Manual stress decomposition with GSD-WUR

In this manual we will guide you through our custom MATLAB app which you can use to analyze dilatational strain and frequency sweeps with a decomposition of the surface stress into four distinct contributions, τ_1 – τ_4, as described in a recent paper by our group (de Groot et al., 2023). Decomposition is achieved with a Fourier analysis of the stress, followed by a separation of the even and odd harmonics. The odd harmonics (τ_1 & τ_2) are shown to be related to network formation and the even harmonics relate to surface density changes within one loop.

This document is meant as a guide for using the app correctly. As a start, we have included an example file that can be used to you get familiar with the software. If you have any questions, please do not hesitate to contact us.

Contents

1 QuickStart

1. Prepare dataset for analysis in excel file.
2. Set the parameters within the software and select your data with ‘browse file’.
3. Decide whether you want to export the results, if so, select export results.
4. Run the software.
5. If you exported the results: Go to the current folder and use Results_GSD_{filename}.xlsx’ to prepare your figures.
6. If you want to use the predefined figures, save those for later use.

2 Which types of data can be analyzed?

The software is built for data that contains multiple sets of oscillations with a short break between each set as shown in Fig. 1. This software can decompose each set of oscillations and calculate GSD parameters from it.

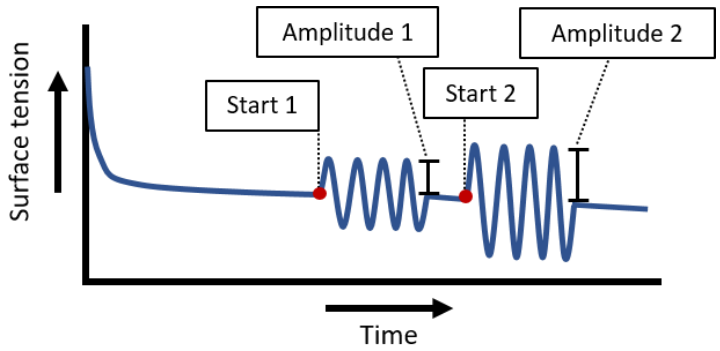

Fig. 1 Data that is suitable for analysis with some important parameters.

3 Preparing for analysis

The GSD software should be installed to MATLAB, see ‘Installation guide general stress decomposition for dilatation’. Now open the software under the Apps section in MATLAB (Fig. 2).

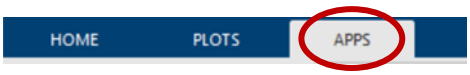

Fig. 2 Apps section in MATLAB.

3.1 Prepare data in excel file

To be able to run the software you must create an .xlsx file with you sample data that should be formatted as the example file (‘Example_GSD.xlsx’) included in the package. It should **only have 3 columns** with contain the following data:

- Column A: Time
- Column B: Surface tension
- Column C: Area

Make sure that these arrays are equally long e.g., if 'time' contains 13400 datapoints, so should 'surface tension' and 'area'.

Remark: When the optimization function of the software is used, the startpoints will automatically be included in column 'F' and 'G' of you excel file.

3.2 Set relevant parameters for the analysis

Once you have the excel file prepared you can start filling in the relevant parameters in the software. All relevant parameters are explained in Table 1, and the panels where these parameters are entered are shown in Fig. 3 & Fig. 4.

Table 1 All parameters within the app with its explanation sorted per section.

Input parameters	**Explanation**
Startpoints	The exact timepoints at which the oscillations start. *When using the optimize function in the software, approximate startpoints suffice.*
Filename	The name of the file you want to analyze, note that the excel file itself should be formatted correctly.
Path	The path where your file is stored.
Browse	Browse can be used to select your file, which will automatically fill in the fields 'Filename' and 'Path' correctly.
Amplitude	The amplitude or amplitudes applied in your experiment. If you performed an amplitude sweep this should be an array of all the applied amplitudes, for example an amplitude sweep from 5 – 30% could look like this: 0.05 0.075 0.1 0.2 0.3.
Frequency	The frequency or frequencies applied in your experiment. If you performed a frequency sweep this should be an array of all the applied frequencies, for example a frequency sweep from 0.01 – 0.1 Hz could look like this: 0.01 0.025 0.05 0.075 0.1.
Equilibrium area	The non-deformed area, A_0, you are oscillating around. (20 mm^2 in the example dataset)

Cycles	The number of cycles in each set of oscillations. (5 in the example dataset)
Number of harmonics	The number of harmonics you would like to use for the analysis. A higher number will include more harmonics but not always give a better fit to the raw data. Harmonics with an intensity at or below the noise level can add spurious oscillations to the fitted loop.
Sweep type	The type of sweep you applied, either an amplitude or frequency sweep.
Output	**Explanation**
Plot data	Indicates which amplitudes or frequencies you want to plot in figure 2.
Export data	Indicates whether you want the results exported to a new excel file named 'Results_GSD_' + filename. For more info see section 4.1.3.
Strain check	Indicates whether you want to plot the strain check. For more info see section 4.1.1.
Optional settings	**Explanation**
Optimize startpoints (strain)	Indicate whether you want the software to optimize the startpoints based on the strain. For more info see section 4.1.2.
Optimize startpoints (τ1)	Indicate whether you want the software to optimize the startpoints based on the area of τ_1. For more info see section 4.1.2.
Ignore optimized startpoints	If you for some reason want to not use the startpoints that are calculated with the optimization function, check this box.
Calculate startpoints manually	**Explanation**
Calculate startpoints	This button will automatically calculate the startpoints based on the start of the oscillations, the frequency and the pause between each set of oscillations.
Start oscillations	The time at which the first set of oscillations starts.
Advanced settings	**Explanation**
Baseline adjusting	This can be used when during oscillations the equilibrium surface tension is still decreasing. If selected, the software will calculate the average surface tension based on this and the next set of oscillations, see also section 4.1.4.
Averaging baseline	The number of seconds to average the surface tension over.

Exclude cycles	The number of cycles to exclude from the outside of each set of oscillations. (example: from a sequence of five cycles, we usually use only the middle three; so first and last are excluded, which is the default here (=1)).
Startpoints addition	The number of seconds to account for when using the optimization function, see also section 4.1.2.
Save settings	Save current parameters and settings.
Load settings	Load parameters and settings that were last saved.

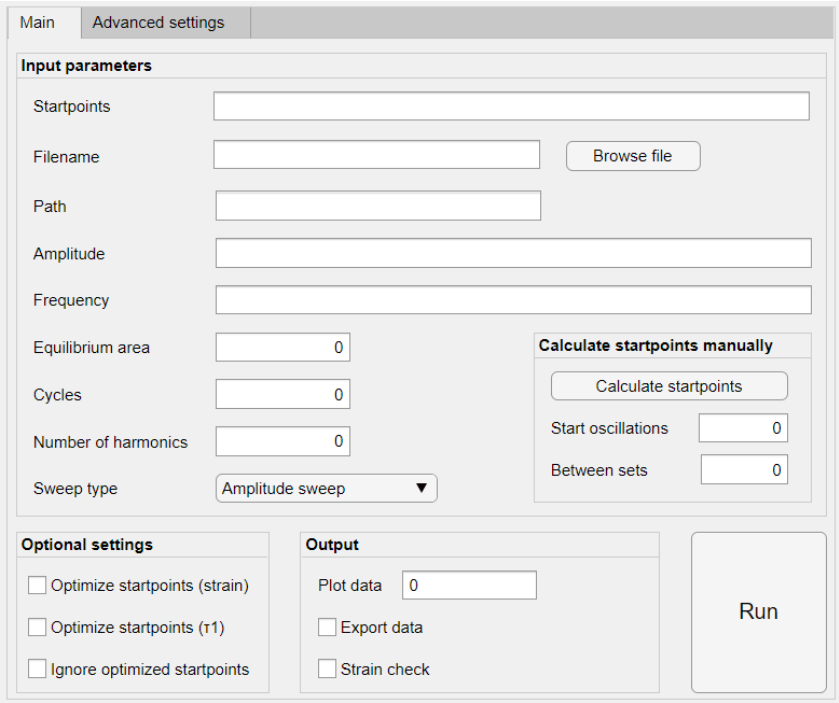

Fig. 3 The main parameters required to fill in before running the software.

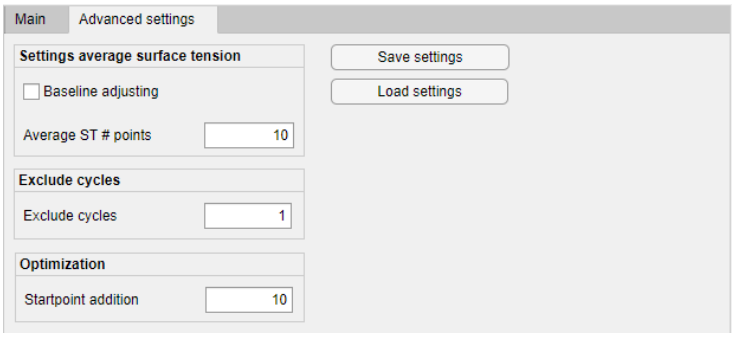

Fig. 4 The advanced setting within the software.

4 Data analysis

Once you have formatted your excel file and set all the parameter correctly, you can run the app. In the first section of the software it will load your data from the excel file. If you have optimized the startpoints with the software before, it will use these startpoints to calculate all parameters. Sometimes it might be necessary to exclude optimized startpoints, which can be done by deleting them from your excel file or by using 'Ignore optimized startpoints'.

The software will start by identifying each interval at which an oscillation starts, as indicated in Fig. 5.

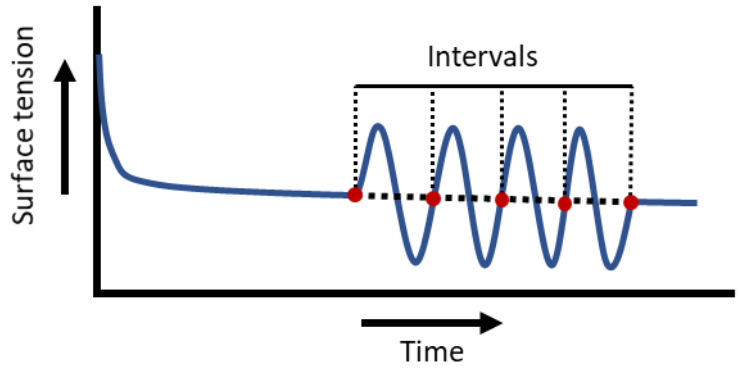

Fig. 5 The intervals within one set of oscillations as identified by the software.

Thereafter, it will calculate the average surface pressure by taking the average surface tension before each set of oscillations, see Fig. 6. When, 'baseline adjusting' is ticked the averaging of surface tension is done for the points immediately before the current set and the next set to adjust for baseline shifting. The last set of oscillations is averaged only over the points immediately before the set as there is no next set.

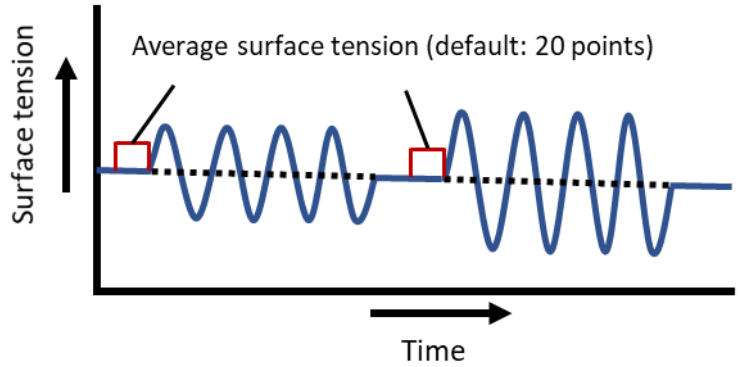

Fig. 6 Calculation of the average surface tension during a set of oscillations.

Subsequently, the intervals are used to identify the middle set of cycles which is interpolated over one period to create a homogeneous assay for the Fourier transformation. By default, the outer oscillations

are excluded to avoid effects created by starting or stopping the oscillations, see Fig. 7. This can be adjusted by changing 'exclude cycles. By default, 'exclude cycles' is set to 1 to exclude only the outer oscillations (see Fig. 7), when set to 0 all oscillations will be included.

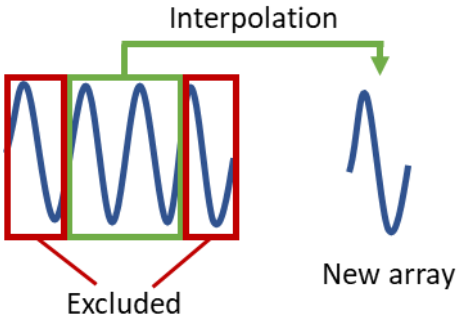

Fig. 7 Interpolation of the middle set of oscillations over one period by default.

Now a Fourier transformation is applied to the interpolated data. From which, a smoothed stress signal is recreated based on the number of harmonics defined in 'parameters'.

Additionally, the strain is smoothed by taking the shift (0^{th} harmonic) and the 1^{st} harmonic to reduce the noise. *Always check if this applied strain indeed follows a sinusoidal curve, if not the data is not reliable!*

From the Fourier transformed stress signal each tau-component is calculated according to Eq. 1 – Eq. 4. Here a'_{2k+1}, b'_{2k+1}, c'_{2k}, d'_{2k} are the coefficients of each harmonic.

$$\tau_1 = \sum_{k=0}^{n} b'_{2k+1}\, sin\big((2k+1)\omega t\big) \quad (1)$$

$$\tau_2 = \sum_{k=0}^{n} a'_{2k+1}\, cos\big((2k+1)\omega t\big) \quad (2)$$

$$\tau_3 = \sum_{k=0}^{n} c'_{2k}\, sin(2k\omega t) \quad (3)$$

$$\tau_4 = \sum_{k=0}^{n} d'_{2k}\, cos(2k\omega t) \quad (4)$$

Subsequently, the software uses Eq. 5 – Eq. 11 to calculate the parameters defining the nonlinearities of the stress response while also providing the traditional dilatational parameters E'_d, E''_d, and $tan\delta$.

$$E_{\tau 1L} = \frac{\sum_{k=0}^{n} b'_{2k+1}(-1)^k}{\varepsilon_0} \quad (5)$$

$$E_{\tau 1M} = \frac{\sum_{k=0}^{n} (2k+1) b'_{2k+1}}{\varepsilon_0} \quad (6)$$

$$S = \frac{E_{\tau 1L} - E_{\tau 1M}}{E_{\tau 1L}} \quad (7)$$

$$E_{\tau 4} = -\frac{\sum_{k=0}^{n} 2d'_{4k+2}}{\varepsilon_0} \quad (8)$$

$$\gamma_s = d'_0 \quad (9)$$

$$U_{d\tau 2} = \pi \varepsilon_0^2 E_1'' \quad (10)$$

$$U_{d\tau 3} = 2\varepsilon_0^2 \sum_{k=1}^{n} \left(\frac{E_{2k\tau 3} * k}{k^2 - 1/4}\right) \quad (11)$$

Now your data has been analyzed, a few plots are made to show you a summary of the analysis. You could use these plots to visualize your data or make use of the export function and make the plots yourself.

4.1 Optional settings in the software

4.1.1 Strain check

This section will only execute if 'Strain check' is ticked (see parameters).

When the data has been analyzed, an important final check is to see if the applied strain was correct, the applied strain should follow a sin curve for this analysis to be valid. Therefore, this section plots the interpolated strain and the smoothed strain over each so you can easily evaluate if the fit is acceptable.

4.1.2 Optimize startpoints automatically

This section will only execute if 'Optimize startpoints' is ticked (see parameters).

'Optimize startpoints automatically' is designed to help you with finding the exact point at which each set of oscillations and will only run if 'optimize startpoints' is checked in the parameters section. After performing optimization once, it is not necessary to do the optimization again as the startpoints are saved automatically in your data file.

Optimization based on strain ('Optimize startpoints (strain)') finds the strain that starts closest to 0 within the next 10 seconds (if 'startpoint addition' = 10). Whereas, optimization based on τ_1 ('Optimize startpoints (τ_1)') finds the lowest area of τ_1 within the next 10 seconds. Ideally the optimization based on strain is used, however if that results in τ_1 plots that are open, one could try to optimize based on τ_1 to improve the analysis. After optimization, the startpoints are exported to your data file and are used in further analysis of the data. If both optimization protocols fail, startpoints should be set manually, to do so you should find the exact time when the oscillations start for each set of oscillations.

4.1.3 Export results

This section will only execute if 'Export data' is ticked (see parameters).

This section summarizes your results and exports them to a new excel file named 'Results_GSD_{filename}.xlsx'. It will include two sheets, with the data for making Lissajous plots in the first and all moduli & dissipated energies in the second.

4.1.4 Baseline adjusting

This section will only execute if 'Baseline adjusting' is ticked (see parameters).

Baseline adjusting will average the surface tension for the points immediately before the current set and the next set of oscillations to adjust for baseline shifting. The last set of oscillations is averaged only over the points immediately before the set as there is no next set.

By default, averaging done over 10 seconds before each set of oscillations, but this can be adjusted by changing 'Averaging baseline' in the Advanced settings section.

5 Data output

Data will only be exported when 'Export data' is ticked (see parameters).

Once you have obtained the exported data in a excel file, you are free to plot the data however you want. The results excel file will provide all required data for making plots and graphs.

For making Lissajous plots the following is exported:

- The time, strain, and stress of middle set of oscillations calculated before data interpolation is exported, which is your raw data but only containing the selected oscillations for each amplitude or frequency.
- Additionally, the smoothed stress and strain data is exported as well as tau-component $\tau_1 - \tau_4$ and the sums: $\tau_1 + \tau_2$ and $\tau_3 + \tau_4$.

For plotting the moduli, dissipated energies etc. the following is exported:

- **Amplitude/frequency**, modulus of τ_1 L (**$E_{\tau 1L}$**), modulus of τ_4 (**$E_{\tau 4}$**), dissipated energy of τ_2 (**$U_{d\tau 2}$**), dissipated energy of τ_3 (**$U_{d\tau 3}$**), shift (**γ_s**), S-factor (**S**), modulus of τ_1 M (**$E_{\tau 1M}$**), storage modulus (**E'_d**), loss modulus (**E''_d**), and the ratio of the latter (**tanδ**).

Within the software itself a built-in function with example graphs will show every time when the software is run, you are free to use these graphs as well.

6 Terminology

Terms	Explanation
Set of oscillations	The set of oscillations that are applied at one amplitude or frequency. In the example file this is a set of 5 oscillations.
Cycle	One oscillation within the set of oscillations.

Terms in data output	Explanation
Time	The time for the middle oscillations that are selected. If 3 cycles of 50 seconds are selected the time will be the time corresponding to these 3 cycles (150 seconds).
Middle strain	The strain corresponding to the selected cycles. If 3 cycles selected this will be the corresponding strain to these three cycles.
Middle stress	The stress corresponding to the selected cycles. If 3 cycles selected this will be the corresponding stress to these three cycles.
Strain sth	The interpolated and Fourier transformed strain as calculated from 'Middle strain'. This results in a smoothed strain.
Stress sth	The interpolated and Fourier transformed stress as calculated from 'Middle stress'. This results in a smoothed stress.
Tau 1	The component τ_1 as calculated from 'Stress sth'.
Tau 2	The component τ_2 as calculated from 'Stress sth'.
Tau 3	The component τ_3 as calculated from 'Stress sth'.
Tau 4	The component τ_4 as calculated from 'Stress sth'.
Tau 1 + Tau 2	The sum of τ_1 and τ_2.
Tau 3 + Tau 4	The sum of τ_3 and τ_4.

7 Analyze example data

We have included an example for you that can help you get familiar with the software. Here we will show step by step you how to analyze the example file 'Example_data.xlsx'.

1. Open GSD software in MATLAB
2. Fill in the parameters and select 'Example_data.xlsx' with the browse file button.
    a. Amplitude: 0.05 0.075 0.1 0.125 0.15 0.2 0.3
    b. Frequency: 0.02
    c. Equilibrium area: 20

d. Cycles: 5
e. Number of harmonics: 6

3. Calculate startpoints manually
    a. Start oscillations: 11700
    b. Between sets: 50
    c. Click ‘Calculate Startpoints’
4. Select ‘Optimize startpoints’
    a. Preferably based on strain, but if this is not suitable, optimization based on τ_1 is also an option.
5. Select ‘Export data’
6. Select ‘Strain check’
7. Fill in ‘Plot data’: 0.05 0.015 0.3

After following all steps your screen should look like Fig. 10.

8. Click ‘Run’.

Now the script will analyze the data based on your calculated startpoints. Then it will optimize these startpoints, include them in the file, plot the results and export them to ‘Results_GSD_Example_data.xlsx’. In this file, all essential data is exported so you can easily make plots as you prefer them.

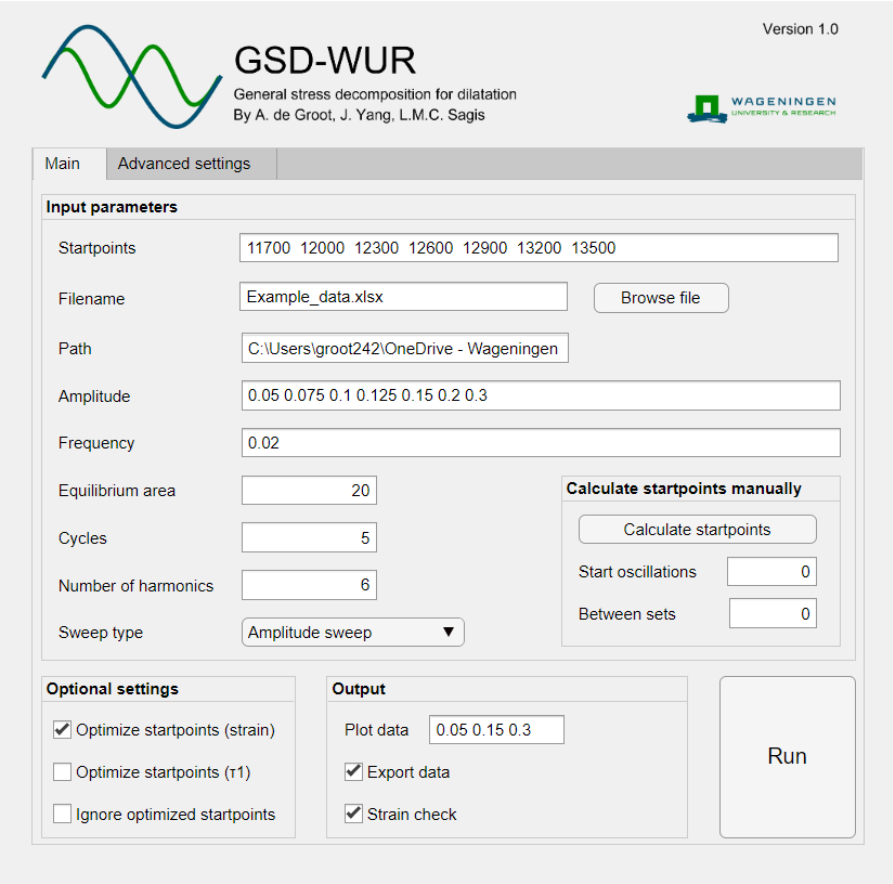

Fig. 8 Parameters to analyze 'Example_data.xlsx'.

8 References

de Groot, A., Yang, J., & Sagis, L. M. C. (2023). Surface stress decomposition in large amplitude oscillatory interfacial dilatation of complex interfaces. *Journal of Colloid and Interface Science*, *638*, 569–581. https://doi.org/10.1016/j.jcis.2023.02.007