

# Rheology Bulletin



## Inside:

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**Phase Angle in Oscillatory Testing**  
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# How do I know if my phase angles are correct ?

$\delta?$

$\delta?$

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## 1. Introduction

A large fraction of rheological testing involves small-amplitude oscillatory shear, sometimes referred to as “dynamic” experiments, which yield the complex modulus  $G^*$  of the sample. The results of such tests are often represented in terms of the storage and loss moduli  $G'$  and  $G''$ , but it is conceptually useful to instead think of  $G^*$  in terms of its magnitude  $|G^*|$  and its phase angle  $\delta$ . How can these quantities be validated? If a rheometer reports, say,  $|G^*| = 12,755$  Pa, and  $\delta = 88.78$  degrees, how closely can the user trust these values?

The magnitude  $|G^*|$  can be validated easily with Newtonian calibration standards of known viscosity. There have also been excellent studies of the reproducibility  $|G^*|$  of molten polymers, which is important for quality control applications of rheometry<sup>1-5</sup>. Even in the absence of any rigorous validation, the specifications on the torque, angular displacement, and frequency range of the rheometer provide guidance on when the range or sensitivity of the instrument is exceeded, and hence large errors in  $|G^*|$  can be expected.

In contrast, it is much more difficult to judge the accuracy of the phase angle,  $\delta$ . We are not aware of studies that evaluate the accuracy of phase angle measurements. Furthermore, rheometer manufacturers do not provide specifications for phase angle, and hence there is no clear guidance on when the range or resolution of the rheometer is exceeded. It is not difficult to understand why phase angle specifications are generally missing: phase angle resolution and accuracy will surely depend on the quality of the torque and angular displacement signals. Approaching the low end of the torque or displacement range, it might still be possible to measure the average magnitudes of these signals (allowing determination of  $|G^*|$  within some well-defined, reasonable certainty), while the signal quality becomes too poor to accurately resolve the phase shift between them. How can a rheologist establish conditions under which his or her rheometer can measure phase angles within some well-defined certainty?

A broad validation of phase angle measurements is beyond the scope of this short article. We will concentrate on

validating phase angle measurements close to 90 degrees. This is important for practical purposes, not least because  $\delta$  approaching 90 degrees corresponds to the terminal region of most viscoelastic materials, where significant connections between the rheology and structure can be made. For example, fluids such as entangled polymer melts and polymer solutions generally show “standard” liquid-like terminal behavior ( $G' \sim \omega^2$  and  $G'' \sim \omega$ ), which can be often be related quantitatively to specific microscale dynamic processes. In other cases, e.g. block copolymers, gels, or particle-filled systems, we are often interested in deviations from standard liquid-like terminal behavior to help identify, for example, an order-disorder transition or a liquid-to-gel transition. A recent article<sup>6</sup> in the *Rheology Bulletin* has also discussed the challenge of measuring terminal viscoelastic properties in the context of calculating the relaxation function  $G(t)$ .

When attempting to validate phase angle measurements, a significant problem is the choice of a viscoelastic standard for calibration: while viscosity standards are readily available, materials with standard viscoelastic properties are less easy to come by. In the absence of standards, some laboratories validate a  $\delta = 90$  degrees using a Newtonian fluid,  $\delta = 0$  degrees using a steel test specimen, and presume that phase angles between 0 and 90 degrees are accurate. Some rheology labs have a standard PDMS putty with a broad spectrum of relaxation times whose phase angle at a particular temperature and frequency has been specified by the supplier. The National Institute for Standards and Technology (NIST) has developed standard reference materials for viscoelastic measurements, most recently the SRM 2490 and SRM 2491 polymer solution and melt<sup>7,8</sup>. However most laboratories do not have these fluids, and some questions have also been raised about the validity of the viscoelastic specifications given for SRM 2490<sup>9</sup>. It would be very useful for experimental rheologists to have a testing protocol, along with different viscoelastic calibration standards, to validate oscillatory measurements on their own rheometers.

Here we show that a linear, monodisperse, and well-entangled polymer melt can serve as an excellent viscoelastic calibration standard when  $\delta$  is close to 90 degrees. Such a material has a sharp transition to its

terminal region as frequency is reduced (see details<sup>†</sup>), and thus is in the terminal region even when  $\delta$  is still far from 90 degrees, and hence still easy to measure. Phase angles close to 90 degrees can then be validated by verifying that the rheometer reproduces the expected terminal behavior ( $\tan\delta$  proportional to  $1/\omega$ ) at lower frequencies.

In essence, this phase angle validation is a test of self-consistency of the rheometer: (1) use the rheometer to characterize the terminal behavior of the fluid when  $\delta$  is not very close to 90 degrees, and (2) use the now-characterized terminal behavior to test the rheometer performance under adverse conditions (e.g.  $\delta$  approaching 90 degrees closely, lower displacements, lower torques, etc.)

## 2. A brief primer on dynamic oscillatory measurements

### Theory

Most dynamic oscillatory tests are performed in controlled strain mode. A sinusoidally-varying strain:

$$\gamma = \gamma_0 \sin(\omega t) \quad (1)$$

is imposed on the sample. Here  $\omega$  is the frequency and  $\gamma_0$  is the strain amplitude. The stress in the sample follows:

$$\sigma = \sigma_0 \sin(\omega t + \delta) = |G^*| \gamma_0 \sin(\omega t + \delta) \quad (2)$$

where  $\sigma_0$  is the stress amplitude and  $|G^*|$  is the magnitude of the complex modulus. Most commonly, analysis is performed in terms of the storage and loss moduli:

$$\sigma = \gamma_0 [G' \sin(\omega t) + G'' \cos(\omega t)] \quad (3)$$

$$\text{where } G' = |G^*| \cos(\delta) \text{ and } G'' = |G^*| \sin(\delta) \quad (4)$$

Even if the tests are performed in controlled stress mode, the same equations can be used to calculate the moduli. We can take the first step in error analysis as:

$$dG' = \cos(\delta) d|G^*| - |G^*| \sin(\delta) d\delta \quad (5)$$

$$\frac{dG'}{G'} = \frac{d|G^*|}{|G^*|} - \tan(\delta) d\delta \quad (6)$$

<sup>†</sup> Any linear viscoelastic fluid can be represented as a sum of Maxwell modes. In a linear, monodisperse, well-entangled polymer, higher order relaxation modes are much faster and much weaker than the longest mode. Therefore the terminal region, i.e. the region in which the longest mode dominates, ranges from  $\tan\delta \rightarrow \infty$  ( $\delta = 90$  degrees) down to about  $\tan\delta \approx 10$  ( $\delta \approx 84$  degrees). In contrast, in most other fluids, higher order modes become important when  $\tan\delta$  is still large ( $\delta$  is still close to 90 degrees).

$$\text{Similarly, } \frac{dG''}{G''} = \frac{d|G^*|}{|G^*|} + \frac{d\delta}{\tan(\delta)} \quad (7)$$

In Eqs. 6 and 7 above, the left hand side is the fractional error in  $G'$  and  $G''$ , the first term on the right hand side is the fractional error in the magnitude of the complex modulus, and the last term reflects the error in measuring phase angle. It is clear that as  $\delta$  approaches 90 degrees, the fractional error in  $G'$  grows without bound even when the error in phase angle  $d\delta$  remains finite. This is just a quantitative way of stating that it is difficult to characterize the elasticity of weakly-viscoelastic materials. The situation is reversed when  $\delta$  approaches 0 degrees: then the error in  $G''$  becomes large, whereas the error on  $G'$  remains finite. In short, when one modulus is much smaller than the other, little of the total signal comes from the response associated with the smaller modulus, and more error is likely in its measurement. Here, we will focus on the case of  $\delta$  approaching 90 degrees, where the elasticity is becoming very weak.

The above equations suggest that rather than  $\delta$  itself, it is better to work in terms of  $\tan\delta$  (or  $1/\tan\delta$ ) since these directly relate to the accuracy and precision of the dynamic moduli. We will reiterate this point at the end of the following section.

### Practical measurements

Assuming a parallel plate geometry with plates of diameter  $2R$  and gap of  $h$ , oscillatory measurements generally depend on applying a displacement:

$$\theta = \theta_0 \sin(\omega t) \quad (8)$$

and measuring a torque:

$$T = T_0 \sin(\omega t + \delta) \quad (9)$$

Here  $\theta_0$  and  $T_0$  are the displacement and torque amplitudes respectively. For the parallel plate geometry, one can obtain<sup>10</sup>:

$$\gamma_0 = \frac{R\theta_0}{h} ; \sigma_0 = \frac{2T_0}{\pi R^3} , \text{ and hence } |G^*| = \frac{\sigma_0}{\gamma_0} = \frac{2T_0 h}{\pi R^4 \theta_0} \quad (10)$$

Slightly different equations can be derived for other measurement geometries<sup>10</sup>. Thus, dynamic oscillatory measurements on rotational rheometers depend on measuring three quantities:  $\theta_0$ ,  $T_0$  and  $\delta$ . Conceptually, these three quantities can be measured by plotting the displacement and torque signals, as illustrated in Fig. 1. The factors limiting the accuracy of  $\tan\delta$  are clear from this diagram: As with any experimentally-determined quantities, there are some errors associated with measuring displacement and torque. For example, if  $\theta_0$  or  $T_0$  are

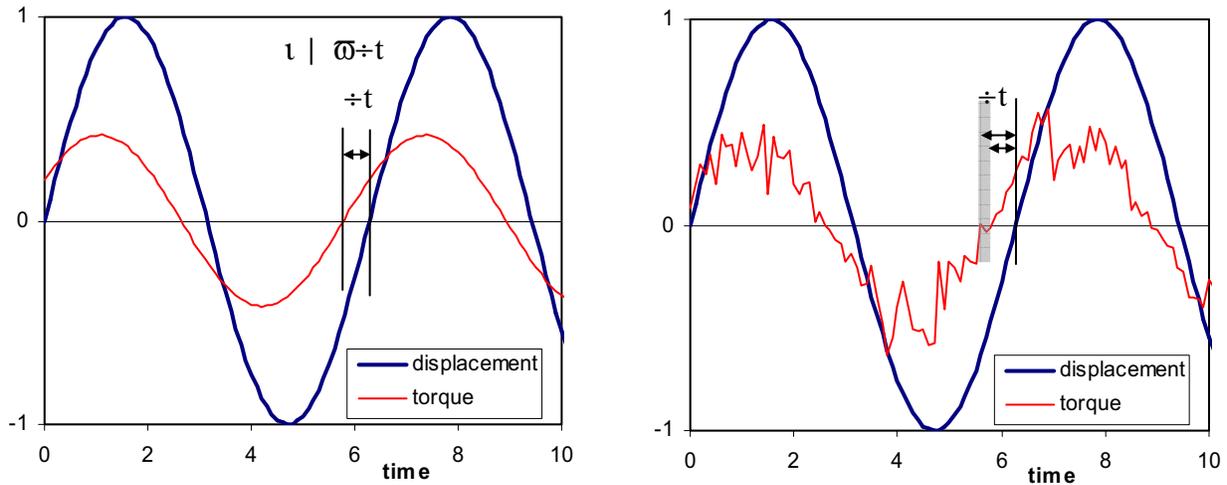


Fig. 1: a. The zero crossing of the sinusoidal displacement and torque signals give the phase lag, from which the phase angle  $\delta$  can be calculated. b. If the one or both of the signals are noisy, it will cause some uncertainty in the zero crossing (illustrated by the shaded line), and hence error in measuring  $\delta$ .

small, the displacement and torque signals can show substantial noise, as illustrated in Fig. 1; such noise was indeed evident in our experiments (discussed below) at small displacements or torques. There may also be minor drifts in the instrument baseline (e.g. the residual torque in an air bearing) over the timescale of a single oscillation. Regardless of cause, these errors in displacement and torque cause errors in the phase angle.

Early rheologists measured  $\theta_0$ ,  $T_0$  and  $\delta$  quite literally as illustrated in Fig. 1 by plotting the torque and displacement signals output from the rheometer on chart paper (see Appendix 2 in Walters<sup>11</sup> for a detailed graphical procedure). Modern rheometers on the other hand use signal processing techniques, often in the digital domain, to obtain phase angles from the raw signals. One approach is to use a cross-correlation method of beating the torque against two reference signals, one in phase with the displacement and the other 90 degrees out of phase with the displacement<sup>10</sup>:

$$S_1 = \frac{\omega}{\pi N} \int_0^{2\pi N} T \sin(\omega t) dt = T_0 \cos \delta \quad ;$$

$$S_2 = \frac{\omega}{\pi N} \int_0^{2\pi N} T \cos(\omega t) dt = T_0 \sin \delta \quad (11)$$

where  $N$  is the number of cycles. Thus, the  $T_0$  and the phase angle can be obtained independently:

$$T_0 = \sqrt{S_1^2 + S_2^2} \quad \text{and} \quad \tan \delta = \frac{S_2}{S_1} \quad (12)$$

Once again we note that it is  $\tan \delta$ , and not  $\delta$ , that is the more natural quantity for analysis. Actual implementation of Eqs. 11 and 12 change from one instrument to another, the raw signals are often digitized before any analysis, and inertial corrections and baseline subtraction may be an integral part of the analysis.

### 3. Experiments and results

The fluid used was Liquid Isoprene Rubber (LIR50), a linear monodisperse 1,4-polyisoprene (high cis content) supplied by Kuraray Corp. This polymer was made by anionic polymerization and had a molecular weight of  $\sim 45000$  kg/mol and polydispersity of less than 1.1. All tests were performed using the AR2000 rheometer with a 40 mm or 25 mm parallel plate geometry with gaps ranging from 0.5 to 2 mm, at a temperature of 25°C maintained with a Peltier plate. The rheometer was mounted on a vibration-isolated platform and leveled. Samples were loaded without air bubbles and excess sample was “trimmed” from the edges when the gap was 10% larger than the desired gap. All tests were performed using the default settings for oscillatory testing (“Continuous oscillation”, conditioning time and sampling time both being 3 s or 1 cycle, whichever is longer).

#### 3.1. Validation of phase angles : Constant-strain frequency sweep experiments

A common oscillatory test sequence involves conducting a single oscillatory measurement at each frequency in a specified frequency range, with the strain amplitude being kept constant throughout the frequency range. This test

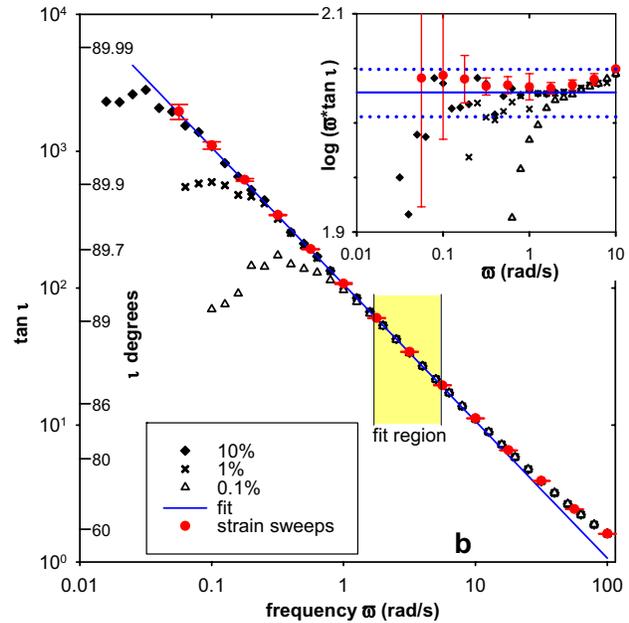
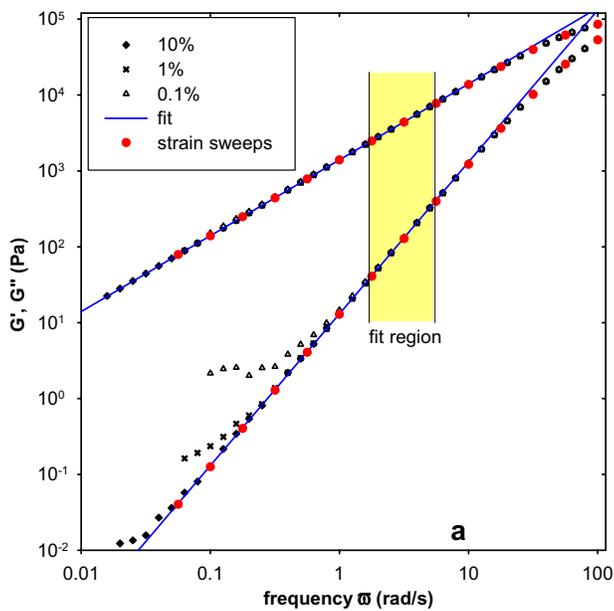


Fig. 2: Black symbols are a. oscillatory moduli from frequency sweep experiments at three different strain amplitudes. b.  $\tan\delta$  from the same experiment. Red symbols are data from strain sweep experiments of Fig. 3. Thin blue lines are terminal behavior (Eqs. 13) fitted to the 0% strain data within the shaded yellow rectangles. Inset to b. shows the  $\tan\delta$  results in a form more suitable to identifying deviation from terminal behavior. In the inset, solid blue line shows the terminal behavior (Eqs. 13), and dotted blue lines show 5% deviation from the terminal behavior.

sequence is often called a “frequency sweep” test in the software associated with many rheometers. The black diamonds in Figs. 2 a&b show the results of a frequency sweep test performed at a strain amplitude of 10%, which is within the linear viscoelastic limit. As expected, this linear, monodisperse, entangled polymer shows terminal behavior down to fairly small  $\tan\delta$  values of about 10. There is therefore a range of frequencies (illustrated by the yellow region in Figs. 2 a&b) in which two conditions are satisfied: the material is in the terminal regime, *and* the instrument can be expected to measure  $\tan\delta$  reliably. We can therefore establish the terminal behavior of this material:

$$G' = 13.13\omega^2 ; G'' = 1401\omega ; \tan\delta = \frac{106.7}{\omega} \quad (13)$$

The accuracy of oscillatory measurements as  $\delta$  approaches 90 degrees can now be tested by examining deviations from this behavior at lower frequencies. Indeed the data do deviate from the expected terminal behavior. Such deviations are more clearly evident when the product of  $\tan\delta$  and frequency – which is expected to be constant in the terminal region – is plotted vs. frequency (see inset to Fig. 2b). If we regard a 5% error on  $\tan\delta$  as acceptable, at 10% strain it appears that oscillatory measurements are accurate up to  $\tan\delta$  on the order of 1000 ( $\delta \approx 89.94$  degrees). This simple test to validate phase angle measurements can be performed *only* because the fluid is monodisperse and well-entangled, i.e. the phase angle validation is crucially dependent on the assumption that

the correct terminal behavior can be captured from phase angle data far from  $\delta = 90$  degrees.

Upon repeating the frequency sweep tests at lower strains, the rheometer makes significant errors at large  $\tan\delta$ , e.g. at 0.1% strain, it is not possible to measure a  $\tan\delta$  of even 100 ( $\delta = 89.4$  degrees) accurately. However, small values of  $\tan\delta$  can still be measured accurately. In other words, as  $\tan\delta$  increases ( $\delta$  approaches 90 degrees), an increasingly larger strain amplitude is necessary for accurate measurements. This immediately suggests that the accuracy of frequency sweep tests can be improved by increasing the strain amplitude as  $\tan\delta$  increases. This will be discussed in more detail below.

### 3.2. Instrumental limits for phase angle accuracy: A strain-sweep protocol

A key finding of Fig. 2 is that at small strain, there can be significant errors in measuring  $\tan\delta$ . It is therefore of immediate interest to find the minimum strain,  $\gamma_{\min}$ , required for measuring  $\tan\delta$  within a specified error, say 5%. To characterize this  $\gamma_{\min}$  as a function of  $\tan\delta$ , we conducted strain sweep tests at several different frequencies. Fig. 3 shows a typical sample of the results. At each frequency, the measured values of  $\tan\delta$  show a plateau at sufficiently high strain amplitude, and a deviation from the plateau at low strain amplitude. We will discuss these features in succession.

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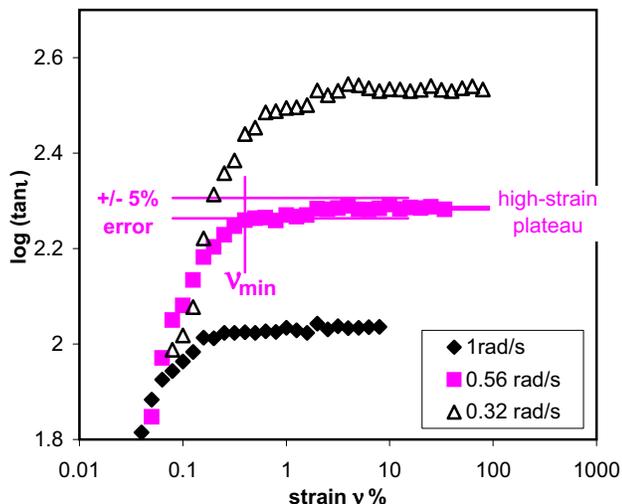


Fig. 3: Typical strain sweep measurements at three different frequencies. The horizontal lines show +/- 5% error limits for  $\tan\delta$  at 0.56 rad/s. The vertical line identifies  $\gamma_{\min}$ , the minimum strain required for reliable phase angle measurement.

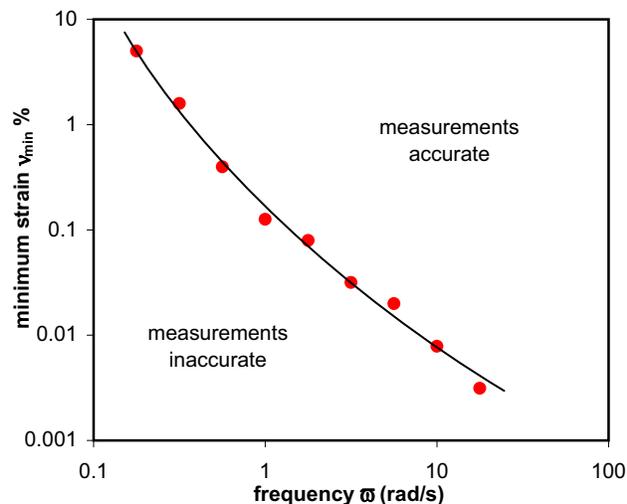


Fig. 4: Minimum strain amplitude,  $\gamma_{\min}$ , as a function of frequency. Red circles are the  $\gamma_{\min}$  values obtained from Fig. 3, and the line is a guide to the eye. For  $\omega \geq 20$  rad/s, the  $\gamma_{\min}$  was smaller than the smallest strain that could be applied by the rheometer for the geometry used. Data at  $\omega \leq 0.1$  have been excluded because the standard deviation on  $\tan\delta$  exceeded 5% (see inset to Fig. 2b).

The mean values of the high-strain plateau at each frequency have been added to Figs. 2a and b (red points). These mean values agree well with the previous frequency sweep data, and are all within 5% error of the expected terminal value. Thus, *on an average*, the AR2000 can measure large  $\tan\delta$  values – exceeding 1000 – accurately. However, the error bars in Fig. 2b show the standard deviation of the various points constituting the plateau. From these error bars it is clear that as  $\tan\delta$  approaches and exceeds about 1000 ( $\omega \sim 0.1$  rad/s), the standard deviation on  $\tan\delta$  increases sharply and can exceed 5% of the mean value (this is more clearly visible in the inset to Fig. 2b), i.e. *a single measurement* of  $\tan\delta$  is not likely to be within 5% error.

Fig. 3 also shows that with decreasing strain, the measured values of  $\tan\delta$  deviate, and reduce systematically from the plateau value. We can immediately identify the strain,  $\gamma_{\min}$ , below which most  $\tan\delta$  values are more than 5% in error; the procedure for doing so is illustrated at the frequency of 0.56 rad/s in Fig. 3. The values of  $\gamma_{\min}$  thus obtained are plotted as a function of frequency in Fig. 4. This diagram is a map of instrumental limitations when measuring phase angles: the region below the solid line, labeled “measurements inaccurate” is to be avoided when conducting measurements.

This map quantifies the observation already made in Section 3.1, viz. accurate phase angle measurements require increasingly larger strain amplitudes at low frequencies. Thus, a simple strategy to improving the accuracy of oscillatory measurements is: don’t conduct a frequency sweep test at *fixed* strain amplitude, instead,

increase the strain amplitude at low-frequency. The same strategy was proposed previously for improving the reproducibility of  $|G^*|^2$ . One convenient way of doing so is to perform a frequency sweep at fixed stress amplitude, so that the strain increases as frequency reduces ( $\gamma \sim \omega^{-1}$  for a material in its terminal region). Another convenient method is to use a “Minimum Torque” option available in some rheometers for strain-controlled frequency sweep tests. This option increases the strain amplitude beyond the specified value if the torque is less than a user-specified minimum value. It would be useful if the software also had provision to specify a maximum strain that should not be exceeded. In all such cases, when increasing the strain to improve the quality of oscillatory data, the rheologist must take care to remain in the linear viscoelastic region.

The form of Fig. 4, viz. the minimum strain vs. frequency, is not very practical because a different material may show a significantly different  $\gamma_{\min}$  vs.  $\omega$  behavior. For example, consider what would happen if the same test were repeated with a less elastic fluid for which  $\tan\delta$  at 1 rad/s is much higher, say 10,000. We certainly do not expect the rheometer to be able to measure accurately a  $\tan\delta$  of 10,000 – no matter how high the strain.

Therefore, we redraw Fig. 4 in a form that directly addresses the question: “What conditions should be met to measure any particular value of  $\tan\delta$  accurately?” In drawing such a map, we must avoid “derived” quantities such as strain, and instead use more basic parameters viz. the torque and the displacement. Accordingly, a better representation of the instrumental limits may be obtained

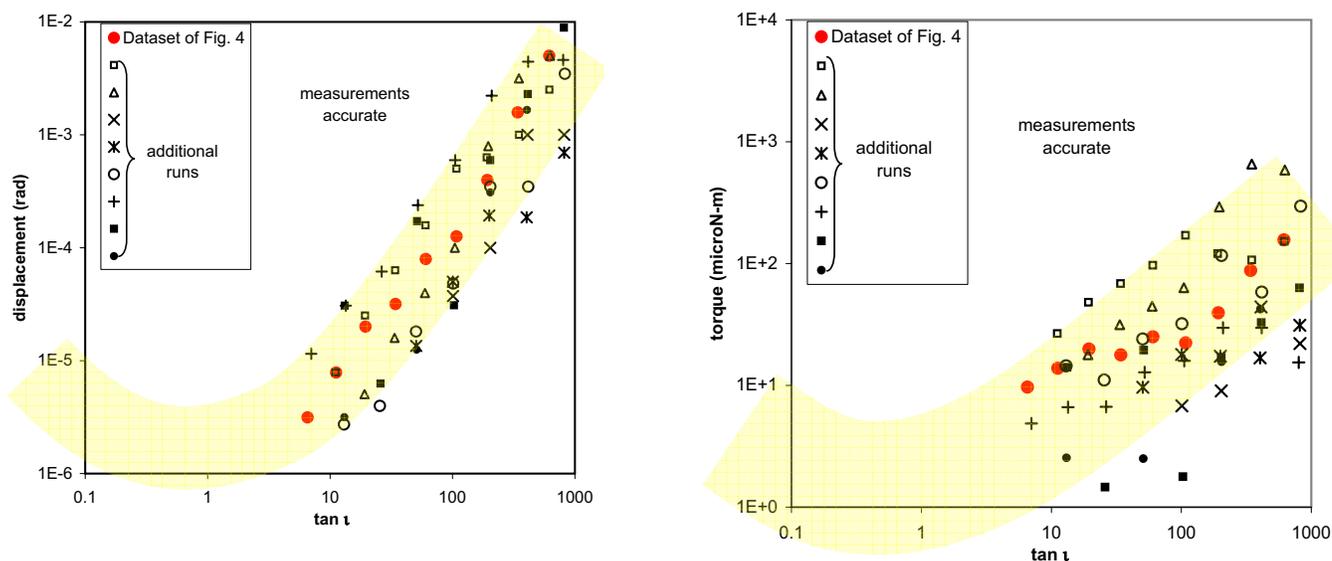


Fig. 5: Maps of instrument limits. Red circles are the torque and displacement corresponding to the same dataset as Fig. 4. Remaining symbols are various runs with different gaps and plate diameters.

by plotting the minimum torque  $T_{\min}$  and minimum displacement  $\theta_{\min}$  corresponding to each  $\gamma_{\min}$ , as a function of the  $\tan\delta$  corresponding to each frequency. Such a representation is shown in Fig. 5, where the red points correspond to the same dataset in Fig. 4.

We repeated the analysis of Fig. 3 several times over a period of a few months using parallel plate geometry with gaps ranging from 2 mm to 0.5 mm, and plate diameters of 40 mm or 25 mm. These data are also shown in Fig. 5. The broad yellow lines through the scattered points show the general trend: measuring higher  $\tan\delta$  requires increasingly higher amplitudes of the basic torque and displacement signals for the same (5%) error limits. There is substantial scatter in the minimum torque and displacement, i.e. in some runs, the specified level of performance (5% error on  $\tan\delta$ ) can be achieved under more adverse conditions, whereas in other runs, the same performance required much larger displacement and torque values. We are not certain why the instrument limits are so inconsistent; it may be due to uncontrollable factors such as minor changes in air bearing pressure, incidental vibrations, possible electrical noise, etc. It is important to emphasize that it is only the *minimum torque and displacement limits* of the rheometer that are not reproducible from one run to another; the  $\tan\delta$  values away from the limits (i.e. the plateaus in Fig. 3) were highly consistent. For accurate measurements, one must conduct experiments substantially above the minimum limits estimated in Fig. 5 so that irreproducibility of the limits does not affect the results.

In this article we have only been concerned with large values of  $\tan\delta$ . As mentioned in Section 2, at large  $\tan\delta$ , oscillatory measurements are limited by the error in  $G'$  which grows proportionately to  $\tan\delta$ . In the other extreme of  $\tan\delta$  approaching zero, oscillatory measurements are limited by the errors in  $G''$ , which grow proportionately to  $(\tan\delta)^{-1}$ . Thus we anticipate that with decreasing  $\tan\delta$ ,  $\theta_{\min}$  and  $T_{\min}$  will rise again; this is the reason why the broad yellow curves in Fig. 5 have been shown to have minima. Experiments with other fluids for which  $G'$  exceeds  $G''$  would be necessary to verify the upturn in the minimum torque or displacement for  $\tan\delta < 1$ .

Of these two parameters,  $\theta_{\min}$  or  $T_{\min}$ , which one is the more fundamental limiting factor? Our results of Figure 5 show a great deal of scatter, both for small changes in geometry and even for repeat tests using the same geometry. Therefore we are unable to answer this question here except to note that the range of scatter is larger for the torque than for the displacement. This argues for a displacement limit that is fundamental. Repeating these experiments with fluids with substantially different viscosity would help determine whether torque or displacement is the fundamental limiting factor.

#### 4. Closing comments

In summary, we have presented procedures to validate the accuracy of phase angle measurements as the phase angle approaches 90 degrees. They are easy to conduct and use readily available materials, viz. linear, monodisperse, well-entangled polymers, as calibration standards. Therefore

the test can be applied easily by any rheologist to test any specific rheometer.

In plotting the instrumental limits in the form of Fig. 5, we have presumed that the most important parameters that affect phase angle accuracy are the torque and the displacement. While this is eminently plausible, other factors may also play a role. For example, at high frequency, the accuracy of any inertial corrections, rather than limitations of torque or displacement, may dominate the performance limits. In the experiments in this paper, inertial effects were negligible over most of the frequency range.

We have used the polyisoprene LIR50, for phase angle validation because this is a linear, monodisperse, room temperature melt which was already available in a large quantity in our laboratory. Other rheologists may find it more convenient to select other model fluids, either polymer melts or solutions, that are more similar to their fluids of interest. As long as the fluid is monodisperse and well-entangled, the terminal region will extend over a wide range of  $\tan\delta$  and the procedure outlined here can be applied. In fact, the strain sweep procedure of Fig. 3 does not even need a model fluid: it will yield the *limits of resolution* of  $\tan\delta$  (Fig. 5) for any material and at any phase angle. However, without a model fluid, there will be no guarantee that the high-strain plateau values of Fig. 3 are correct; whereas with a linear monodisperse fluid such as LIR50, the same experiment will also validate the *accuracy* of  $\tan\delta$  as  $\delta$  approaches 90 degrees.

It is worth noting that in our strain-controlled experiments, while the AR2000 could measure phase angles quite close to 90 degrees, it never reported  $\delta$  values exceeding 90 degrees (i.e. negative values of  $\tan\delta$ ). This is somewhat surprising; the simple-minded expectation would be that the rheometer makes *random* errors in measuring phase angle, and hence as  $\delta$  approaches close to 90 degrees, measured values of  $\delta$  will fall on both sides of 90 degrees. We are not sure why the measured values of  $\delta$  remain below 90 degrees, but this may also be the reason why there are systematically-negative deviations of  $\tan\delta$  at low strain in Fig. 3.

The minimum torques and displacements required for accurate phase angle measurements (Fig. 5) are substantially larger than the minimum torque and displacement specifications quoted by the manufacturer. We suspect that specifications given for the AR2000, and perhaps for other rheometers, are only intended for  $G^*$  or  $\eta^*$ , and not for phase angle measurements. If so, the given specifications are of only limited use since oscillatory measurements *must* include the phase angle to give any information about viscoelasticity.

Despite this criticism, we want to comment that the AR2000 rheometer, and perhaps other comparable instruments, can measure very high values of  $\tan\delta$ —roughly on the order of 1000—within 5% accuracy,

provided signals are maintained above limits such as those of Fig. 5. This is remarkable performance, and better than we had expected prior to performing these tests. This level of performance was realized using the default test settings of the rheometer, and without taking any special precautions in sample loading, except to avoid bubbles: bubbles could give a large error in  $G'$  in the terminal region due to their surface tension elasticity.

### Acknowledgement

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