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Measuring and Evaluating Oscillation Data

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SCOPE

In an oscillation shear experiment, the material is subjected to either a sinusoidal strain or stress and the corresponding response is measured. The ratio of the output and input signals is referred to as the transfer function or material function (Figure 1). When a sinusoidal deformation or deformation rate is applied, the material's response is the stress. The resulting material function is either the modulus or the viscosity; if a stress is applied and the strain measured, the material function is the compliance.

In an oscillation experiment, the excitation and the response signals are sinusoidal in the time domain. The parameters describing the material's behavior are complex in the frequency domain and are represented by the storage and loss modulus, or the magnitude of the modulus and the loss tangent.

It is not a necessity to know the details of how the final results in a rheometer are derived from the raw experimental data in the time domain in order



Figure 1: Material functions are defined based on the input and ouput signals.



Figure 2: Sinusoidal shear train applied to a material

to apply rheology in material testing, however this knowledge provides insight into the physical meaning of the measured dynamic material parameters and the limitations of the measurement.

Usually materials are analyzed in the so-called "linear region" at steady state. Under these conditions, the material's response to a sinusoidal excitation is also sinusoidal with the same frequency. The ratio of the amplitudes of the output and input functions and the relative offset of the two sinusoidal waves fully describe the material's behaviour. In the linear regime, the rheological material functions are only dependent on frequency at constant temperature.

CONVERTING TIME DEPENDENT STRAIN AND STRESS TO G'AND G"⁽¹⁾

During an oscillation test, a sinusoidal strain (or stress) is forced onto a material (Figure 2) and within a few cycles or less, the responding stress (or strain) will oscillate along with the input strain sinusoidally

THE DISCRETE FOURIER TRANSFORM⁽²⁾

The Fourier transform arranges the time dependent periodic signal x(t) with respect to the different frequencies X(f), which are present in the time domain. The Fourier transform is a linear transformation – that means that any superposition of different frequencies in time will be resolved in the frequency domain. The FT is inherently complex. X(f) is a complex spectrum with a real and imaginary part and usually represented by a magnitude and a phase. The Fourier transform of a continuous signal x(t) is:

$$X(f) = \int_{-\infty}^{+\infty} x(t) e^{-i2\pi f t} dt$$
$$X(\omega) = \int_{-\infty}^{+\infty} x(t) e^{-i\omega t} dt$$

For a discrete series x(n) with *N* samples, x(t) becomes $x(n\Delta t)=x(n)$ with *n* the sample number and Δt the sampling time and ωt becomes $2\pi k\Delta fn\Delta t$ (*k* is the number of the harmonic frequencies) and with $\Delta f = 1/(N\Delta t)$ (the inverse of the period), ωt reduces to $2\pi kn/N$. The Fourier transform $X(\omega)$ becomes $X(k\Delta \omega)=X(k)$ with

$$X(k) = \frac{1}{N} \sum_{n=0}^{N-1} x(n) e^{\frac{-i2\pi kn}{N}}$$

with

The results of X(k) are complex, even when the input data from the time domain are not complex. The resulting spectrum is represented by the magnitude and the phase as:

$$|X(k)| = \sqrt{X'^2 + X''^2}$$

$$\phi = \arctan\left|\frac{X''(k)}{X'(k)}\right|$$

$$X'(k) = \frac{1}{N} \sum_{n=0}^{N-1} x_r(n) \cos\left(\frac{-2\pi nk}{N}\right)$$

$$- x_{im}(n) \sin\left(\frac{-2\pi nk}{N}\right)$$

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If the input time signal is real, the second term of the equations is dropped. For k=1, the magnitude and phase for the fundamental frequency is obtained. The response for k>1 provides a magnitude and a phase for the harmonic frequencies.



Figure 3: Decomposition of the measured stress into an in phase and out of phase component

at the same frequency, but with a phase lag δ .

$$\gamma(t) = \hat{\gamma} \sin \omega t$$

 $\sigma(t) = \hat{\sigma} \sin(\omega t + \delta)$

The responding stress wave $\sigma(t)$ can be decomposed into two waves with the same frequency; one in phase, the other out of phase (90°) with the input strain wave (Figure 3). The measured stress signal $\sigma(t)$ is the sum of the two waves according to:

$$\sigma(t) = \sigma'(t) + \sigma''(t)$$

in phase out of phase
$$= \hat{\sigma}' \sin \omega t + \hat{\sigma}'' \cos \omega t$$

The prime and double prime notation here has its origin in the complex numbers. According to the Euler equation (Figure 4) the applied sinusoidal strain $\gamma(t)$ can be rewritten as the imaginary part of a complex strain γ^* :

$$\gamma(t) = \operatorname{Im}\left\{\hat{\gamma} e^{i\omega t}\right\} = \operatorname{Im}\left\{\gamma^*\right\}$$

Similar the in and out of phase stress waves σ'

$$e^{i\alpha} = \cos\alpha + i\sin\alpha \quad \text{with} \quad i = \sqrt{-1}$$
$$\gamma^* = \hat{\gamma}e^{i\omega t} = \hat{\gamma}\,\cos\omega t + i\hat{\gamma}\,\sin\omega t$$
$$\gamma(t) = \operatorname{Im}\{\hat{\gamma}e^{i\omega t}\}$$

Figure 4: Euler equation. The applied sinusoidal strain is the imaginary part of the complex strain

and σ "can be expressed as:

$$\sigma'(t) = \operatorname{Im}\left\{\hat{\sigma}' e^{i\omega t}\right\}$$
$$\sigma''(t) = \operatorname{Re}\left\{\hat{\sigma}'' e^{i\omega t}\right\}$$

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The strain and stress functions can be extended to a complex function as:

$$\gamma^* = \hat{\gamma} e^{i\omega t}$$
$$\sigma^* = \hat{\sigma} e^{i(\omega t + \delta)}$$

The ratio of complex stress and strain provides a complex modulus G^* :

$$G^* = \frac{\sigma}{\gamma} \frac{\sigma}{*} = \frac{\hat{\sigma} e^{i\omega t} e^{i\delta}}{\hat{\gamma} e^{i\omega t}} = \frac{\hat{\sigma}}{\hat{\gamma}} e^{i\delta}$$
$$= \frac{\hat{\sigma}}{\hat{\gamma}} \cos\delta + i\frac{\hat{\sigma}}{\hat{\gamma}} \sin\delta$$
$$= |G^*|\cos\delta + i|G^*|\sin\delta$$
$$= G' + iG''$$

G' and *G*" are the real and imaginary parts of the complex modulus and represented in the complex plane as shown in figure 5. Simple trigonometry shows that the magnitude of G^* and the phase δ can be obtained from:

$$|G^*| = \sqrt{G'^2 + G''^2}$$
$$\delta = \arctan\left(\frac{G''}{G'}\right)$$

There is nothing imaginary about G", in fact it is a measure of the energy dissipated per cycle of deformation per unit volume:

$$E_d = \pi G'' \hat{\gamma}^2$$

HOW TO DETERMINE THE COMPLEX MATERIAL PARAMETERS? – DISCRETE FOURIER ANALYSIS AND CROSS CORRELATION

In the rheometer the strain and stress signals are digitized and are available to the instrument computer as an array of *n* measured quantities sampled over an equal time interval Δt .

$$\sigma(t) = \{\sigma_0, \sigma_1, \dots, \sigma_n, \dots, \sigma_{N-1}\}$$

$$\gamma(t) = \{\gamma_0, \gamma_1, \dots, \gamma_n, \dots, \gamma_{N-1}\}$$

The method used to convert the discrete raw signal from the time into the frequency domain is the discrete Fourier transformation (DFT). The expression for the transformation of a real discrete



Figure 5: Vector representation of the complex modulus in the complex plane

periodic function in time x(n) into the frequency spectrum X(k) is (see DFT section):

$$X(k) = \frac{1}{N} \sum_{n=0}^{N-1} x(n) e^{-\frac{i2\pi n h}{N}}$$

When the strain and stress wave functions are sinusoidal, real and oscillating at the same frequency in the linear regime, the only significant frequency is the fundamental (k=1). The transformation provides an in phase and out off phase (quadrature) term for the strain and stress functions as follows:

$$\sigma' = \frac{1}{N} \sum_{n=0}^{N} \sigma_n \cos\left(\frac{-2\pi n}{N}\right)$$
$$\sigma'' = \frac{1}{N} \sum_{n=0}^{N} \sigma_n \sin\left(\frac{-2\pi n}{N}\right)$$
$$\gamma'' = \frac{1}{N} \sum_{n=0}^{N-1} \gamma_n \cos\left(\frac{-2\pi n}{N}\right)$$
$$\gamma'' = \frac{1}{N} \sum_{n=0}^{N-1} \gamma_n \sin\left(\frac{-2\pi n}{N}\right)$$

N is the total number of data points per cycle and n the nth data point.

In the rheometer, the digitized data σ_n , γ_n are multiplied with the sine and cosine reference signals and the sum for the *N* data points stored as in phase and quadrature terms. The magnitude of the complex strain, stress vectors as well as the phase are derived as (Figure 6):

$$\begin{vmatrix} \gamma * \\ \gamma * \end{vmatrix} = \sqrt{\gamma'^2 + \gamma''^2} \qquad \delta_{\gamma} = \arctan\left(\frac{\gamma''}{\gamma'}\right)$$
$$\begin{vmatrix} \sigma * \\ \sigma * \end{vmatrix} = \sqrt{\sigma'^2 + \sigma''^2} \qquad \delta_{\sigma} = \arctan\left(\frac{\sigma''}{\sigma'}\right)$$

The magnitude of the complex modulus G^* is the ratio of the magnitude of the complex stress and strain vectors and the phase δ , the sum of the component's phase.



Figure 6: Complex modulus derived from the complex strain and stress wave function

$$|G^*| = \frac{|\sigma^*|}{|\gamma^*|}$$
$$\delta = \delta_{\sigma} - \delta_{\gamma}$$

<u>Note:</u> Because of symmetry, only a quarter of a cycle worth of raw data needs to be collected in order to calculate phase and magnitude. The disadvantage of this approach is that drifts of the raw signals are not eliminated and the experimental errors increase.

NOISE, RANDOM AND SYSTEMATIC ERRORS

Rheological measurements made in oscillation in general operate on strong signals, both strain and stress. This means that for many applications, few raw data points are sufficient to obtain accuracy test results. However in order to monitor large modulus changes under the same testing conditions or to improve the phase angle resolution, the measurable signal range has to be extended and the sensitivity of the oscillation measurement improved.

A high raw data acquisition rate and optimized data handling can significantly enhance the signal's dynamic range i.e. increase the sensitivity of the strain and stress signals.

The sensitivity is the ratio of detected signal to noise. The noise is the uncertainty of the measured signal and can be obtained from the base line of the Fourier transformed time signal. This information is not readily available from a simple correlation. The uncertainty can also be obtained from the variance of a series of repeated measurements of the modulus and phase. The signal to noise ratio (S/N) increases when averaging over a larger population of raw data. The S/N increases, for random noise only, with the square root of the number of measured transient data points $S/N \sim n^{1/2}$ ⁽³⁾.



Figure 7: Effect of sampling rate, quantified by the number of raw data pts /cycle, on the accuracy of the modulus and phase $^{\rm (4)}$

How the accuracy and the sensitivity of the modulus and phase improves with increasing the sampling rate and the number of sampled data pts/ cycle is demonstarted in figure 7. The small strain amplitude measurements have significant scatter in the modulus and phase with a sampling rate of only 100 pts/cycle. The variance clearly decreases when 1000 i.e. 10 000 data pts/cycle are sampled ⁽⁴⁾.

The noise here is defined as the standard deviation, calculated from 50 consecutive measurements of modulus and phase. The S/N ratio in figure 8 however is increasing slower with the number of data pts/cycle than expected for random noise. This is due to systematic errors: by reducing random



Figure 8: Signal to noise ratio, actual data and theoretical expectations for random noise only.

noise, systematic errors become visible and can be corrected for - thus further improving the operation range of the instrument.

FAST DATA ACQUISITION

Many materials experience rapid changes in structure as a result of thermal conditioning, chemical or physical reaction processes and of the nature of the structure itself. When these changes occur fast during long testing times, these changes will affect the test results. In the following two methods, "MultiWave" and "Window Correlation", frequently used to speed up oscillation testing, are presented.

Multiwave

Multiwave is a method, that allows superposition of a series of test frequencies over typically a range of two decades. The advantage is a significantly reduced test time, a must when testing materials which experience significant changes in structure during the time of the experiment.

Multiwave enables testing of a material at one fundamental frequency and its higher harmonics, each with its own strain (stress) amplitude. When correlating the strain and stress waves at the imposed harmonic frequencies, the material's response at these frequencies is obtained. Multiwave takes advantage of the fact, that two or more mechanical waves can pass through a material at the same time, independent of each other. The Fourier transformation is a linear transformation, and any superposition of different frequencies in the time domain will be



Figure 9: Discrete waveform at 1, 2, 8 rad/s and the superposition (MultiWave) of the three waveforms



Figure 10: Frequency dependence of the modulus, obtained from a multiwave and a standard frequency sweep test

resolved in the frequency domain, independent of the other frequencies applied at the same instant.

<u>Note</u>, that the individual strains add up and the total strain has to be small enough for the material to behave linear viscoelastic, i.e. the test response is independent of the strain amplitude.

Figure 9 shows three discrete strain waveforms at 1, 2, 8 rad/s with the same strain amplitude. The superposition of these same frequencies is given below. The time dependent strain function, applied to the materials is very unregular. The limitation to the higher frequencies is governed by the response of the motor.

The correlation at the discrete harmonic frequencies applied to the material provides for each excitation frequency the corresponding phase and out off phase modulus (G' and G''), from which the magnitude and the phase can be easily calculated. The results are shown in figure 10 and compared with the data obtained in a standard frequency sweep test. Excellent agreement is obtained between the two test methods.

The ability to decrease test time in general is an advantage, especially when large numbers of tests within a limited time span needs to be performed. Multiwave speeds up frequency temperature sweeps, allowing rapid master curve generation. In figure 10, the frequency sweep took 50 minutes in discret mode, the same data was obtained using MultiWave in only 16 minutes.

The determination of the instant of gelation in crosslinking polymers becomes easy with Multi-



Figure 11: Evolution of the loss tangent during a curing reaction. The gel point is the point, when tan δ becomes independent of frequency

wave. At the gel point, these materials show a constant loss tangent over a wide range of frequencies ⁽⁵⁾. Using the multiwaves's ability to generate many frequencies simultaneously, it becomes easy to determine the point at which a material's loss tangent becomes independent of frequency (Figure 11).

<u>Note:</u> The number of frequencies tested at the same time can be extended significantly by a applying a step function or better an exponential pulse to the material. From the strain and stress response, via DFT, the frequency dependance of the modulus can be obtained. The frequency range of the resulting modulus depends on the width of the pulse and the sampling rate of the time dependent stress and strain signals. Figure 12 exhibits an example of a two pulse strain excitation an the frequency dependent moduli



Figure 12: Exponential pulse and frequency response, Results are compared to data obtained using a standard frequency test.



Figure 13: Window correlation and under-sampling

G', G" and for comparison the data obtained from a standard frequency sweep test.

Window Correlation and under-sampling

Oscillation measurements are usually done over one period of oscillation. At an excitation frequencies above 1 Hz, typically one dynamic data point per second is obtained using standard correlation techniques. Operating at a quarter of a cycle, allows more data points to be determined in the same time interval, however increasing noise and experimental errors. At higher frequencies, even when limiting to a quater cycle correlation, much faster acquisition is usually not possible because of the overhead tasks of the control computer.

For materials such as UV curing adhesives or coatings which cure within seconds, faster data acquisition however is necessary in the order to monitor the cure behavior. 100 and more dynamic data points per second are required to measure the gel time accurately.

Fast data acquisiton can be achieved using the "window correlation" technique. This method stores the raw data coming from the A/D converter in a dynamic buffer, the size given by the product of the number of correlation cycles and data pts. per



Figure 14: Trace of G' and G" obtained with the windows correlation technique and the ARES rheometer correlator

cycle. The buffer is continuously filled with new data, while the oldest data drop out. The correlation of the data in the buffer can be invoked anytime as fast as the processor allows, typically between 10 and 1000 times per second.

The operation of the "Window Correlation" is explained in figure 13. Suppose, you are probing a sample at a frequency of 10 Hz, and would like to generate 20 G', G" data sets per second, i.e. one data point every 50 ms, while maintaing one full cycle for the correlation. Since at a frequency of 10 Hz, 100 ms are required to complete one cycle, the buffer contains the raw data sampled over the last 100 ms. With a correlation performed every 50 milliseconds, half of the experimental data in the buffer are new, half have been used in the previous



 $-\mathbf{s} - \mathbf{G}'(4\text{cycl}) - \mathbf{s} - \mathbf{G}'(4\text{cycl}) - \mathbf{s} - \mathbf{G}'(8\text{cycl}) - \mathbf{g} - \mathbf{G}'(8\text{cycl}) - \mathbf{g} - \mathbf{G}'(8\text{cycl}) - \mathbf{g} - \mathbf{G}'(8\text{cy$

Figure 15: Fast data acquisition using the undersampling technique. Time resolution is decreased by performing 1, 2, 4, 8 correlations per cycle at constant frequency

correlation already. This is technique is referred to as "under-sampling". Figure 14 shows a fast curing reaction, monitored using the window correlation technique and the standard correlator of the ARES rheometer. The cross over point (characterizing the gel point) can be accurately resolved. The standard rheometer correlator provides a data point only every few seconds and therefore misses the gel time completely.

Note: The resolution of the measured modulus in time is determined by the correlation period, i.e. the time to renew the correlation buffer. The correlation period has to be small compared to the overall time of change. Test frequency and correlation cycles (typically one) have to be chosen accordingly. The under-sampling technique enhances the time resolution and allows more dynamic data points to be taken. However this technique has its limits, due to the averaging effect of the correlation. This is shown in figure 15. The moduli G' and G" of an UV curable adhesive are measured using 1, 2, 4, 8 correlation cycles - thus increasing the correlation period (time). The reaction time constant (63% of full cure) for the material under the chosen conditions is 20 seconds. With increasing correlation cycles i.e. averaging time (1 cycle i.e. 0.1 s; ... 8 cycles i.e. 0.8 s), the modulus shifts to shorter time, the time reference referring to the mid point of the correlation period. For 1, 2 and 4 cycles, the ratio of averaging and reaction time is 0.5, 1 and 2%. The shift of the cross over modulus to earlier time is 0.14 s (2 cycles) and 0.23 s (4 cycles) in reference to 1 cycle correlation. For 8 correlation cycles, the averaging time is 0.8 seconds and the cross over shift 0.7 seconds, which corresponds to a relative shift of 2.2%. In order to record the modulus accurately and in a timely fashion, the averaging or correlation time has to be chosen to be less than 1% of the total process time.

HIGHER HARMONICS

DMA (Dynamic Mechanical Analysis) measurements are performed in the linear testing regime. Multiwave tests have to be designed, such that the total strain is small and the condition of linearity is conserved. Only under this condition, can the higher harmonic content of the stress response directly be related to the harmonics of the excitation strain oscillation.



Figure 16: Non linear stress reponse to a sinusoidal strain excitation

If the input strain amplitude exceeds a critical value, the response of the material to a sinusoidal oscillation is not a simple sine wave anymore, i.e. the material behaves non linear (Figure 16).

The non linear response of the material shows as a non symetric distorsion of the responding wave form and can be described by a series of odd harmonics.

The highest harmonic frequency, which can be resolved is the Nyquist frequency and depends on the raw data sampling rate as

$$f_{Nva} = n/27$$

with n the number of sampled discrete data points during a period T⁽⁷⁾. When 100 data points per cycle are sampled at an oscillation of 1Hz, for example, the Nyquist frequency is 50 Hz. The higher the sampling rate, the higher the the Nyquist frequency or spectral resolution.

Figure 16 shows the stress response of a cosmetic



Figure 17: Linear Non linear stress reponse to a sinusoidal strain excitation with strain amplitude

lotion to a sinusoidal strain excitation for different strain amplitudes. With increasing strain, the material behaves more and more non-linear, which shows in the distorsion of the stress response.

<u>Note:</u> While in the linear regime, a steady state oscillation establishes fast, it takes usually several cycles to establish steady state conditions during non linear testing. Also is it important to select the shear geometry carefully to avoid edge effects ⁽⁸⁾.

Using DFT, the stress response can formaly be described by the higher harmonic content in terms of magnitude and phase. Typically, the magnitude of the harmonics of the stress response is normalized with the magnitude of the fundamental and the phase and scaled to the cosine of the fundamental of the stress response.

Figure 17 shows the evolution of the magnitude of the the 3rd harmonic as a function of the strain amplitude for the cosmetic lotion. For small strain, the measured moduli *G* and *G* are strain inde-pendent and all harmonics are zero. With the modulus decreasing beyond a strain amplitude of 1%, the 3^{rd} harmonic grows to reach a contribution of 30% of the fundamental at higher strain amplitude.

CONCLUSION

The discrete Fourier transformation (DFT) is a powerfull method to analyze oscillation data and to calculate the complex material parameters such as the storage (G') and loss (G'') modulus. Variations of correlatioon conditions as well as the analysis of the harminic content allow 1- increase of accuracy and sensitivity of the obtained results, - 2 superposition of different frequencies for faster testing over wide frequency ranges, 3 - monitoring of fast changing systems and 4 - quantitative description of the non linear behavior

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