Unique Feature for Easier Rheological Measurements: Harmonic Distortion

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Introduction

Oscillation measurements, which can be performed with the Kinexus rotational rheometer, are used to characterize the viscoelastic properties of materials, for example, soft solids like gels or pastes, or complex fluids such as polymers, emulsions, or suspensions. In these experiments, a sinusoidal shear deformation (strain-controlled) or shear stress (stress-controlled) is applied, and the material's response is subsequently analyzed.

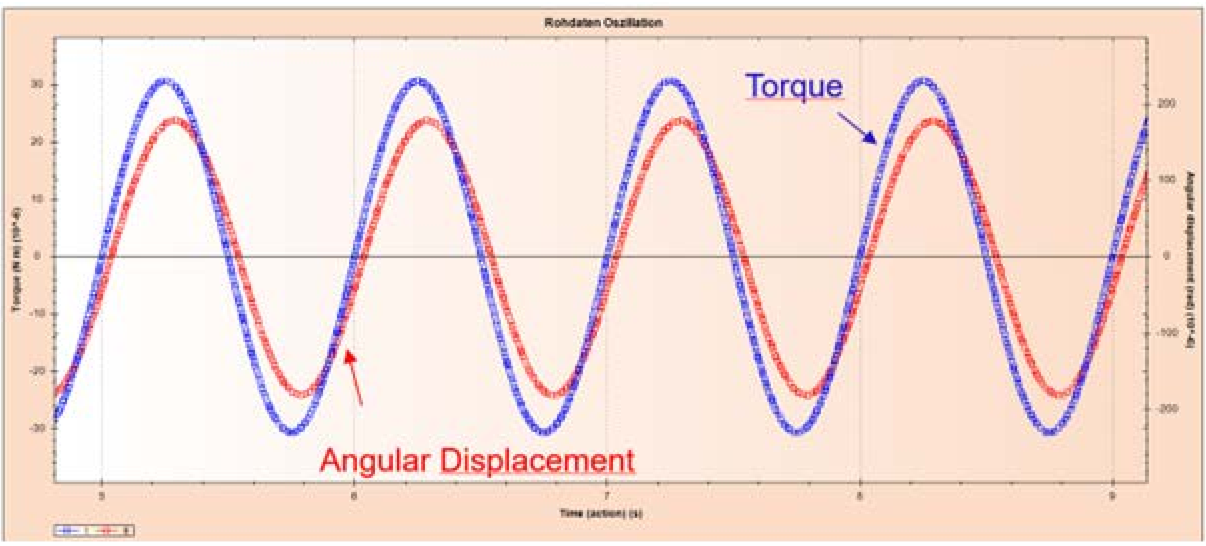
The main parameters obtained are:

- Storage shear modulus (G'), giving information about the "solid-like" behavior of the material.
- Loss shear modulus (G"), related to the "liquid-like" behavior of the material.
- Phase angle (δ): This parameter is indicative of the lag between the applied stress and strain, thereby facilitating determination of the material's behavior as either that of a solid (δ ≈ 0°) or that of a liquid (δ ≈ 90°).

Amplitude Sweep: Determination of the LVER (Linear Viscoelastic Region)

Oscillatory measurements are generally conducted within the linear viscoelastic region (LVER), where the material structure remains unaffected by the applied deformation. The LVER is determined by means of an amplitude sweep. This test determines the maximum deformation amplitude that can be used without leading to a breakdown of the material's structure for a defined frequency and temperature.

Within the LVER, input and output oscillation frequencies are the same (see figure 1).



1 Input signal (angular displacement, red) and output signal (torque, blue) within the linear range. Both signals have the same frequency.

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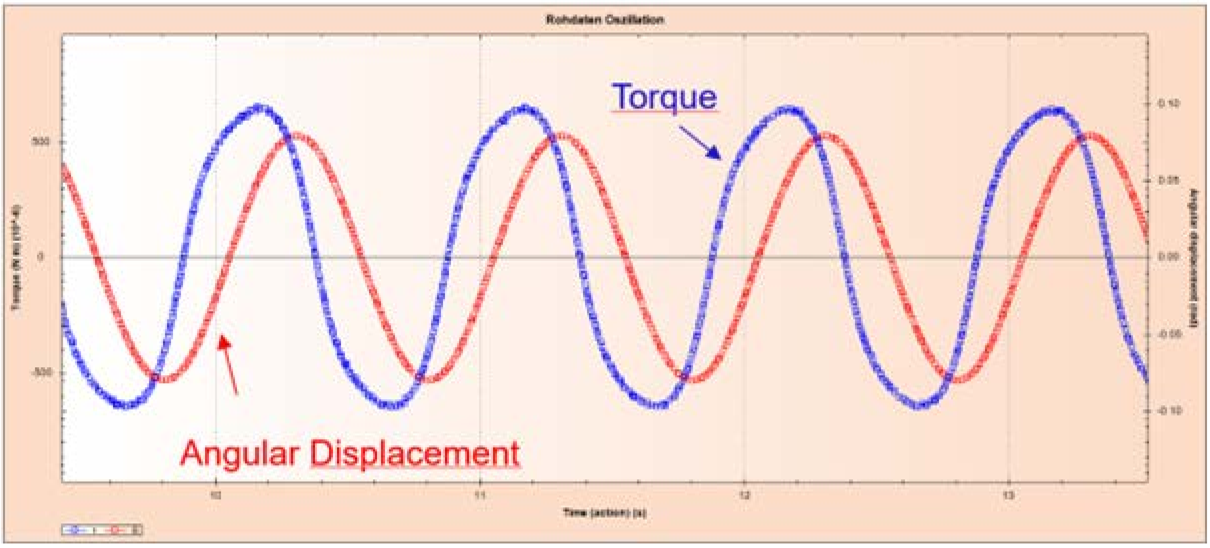
In contrast, beyond the LVER, excitation with sinusoidal shear wave leads to a non-sinusoidal response (figure 2). The input oscillation (for example, with a base frequency of 1 Hz) breaks down to oscillations of different harmonic frequencies; see figure 3.

Harmonic distortion is defined as follows:

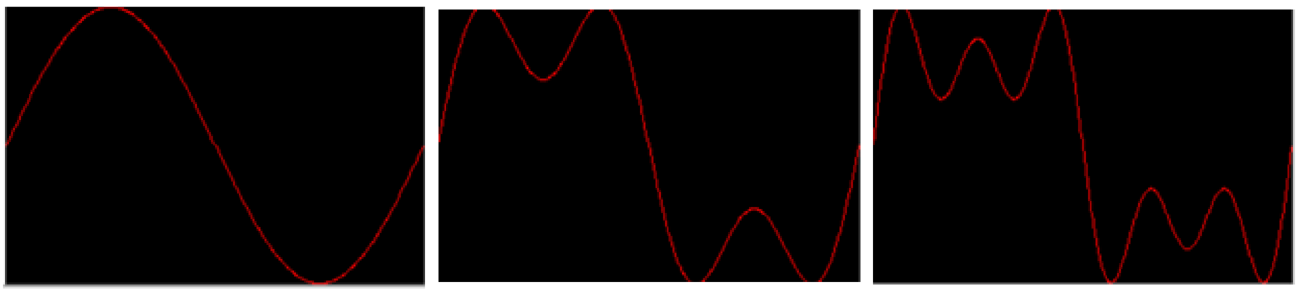
$$Harmonic\ Distortion\ HD\ [\%] = \frac{\sum_{n=2}^{\infty} I_n}{I_1} \cdot 100\%$$

I_1: Amplitude of the input frequency
I_n: Amplitude of the nth harmonic component of the oscillatory response

Harmonic distortion of 0% means perfect linearity of the signal. This parameter can be displayed in the Kinexus measurement and evaluation software, rSpace, to check the correctness of the oscillatory data.



2 Input signal (angular displacement, red) and output signal (torque, blue) outside the linear range. The response signal contains odd higher harmonic frequencies.



3 Input signal with a frequency of 1 Hz (left) and resulting harmonic frequencies outside the linear range (middle and right)

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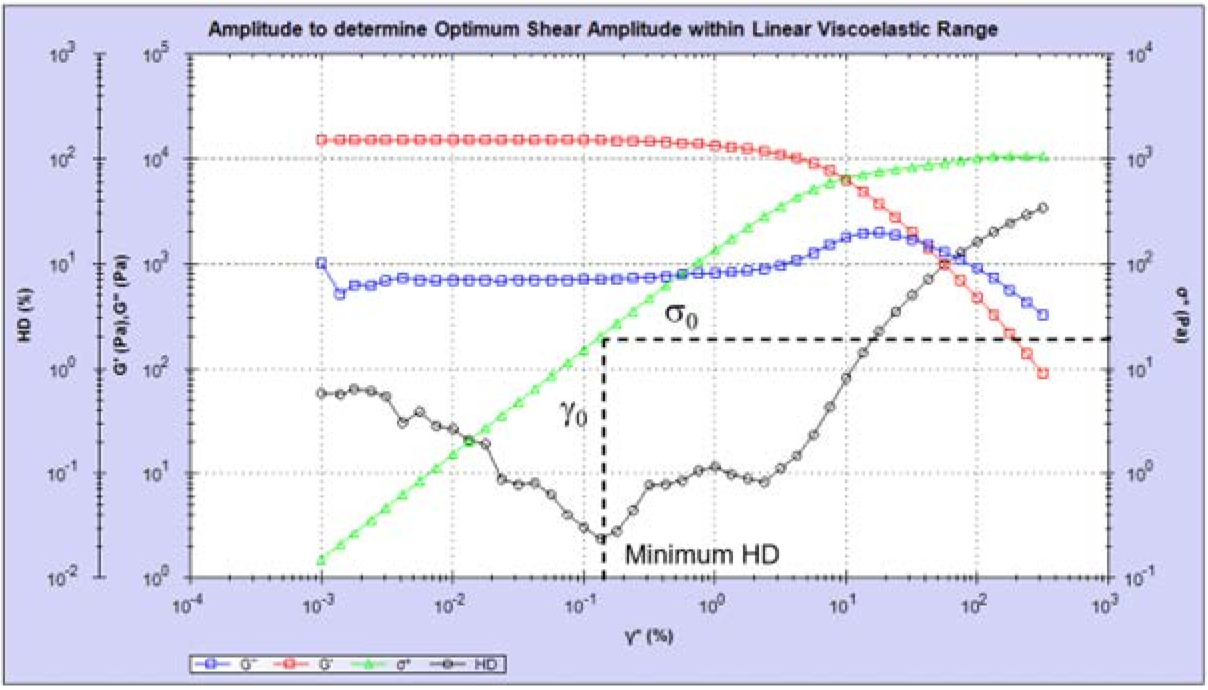
Minimum of Harmonic Distortion (HD) = Best Signal-to-Noise Ratio

An example is depicted in figure 4: The curves of elastic shear modulus (G', red), viscous shear modulus (G'', blue), amplitude of shear stress (σ, green), and harmonic distortion (HD, black) during an amplitude sweep. The shear strain, γ, detected at minimum HD corresponds to the deformation for the optimum signal-to-noise ratio. This value can be used for the following oscillatory measurements (frequency sweep, temperature sweep, etc.).

Harmonic Distortion to Check Linearity during Temperature or Frequency Ramps

The linear viscoelastic region (LVER) depends on measurement conditions such as frequency and temperature. In an amplitude sweep, these parameters are kept constant to determine the appropriate strain within the LVER. During a frequency sweep, however, the frequency varies throughout the test, and the LVER may change accordingly. To ensure that the material remains within the LVER over the entire frequency range, the harmonic distortion signal can be monitored as an indicator of the linear behavior.



4 Determination of the amplitude for the best signal-to-noise ratio in the rSpace software

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Conclusion

Harmonic distortion is an important signal to check if oscillations measurements are performed in the linear viscoelastic region. It concerns the polymer field as well as the food and pharmaceutical field:

- **Thermoplastics:** Determining the LVER is crucial for capturing only the intrinsic material properties during frequency or temperature sweeps of polymers and plastics. If measurements were taken outside the LVER, additional structural changes such as chain orientation, disentanglements, or even damage to the polymer network could occur. This would lead to distorted measurement data and make the evaluation of processing or aging studies unreliable.

- **Thermosets, coatings and adhesives:** These systems often contain sensitive networks of polymers or fillers that can be destroyed under excessive stress. If the LVER is not considered, the materials appear either too soft or too hard, which can lead to incorrect decisions in application and process design (e.g., incorrect viscosity windows for application or inaccurate predictions of adhesion).

- **Food (e.g., gels, emulsions, spreadable fats):** Here, it is particularly important not to destroy the fragile microstructure (e.g., emulsion networks, protein gels, fat crystals) by excessive shearing. Measurements outside the LVER could, for example, break up a gel or rearrange fat crystals, making the texture appear "artificially" softer than it actually is. This would have direct consequences for product development and quality control, as stability, mouthfeel, or spreadability would be incorrectly assessed.

- **Pharmaceutical formulations (e.g., creams, pastes, suspensions):** Here, too, structural integrity is key, especially when assessing storage stability or the release of active ingredients. If measurements are taken outside the LVER, shearing could alter the particle or carrier structures, leading to a misjudgment of the flow and application properties. In the worst case, this could have an impact on efficacy or patient safety.

The distortion factor ensures that rheological investigations are carried out in a range where the material structure remains intact. This prevents the measurement itself from distorting the result – a prerequisite for reliable, comparable, and practice-relevant data.

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