH, Soenen H, Seppälä J (2016b) Rheological Analysis of Bitumen as
34 a Complex Glass-Forming Liquid and Comparison with some Simple Glass-Forming
35 Liquids. *Annu Trans Nord Rheol Soc* 24:17-21
- 36 Laukkanen O (2015). Low-temperature rheology of bitumen and its relationship with
37 chemical and thermal properties. Master's thesis. Aalto University. Espoo, Finland.

- 1 Laukkanen O, Winter HH, Soenen H (2015) Rheological Analysis of the Low-Temperature
2 Dynamics of Bitumens. *Annu Trans Nord Rheol Soc* 23:23-26
- 3 Liu C, Yao M, Garritano RG, Franck AJ, Bailly C (2011) Instrument Compliance Effects
4 Revisited: Linear Viscoelastic Measurements. *Rheol Acta* 50(5-6):537-546
- 5 Lu X, Uhlback P, Soenen H (2016) Investigation of Bitumen Low Temperature Properties
6 using a Dynamic Shear Rheometer with 4mm Parallel Plates. *Int J Pavement Res Technol*.
7 <http://dx.doi.org/10.1016/j.ijprt.2016.08.010>
- 8 Lu X, Soenen H, Redelius P (2011) Rheological Characterization of Polymer Modified
9 Bitumens. *Ann Trans Nordic Rheol Soc* 19:77-84
- 10 Macosko C, Davis W (1974) Dynamic Mechanical Measurements with the Eccentric
11 Rotating Disks Flow. *Rheol Acta* 13(4-5):814-829
- 12 Maeda A, Inoue T, Sato T (2013) Dynamic Segment Size of the Cellulose Chain in an Ionic
13 Liquid. *Macromolecules* 46(17):7118-7124
- 14 Marin G (1988) Oscillatory Rheometry. In: Collyer AA and Clegg DW (ed) *Rheological*
15 *Measurements*, Elsevier, London, UK, pp. 297-343
- 16 Möbius M, Xia T, van Saarloos W, Orrit M, Van Hecke M (2010) Aging and Solidification
17 of Supercooled Glycerol. *J Phys Chem B* 114(22):7439-7444
- 18 Nill T (2014) Extended Application Report: Measurement of Glycerol in the Glassy State.
19 Investigation and Correction of Instrument Radial Compliance. Application report, Anton
20 Paar Germany GmbH
- 21 Piccirelli R, Litovitz T (1957) Ultrasonic Shear and Compressional Relaxation in Liquid
22 Glycerol. *J Acoust Soc Am* 29(9):1009-1020
- 23 Pogodina N, Nowak M, Läger J, Klein C, Wilhelm M, Friedrich C (2011) Molecular
24 Dynamics of Ionic Liquids as Probed by Rheology. *J Rheol* 55(2):241-256
- 25 Rides M, and Olusanya A (1996) Appendix A.2. Compliance Correction. In: Olusanya A (ed)
26 *A Comparison of Techniques for Monitoring the Cure of Adhesives*. MTS Adhesives Project
27 5, Measurements for Optimising Adhesives Processing Report 10, NPL Report
28 CMMT(B104), National Physical Laboratory, Teddington, Middlesex, UK, pp. 33-39
- 29 Scarponi F, Comez L, Fioretto D, Palmieri L (2004) Brillouin Light Scattering from
30 Transverse and Longitudinal Acoustic Waves in Glycerol. *Physical Review B* 70(5):054203
- 31 Schrag JL (1977) Deviation of Velocity Gradient Profiles from the “gap Loading” and
32 “surface Loading” Limits in Dynamic Simple Shear Experiments. *Trans Soc Rheol*
33 21(3):399-413
- 34 Schröter K, Hutcheson S, Shi X, Mandanici A, McKenna G (2006) Dynamic Shear Modulus
35 of Glycerol: Corrections due to Instrument Compliance. *J Chem Phys* 125(21):214507

- 1 Schröter K, Donth E (2000) Viscosity and Shear Response at the Dynamic Glass Transition
2 of Glycerol. *J Chem Phys* 113(20):9101-9108
- 3 Shi X, Mandanici A, McKenna GB (2005) Shear Stress Relaxation and Physical Aging Study
4 on Simple Glass-Forming Materials. *J Chem Phys* 123(17):174507
- 5 Soenen H, Lu X, Redelius P (2008) The Morphology of Bitumen-SBS Blends by UV
6 Microscopy: An Evaluation of Preparation Methods. *Road Mater Pavement* 9(1):97-110
- 7 Sui C, Farrar MJ, Harnsberger PM, Tuminello WH, Turner TF (2011) New Low-
8 Temperature Performance-Grading Method. *Transp Res Rec* 2207(1):43-48
- 9 Sui C, Farrar MJ, Tuminello WH, Turner TF (2010) New Technique for Measuring Low-
10 Temperature Properties of Asphalt Binders with Small Amounts of Material. *Transp Res Rec*
11 2179(1):23-28
- 12 Williams G, Watts DC (1970) Non-Symmetrical Dielectric Relaxation Behaviour Arising
13 from a Simple Empirical Decay Function. *Trans Faraday Soc* 66:80-85
- 14 Winter HH (1997) Analysis of Dynamic Mechanical Data: Inversion into a Relaxation Time
15 Spectrum and Consistency Check. *J Non Newtonian Fluid Mech* 68(2-3):225-239
- 16 Xia T, Xu J, Huang T, He J, Zhang Y, Guo J, Li Y (2016) Viscoelastic Phase Behavior in
17 SBS Modified Bitumen Studied by Morphology Evolution and Viscoelasticity Change.
18 *Constr Build Mater* 105:589-594
- 19 Zhu J, Lu X, Balieu R, Kringos N (2016a) Modelling and Numerical Simulation of Phase
20 Separation in Polymer Modified Bitumen by Phase-Field Method. *Mater Des* 107:322-332
- 21 Zhu J, Lu X, Kringos N (2016b) Experimental Investigation on Storage Stability and Phase
22 Separation Behaviour of Polymer-Modified Bitumen. *Int J Pavement Eng*.
23 <http://dx.doi.org/10.1080/10298436.2016.1211870>
- 24