Electronic supplementary information

A Sensitivity Metric and Software to Guide the Analysis of Soft Films Measured by a Quartz Crystal Microbalance

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S1. Comparison of Model Output to Plots from *Phys. Scr.* 1999, 59, 391–396

Figure S1 shows two plots which match those created by Voinoiva *et al.*[1] as a validation of the code used in this work.

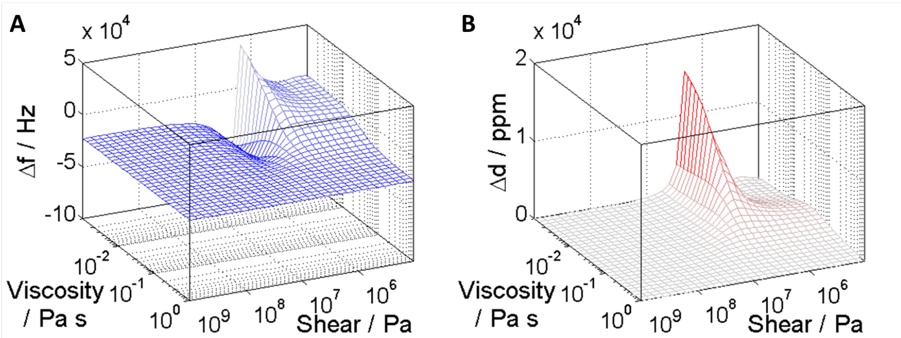


Figure S1. **A** fundamental frequency and **B** dissipation responses from a modelled layer. Fixed model parameters: h_{film} = 1 µm, $\rho_{film} = 1.0 \times 10^3$ kg m^{-3}, $\rho_{bulk} = 1.0 \times 10^3$ kg m^{-3}, η_{bulk} = 1 mPa s, f_0 = 10 MHz, N = 1.

S2. TPM-sensitivity Based on Linear Changes to Shear and Viscosity

The TPM-sensitivity plots in the main manuscript were based on the gradient of QCM-D responses with respect to the natural logarithm of shear and viscosity. Figure S2 compares the appearance of a TPM-sensitivity surface calculated with respect to the natural logarithm of shear and viscosity (Figure S2A) and with respect to the unmodified value (Figure S2B). All other aspects of the plots are identical.

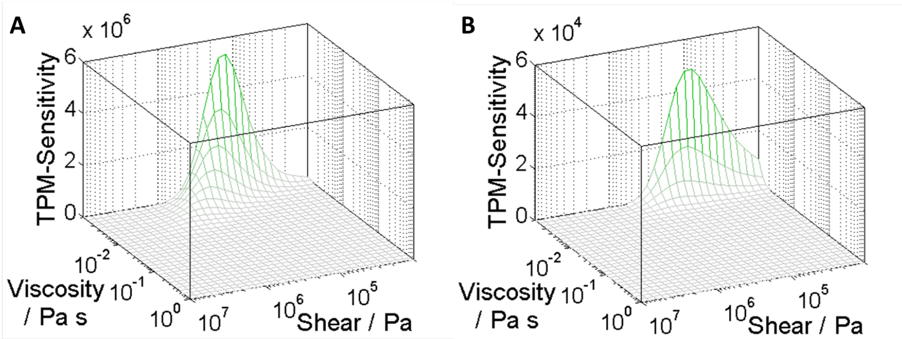


Figure S2. TPM-sensitivity calculated based upon **A** log spacing and **B** a linear spacing of the shear and viscosity values. Fixed model parameters: h_{film} = 5 nm, ρ_{film} = 1.45 × 10^3 kg m^{-3}, ρ_{bulk} = 1.0 × 10^3 kg m^{-3} η_{bulk} = 0.89 mPa s, f_0 = 4.95 × 10^6 Hz, N = 7. Sensitivity weightings (see text): $\sigma_{\Delta f}$ = 0.053 Hz, $\sigma_{\Delta d}$ = 0.021 ppm.

Equations S1 define the frequency and dissipation vectors with respect to logarithmic changes in shear modulus and viscosity.

$$\begin{cases} \nabla f_N^{\ \ln} = \mu_{\mathrm{film}} \dfrac{\partial f_N}{\partial \mu_{\mathrm{film}}} \hat{\boldsymbol{\mu}}_{\mathbf{film}} + \eta_{\mathrm{film}} \dfrac{\partial f_N}{\partial \eta_{\mathrm{film}}} \hat{\boldsymbol{\eta}}_{\mathbf{film}} = \dfrac{\partial f_N}{\partial (\ln \mu_{\mathrm{film}})} \hat{\boldsymbol{\mu}}_{\mathbf{film}} + \dfrac{\partial f_N}{\partial (\ln \eta_{\mathrm{film}})} \hat{\boldsymbol{\eta}}_{\mathbf{film}} \\ \nabla d_N^{\ \ln} = \mu_{\mathrm{film}} \dfrac{\partial d_N}{\partial \mu_{\mathrm{film}}} \hat{\boldsymbol{\mu}}_{\mathbf{film}} + \eta_{\mathrm{film}} \dfrac{\partial d_N}{\partial \eta_{\mathrm{film}}} \hat{\boldsymbol{\eta}}_{\mathbf{film}} = \dfrac{\partial d_N}{\partial (\ln \mu_{\mathrm{film}})} \hat{\boldsymbol{\mu}}_{\mathbf{film}} + \dfrac{\partial d_N}{\partial (\ln \eta_{\mathrm{film}})} \hat{\boldsymbol{\eta}}_{\mathbf{film}} \end{cases} \tag{S1}$$

S3. TPM-sensitivity Defined for Greater Than Two Unknown Parameters

Equations S2 present a generalised definition of TPM-sensitivity that permits a multidimensional sensitivity analysis that considers multiple harmonics (abbreviated as N, M and O) and all the film and fluid parameters.

$$\begin{cases} \nabla = \hat{\boldsymbol{\mu}}_{\mathbf{film}} \dfrac{\partial}{\mathrm{d}\mu_{\mathrm{film}}} + \hat{\boldsymbol{\eta}}_{\mathbf{film}} \dfrac{\partial}{\mathrm{d}\eta_{\mathrm{film}}} + \hat{\boldsymbol{\rho}}_{\mathbf{film}} \dfrac{\partial}{\mathrm{d}\rho_{\mathrm{film}}} + \hat{\boldsymbol{h}}_{\mathbf{film}} \dfrac{\partial}{\mathrm{d}h_{\mathrm{film}}} + \hat{\boldsymbol{\rho}}_{\mathbf{bulk}} \dfrac{\partial}{\mathrm{d}\rho_{\mathrm{bulk}}} + \hat{\boldsymbol{\eta}}_{\mathbf{bulk}} \dfrac{\partial}{\mathrm{d}\eta_{\mathrm{bulk}}} \\ \text{TPM-sensitivity} = \left| \det\left[\nabla f_N \; \nabla d_N \; \nabla f_M \; \nabla d_M \; \nabla f_O \; \nabla d_O\right] \right| \end{cases} \tag{S2}$$

S4. Description of MATLAB Functions Used for Modelling and Optimisation

There are three functions intended for general use listed below with their sample inputs and outputs (graphs inclusive). With each code there is an example to assist other users to use this code. The values set in the controls should be changed to the specific system under investigation and by default are set to the example values given below.

S4.1.voigt_responses

The function `voigt_responses` generates frequency, dissipation, TPM-sensitivity and missing mass plots for the harmonic specified. The TPM-sensitivity here is for the frequency and dissipation combination for that harmonic.

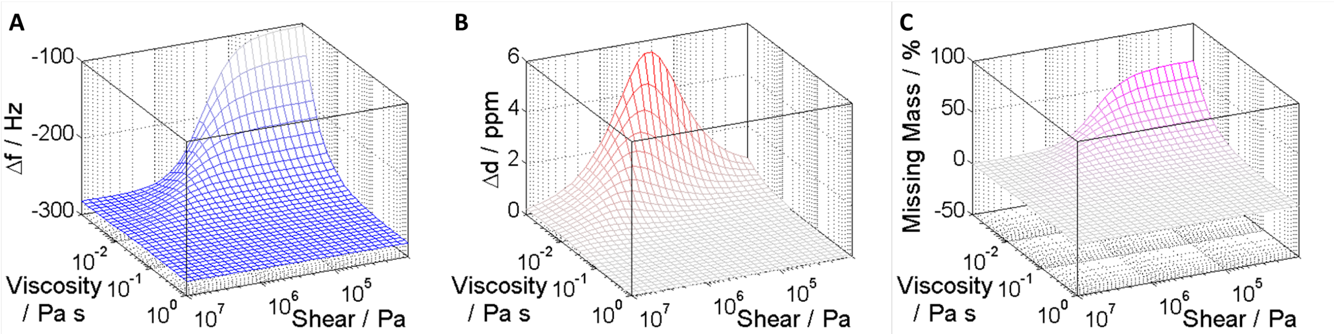
Syntax:

```
[output]=voigt_responses(controls)
```

Input:

Variable	Sample value	Description
`controls.x`	`'film shear'`	Variable to use as the x axis. Choose from `'film height'`; `'film density'`; `'bulk density'`; `'film viscosity'`; `'bulk viscosity'`; `'film shear'`
`controls.y`	`'film viscosity'`	Same as above with same choices, but for the *y* axis.
`controls.x_range`	`[1e4,1e7]`	Range of the *x* axis. Start to finish
`controls.y_range`	`[1e-03,1]`	Range of the *y* axis. Start to finish
`controls.steps`	`30`	Number of points along each axis
`controls.f0`	`4.95e6`	Fundamental frequency in Hz
`controls.harmonic`	`7`	Harmonic/overtone number. Choose from odd positive integers.
`controls.height_film`	`5e-09`	Height of the film in m
`controls.density_bulk`	`1.45e3`	Density of the film in kg m^{-3}
`controls.viscosity_film`	`3.2e-3`	Viscosity of the film in Pa s
`controls.shear_film`	`3.2e+05`	Shear modulus as the film in Pa
`controls.density_bulk`	`1e3`	Density of the bulk in kg m^{-3}
`controls.viscosity_bulk`	`8.9e-04`	Viscosity of the bulk in Pa s
`controls.normalise`	`0`	Boolean. Set to 0 (false) for the true harmonic response or set to 1 (true) for that overtone to be normalised by division by its overtone number
`controls.d_sensitivity`	`2.1e-08`	The error/weighting for the dissipation response
`controls.f_sensitivity`	`5.3e-2`	The error/weighting for the frequency response in Hz
`controls.z_range_f`	`[0,0]`	Set to [0,0] to let the frequency response graph auto-scale. Set to desired *z*-axis range if specific range of the graph is needed
`controls.z_range_d`	`[0,0]`	As above but for dissipation response graph scale.
`controls.z_range_s`	`[0,0]`	As above but for TPM-sensitivity graph scale.
`controls.z_range_mm`	`[0,0]`	As above but for missing mass graph scale.
`controls.publication`	`1`	Set to 0 for general use and auto formatting of the graph. Set to 1 to use static code in sub routine sketch which can be edited to obtain a tailored graph for publication

Output:



Variable	**Sample output**	**Description**
`output.f_surface`	`<31x31x7 double>`	Grid of points constituting the frequency response surface. Regardless of harmonic selected in `controls`, all overtone responses are calculated: Δf_1 = [*n*,*n*,1]; Δf_3 = [*n*,*n*,2]; Δf_5 = [*n*,*n*,3]; Δf_7 = [*n*,*n*,4]; etc. The value of n is equal to `controls.steps` + 1.
`output.d_surface`	`<31x31x7 double>`	Same as `output.f_surface`, but for the dissipation responses.
`output.variables`	`<31x31x6 double>`	Matrix of all the system properties for each point of the surface. [n, n, 1] film density; [n, n, 2] film shear; ; [n, n, 3] film viscosity; [n, n, 4] film height; [n, n, 5] bulk density ; [n, n, 6] bulk viscosity
`output.f_vector`	`<31x31x4 double>`	Matrix of frequency response vectors used for the 2D TPM-sensitivity calculation. [*n*,*n*,1] and [*n*,*n*,2] *x* and *y* components of the vector respectively; [*n*,*n*,3] is the vector's magnitude; and [*n*,n,4] is vector's angle.
`output.d_vector`	`<31x31x4 double>`	Same as `output.f_vector`, but for the dissipation response vectors.
`output.missing_mass`	`<31x31x7 double>`	Grid of points constituting the missing mass surface. Regardless of harmonic selected in controls, all overtone responses are calculated, indexed as for `outputs.f_surface`.

S4.2.TPM_sensitivity

The function `TPM_sensitivity` generates a TPM-sensitivity plot for the combination selected. These plots can be any combination of harmonics, frequencies and dissipations.

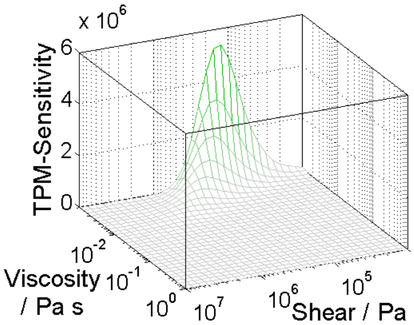
Syntax:

```
[output] = TPM_sensitivity(controls,properties,fixed_properties)
```

Input:

Variable	Sample value	Description
`controls.x`	`'film shear'`	Variable to use as the *x* axis. Choose from `'film height'; 'film density'; 'bulk density'; 'film viscosity'; 'bulk viscosity'; 'film shear'`
`controls.x_range`	`[10000,10000000]`	Range of the *x* axis in SI base units. Start to finish.
`controls.y`	`'film viscosity'`	Same as `controls.x`, but for the *y* axis. Same choices as `controls.x`
`controls.y_range`	`[1e-03,1]`	Range of the *y* axis. Start to finish
`controls.steps`	`30`	Number of points along each axis
`controls.harmonic`	`[5,13]`	The pair of harmonic numbers used to calculate the TPM-sensitivity. Must be odd integers ≤13.
`controls.harmonic_type`	`'FF'`	Sets the harmonic types, e.g. FF sets harmonic one and two both to frequency, FD would set harmonic one to frequency and harmonic two to dissipation, etc. This input is case sensitive.
`controls.z_range`	`[0,0]`	Set to [0,0] to let the TPM-sensitivity graph auto-scale. Set to desired *z* axis range if manual *z* range of the graph is needed
`controls.publication`	`1`	Set to 0 for general use and auto formatting of the graph. Set to 1 to use static code in sub routine sketch which can be edited to obtain a tailored graph for publication
`controls.linear`	`0`	Boolean operator. Set to 0/false for the derivatives underpinning TPM-sensitivity to be calculated with respect to based logarithmic changes in materials properties.
`controls.f0`	`4.95e6`	Fundamental frequency in Hz
`controls.f_sensitivity`	`[5.3e-2, 5.3e-2, 5.3e-2, 5.3e-2, 5.3e-2, 5.3e-2, 5.3e-2]`	The error/weighting for the frequency response in Hz. Independent errors for odd harmonics 1–13 inclusive.
`controls.d_sensitivity`	`[2.1e-8, 2.1e-8, 2.1e-8, 2.1e-8, 2.1e-8, 2.1e-8, 2.1e-8]`	The error/weighting for the dissipation response. Independent errors for odd harmonics 1–13 inclusive.
`properties`	`[5e-09, 1.45e3, 3.2e3, 3.2e5, 1e3, 8.9e-04]`	Properties of the system in SI base units. Order: film height; film density; film viscosity; film shear modulus; bulk density; bulk viscosity.
`fixed_properties`	`[1, 1, 0, 0, 1, 1]`	Boolean vector for which properties of the system are fixed during calculation. Set to 0 to allow the property to vary. Has the same ordering of system properties as `properties`.

Output:



Variable	Sample output	Description
`output.score_surface`	`<31x31x91 double>`	The TPM-sensitivity scores that constitute the plots surface. Third index is the combination that created that score surface, $^{14}C_2 = 91$
`output.max_index`	`<31x31 double>`	The maximum scoring TPM-sensitivity harmonic combination for that location on the *x* and *y* axis
`output.max_score`	`<31x31 double>`	The maximum TPM-sensitivity score for that location on the *x* and *y* axis

S4.3.combo

The function combo creates a list of the highest scoring TPM-sensitivity combinations with their corresponding scores. This code optimises for a specific set of physical conditions of the film, so multiple runs may be necessary to probe an area of the surface of a TPM-sensitivity plot.

Syntax:

```
[combinations,score,fd_derivative] = combo(controls)
```

Input:

Variable	**Sample value**	**Description**
`controls.f0`	`4.95e6`	Fundamental frequency in Hz
`controls.f_sensitivity`	`[5.3e-2, 5.3e-2, 5.3e-2, 5.3e-2, 5.3e-2, 5.3e-2, 5.3e-2]`	The error/weighting for the frequency responses in Hz. Independent errors are assigned for all the harmonics. Harmonics are ordered as odd integers from 1 to 13.
`controls.d_sensitivity`	`[2.1e-8, 2.1e-8, 2.1e-8, 2.1e-8, 2.1e-8, 2.1e-8, 2.1e-8, 2.1e-8]`	The error/weighting for the dissipation response, with details as for `controls.f_sensitivity`.
`controls.linear`	`0`	Boolean operator. Set to 0/false for the derivatives underpinning TPM-sensitivity to be calculated with respect to based logarithmic changes in materials properties.
`controls.tophits`	`5`	Number of top scores to show
`controls.properties`	`[5e-9, 1.45e3, 3.2e-3, 3.2e5, 1e3, 8.9e-4;1, 1, 0, 0, 1, 1]`	First row: properties of the system. Second row: Boolean determining whether a property is constant (set to 0 to allow it to vary). Order of properties, by column: film height; film density; film viscosity; film shear modulus; bulk density; bulk viscosity

Output:

To command window:

```
Top Score 4.89e+05 (row 29) using f5 f13
Top Score 4.01e+05 (row 39) using f7 f13
Top Score 3.85e+05 (row 18) using f3 f13
Top Score 3.66e+05 (row 28) using f5 f11
Top Score 3.03e+05 (row 17) using f3 f11
```

Variable	**Sample output**	**Description**
`combinations`	`<91xn double>`	All of the combinations of the harmonics for the number of parameters set to vary. Values of 1–7 the frequency response for harmonic ($2N$–1); Values of 8–14 represent the dissipation response for harmonics ($2N$–15). The number of columns depends on the number of free properties (n) set in `controls.properties`.
`score`	`<91x1 double>`	The TPM-sensitivity score for the corresponding harmonic combination in the combinations matrix
`fd_derivative`	`<14xn double>`	Derivative of QCM-D response with respect to properties that are set to vary (n). Row number indexed as for `combinations`. In this example, row 9 column 2 would give $\partial\Delta d_3/\partial\mu_{film}$.

S5. Experimental Materials and Methods

A stock solution (24 mg ml^{-1}), of bilirubin oxidase from *Myrothecium verrucaria* (*Mv*BOx) (Amano Enzyme EU, Chipping Norton, UK) was made by dissolving freeze dried MvBOx in 0.1 M sodium phosphate pH 6.0 at 25 °C. This stock solution was purified by centrifugation through polyethersulfone membrane (Vivaspin, 30 kDa MWCO) to remove low molecular weight contaminants. The concentration was determined to be 14 mg ml^{-1} by UV-vis absorption spectroscopy ($\varepsilon_{280nm} = 9.52 \times 10^4$ cm^{-1} M^{-1}).[2] Enzyme adsorption data was followed using a Q-sense E1 QCM-D system (Biolin Scientific, Stockholm, Sweden), with a Q-Sense QFM401 flow module. A silica-coated QCM sensor (QSX 303 SiO_2) was first treated with ozone for 20 min prior to being modified by 3-(trihydroxysilyl)propane-1-sulfonic acid (30 – 35 wt % in water, Fluorochem), diluted to 5 wt% in a 6 to 1 by volume ethanol and water solution for 1 h. The crystal was then washed with ultra-pure water (Millipore, 18.2 MΩ cm at 25 °C) and dried with a stream of house N_2. A temperature-controlled water recirculator was used in conjunction with the system's built-in Peltier cooler; both were set to 25 °C. Enzyme adsorption to the crystal was accomplished by pausing the flow pump, reversing it for long enough to produce a pendant droplet from the end of the inlet tube, immersing the tube into the purified enzyme solution and running in the forward mode for 15 s (25 µl *Mv*BOx) before repeating the procedure to resume flow of buffer solution.

Frequency and dissipation responses were acquired for all odd harmonics from 1 to 13, inclusive. The acquisition was set for "maximum stability" on the QSoft control software, resulting in a variable data spacing of (1.599 ± 0.049) s. The full data set is shown in Figure S3. The responses from the first harmonic are sensitive to mounting effects, and were excluded from all analyses.[3] The uncertainty in the frequency and dissipation measurements was calculated using QTools built-in algorithm, resulting in mean uncertainties of $\sigma_{\Delta f}$ = (0.053 ± 0.018) Hz and $\sigma_{\Delta d}$ = (0.021 ± 0.008) ppm. The values were similar for all harmonics measured.

The β sensitivity function for a single Kelvin–Voigt viscoelastic adlayer in a Newtonian fluid was based on the derivation from Voinova and co-workers.[1] Partial derivatives of the complex β function with respect to the four film and two bulk material parameters were calculated analytically using Mathematica 10. For the derivation, the material parameters were assumed to be real and positive, and the harmonic number was fixed as an integer. The expressions were simplified using Mathematica's built-in FullSimplify and Simplify functions. The β function was converted into Δf_N and Δd_N responses using eqs S1a and S1b:

$$\Delta f_N = \mathrm{Im}\left(\frac{\beta}{2\pi\rho_{\mathrm{quartz}}h_{\mathrm{quartz}}}\right) \tag{S1a}$$

$$\Delta d_N = -\mathrm{Re}\left(\frac{\beta}{\pi N f_1\rho_{\mathrm{quartz}}h_{\mathrm{quartz}}}\right) \tag{S1b}$$

where N is the harmonic number, f_1 is the fundamental frequency of the quartz resonator, and ρ_{quartz} and h_{quartz} are the density and thickness of the resonator, respectively.

MATLAB version R2013a was used to calculated TPM-sensitivity values and optimum combinations of QCM-D responses, as well as to generate response and sensitivity surfaces. The functions are compatible with version 2015a. These MATLAB functions are described in Section S4.

Figure S3 shows the full dataset obtained from the QCM-D. The sensor was first equilibrated in 0.1M pH 6.5 sodium phosphate buffer until a baseline of at least 25 mins was achieved in a flow cell at a flow rate of 0.1 ml min^{-1}, after which the sensor was exposed to a 25 µl volume of *Mv*BOx for 15 seconds before being changed back to buffer once more. The discontinuities in the plots are due to the associated pump reversals (and so pressure changes) when changing over the flow streams. The greatest discontinuity is in the fundamental trace as this is effected more greatly by mounting and other similar effects and is why it was not used in the fitting performed by QTools.[3] The dead time between solution change and interaction with the sensor surface is approximately 60 s. The data inside the dashed boxes were used for modelling in QTools as this represented a regime whose thickness and relative density changes with time had been previously determined.[4] This allowed results from the modelling to be directly compared and the effectiveness of the modelling quantified.

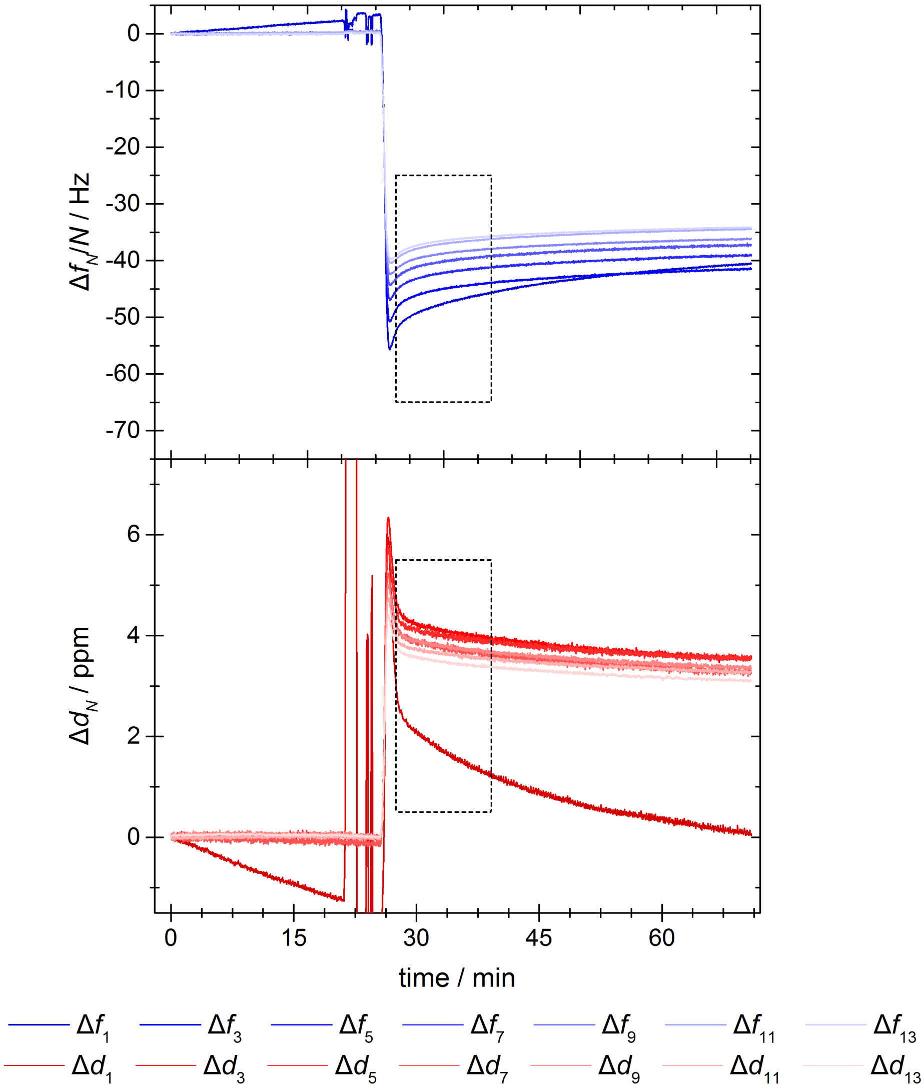


Figure S3. Frequency and dissipation responses from *Mv*BOx adsorption onto a silica-coated QCM-D sensor modified with 3-(trihydroxysilyl)propane-1-sulfonic acid. Data range used for fitting in QTools and shown in Figure 5 and 6 in the main text is shown by dashed boxes. Conditions: *Mv*BOx concentration 14 mg ml^{-1}, volume of *Mv*BOx addition 25 µl, pump flow rate 0.1 ml min^{-1}, cell temperature 25 °C.

S6. TPM-sensitivity values for Figure 4

Table S1. TPM-sensitivity values for points on surfaces shown in Figure 4 of the main text. Shaded fields indicate the optimum harmonic combination for a given point.

Response combination	Point B η_{film} = 31 mPa s μ_{film} = 0.31 MPa	Point C η_{film} = 3.1 mPa s μ_{film} = 3.1 MPa	Point D η_{film} = 3.1 mPa s μ_{film} = 0.31 MPa
$\Delta f_7\ \Delta d_7$	0.8×10^2	1.7×10^3	5.6×10^4
$\Delta f_{13}\ \Delta d_3$	3.4×10^2	3.5×10^3	0.5×10^4
$\Delta f_{13}\ \Delta d_{13}$	0.9×10^2	17.9×10^3	7.4×10^4
$\Delta f_5\ \Delta f_{13}$	1.4×10^2	1.7×10^3	50.0×10^4

S7. Relationship Between Quality of Fit and QCM-D Responses Used in Fitting

The harmonic combinations shown in Table S2 were used as the basis for fitting in QTools. This fitting settings used are shown in Figure S4. The fits to adlayer shear, viscosity and thickness (Figure 5 in the main text and Figure S5) were used to model Δ*f* and Δ*d* responses for odd harmonics 1–13 (Figure S6 and Figure S7). Fits to fewer QCM-D responses produce, as expected, higher goodness-of-fit (χ^2) values, but much more realistic values and trends in the physical properties. For example, using three pairs of Δ*f* and Δ*d* responses (Figure S5(c)) leads to a gross underestimate of shear modulus and a thickness estimate 2–3 times higher than TPM-sensitivity–optimised fits predict.

Table S2. Comparison of goodness of fit (χ^2) for all QCM-D responses based on fits to the indicated responses.

Responses fit	$\chi^{2\,a}$	**Notes**
All responses $N \geq 3$	2.0×10^6	b
Δd_3 Δf_5 Δf_{13}	5.6×10^6	b, c
Δf_3 Δf_7 Δf_{13}	12.1×10^6	b, d
Δf_3 Δf_5 Δf_{13}	13.5×10^6	d, e
Δd_3 Δf_7 Δf_{13}	3.2×10^6	e
Δf_3 Δd_3 Δf_7 Δd_7 Δf_{13} Δd_{13}	2.2×10^6	e

[a] Fitting range is indicated by the dashed boxes in Figure S3. The number of points in each comparison is the same in all cases (5268). Frequency and dissipation responses from the first harmonic were not included.. [b] Shown in Figure 5 in main text and Figure S6. [c] Combination gives maximum TPM-sensitivity for *Mv*BOx protein film on silica. [d] Combination uses only frequency responses. [e] Shown in Figure S7 and Figure S5.

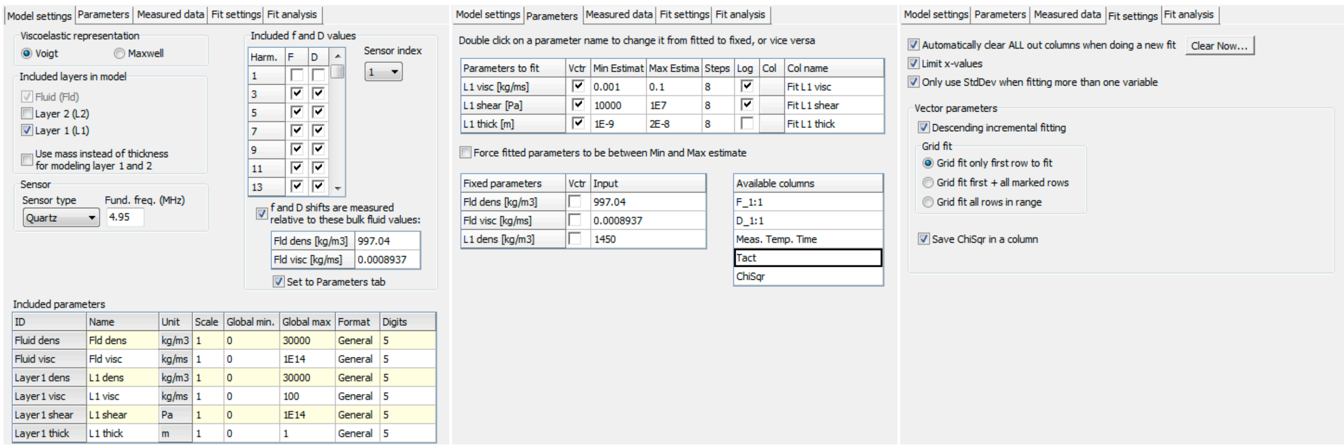


Figure S4. Settings used in QTools to fit QCM-D responses shown in Figure S3.

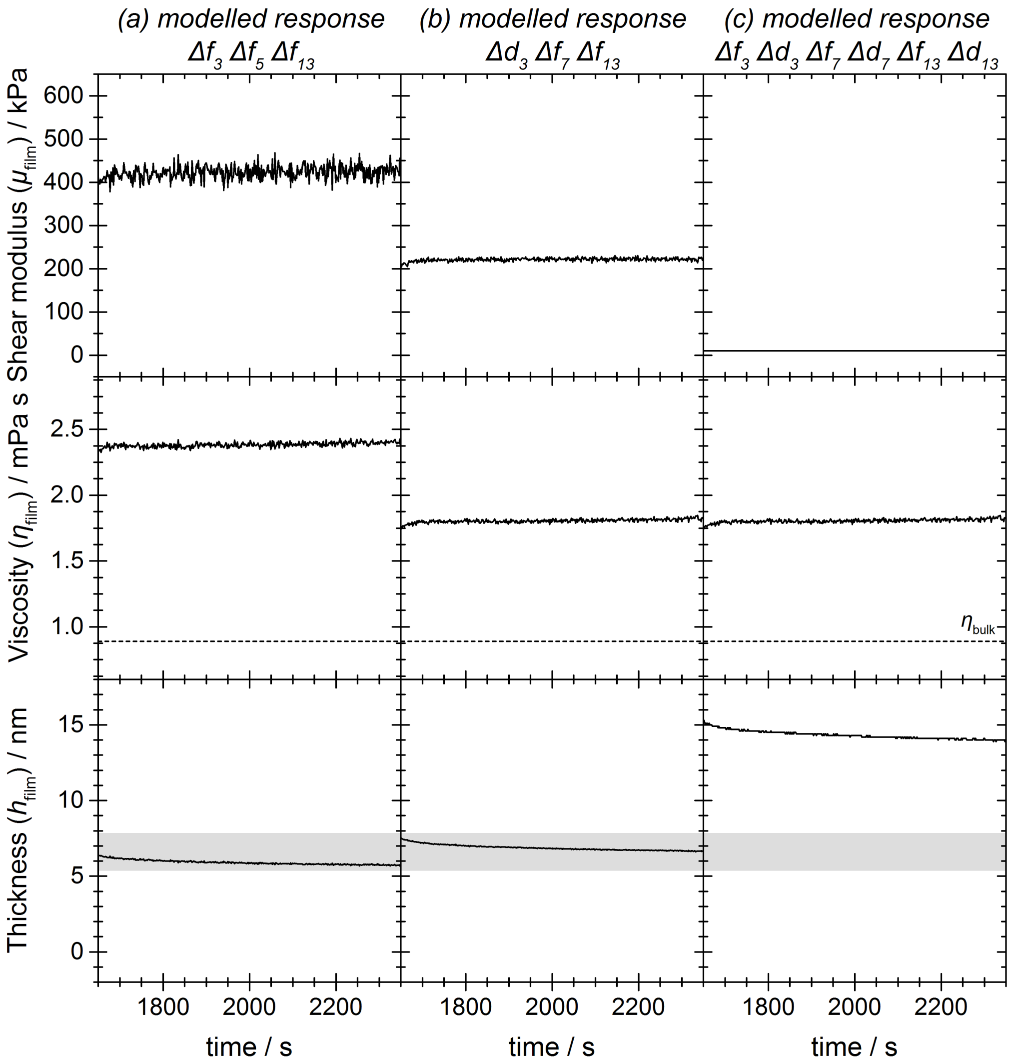


Figure S5. Modelled shear, viscosity and thickness values from the alternative three response combinations noted in Table S2 using the settings shown in Figure S4. The grey box represents the range of values from an independent measurement using dual polarisation interferometry.[4]

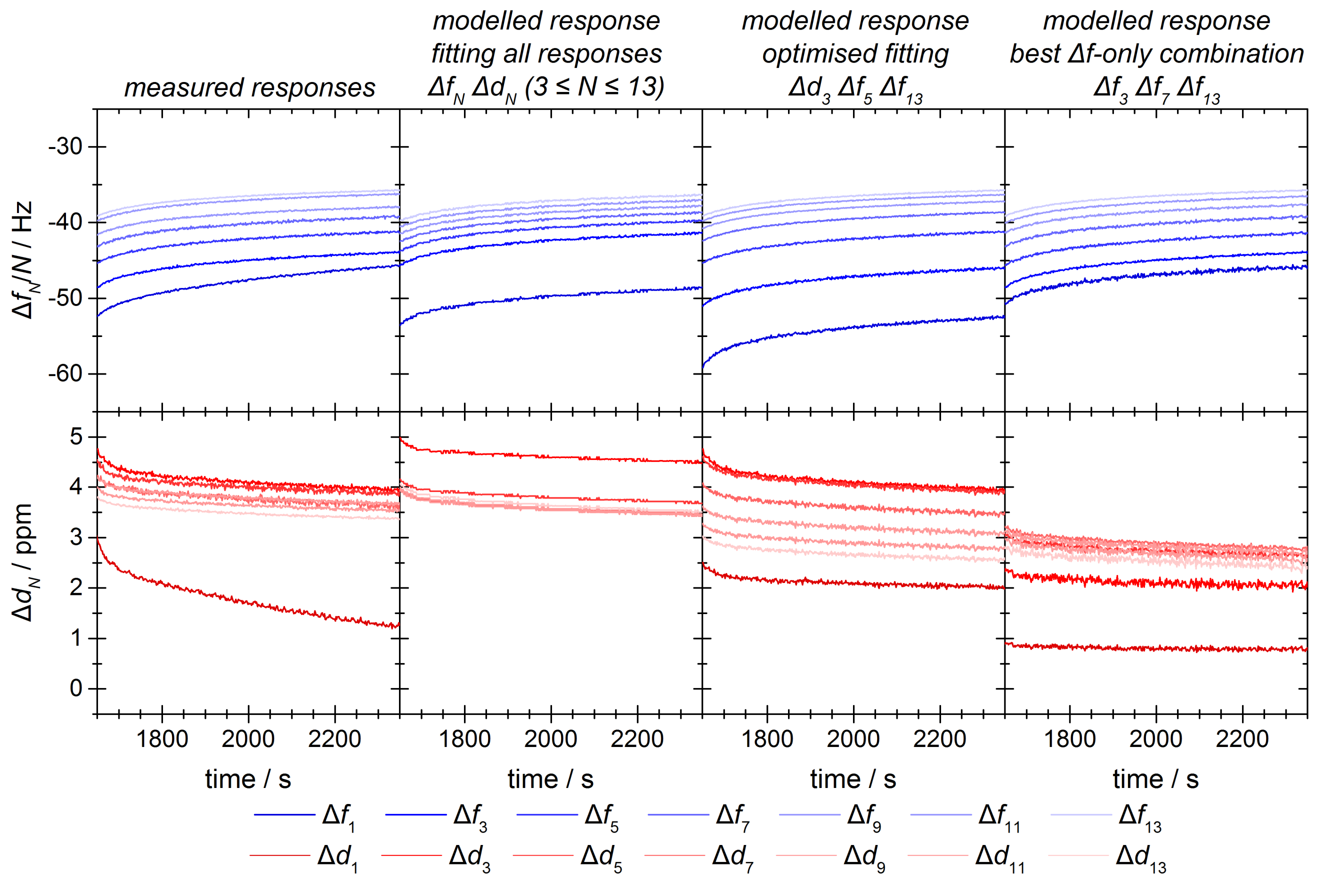


Figure S6. Measured QCM-D response from an adlayer *Mv*BOx on a silica-coated QCM-D sensor. From left to right: the measured responses, the modelled responses after fitting to all Δf and Δd responses for odd harmonics 3–13 ($\Delta d_1 > 9$ and out of frame); modelled response after fitting to TPM-sensitivity optimised selection of harmonics (Δd_3 Δf_5 Δf_{13}); modelled responses after fitting to TPM-sensitivity optimised selection of frequency responses only (Δf_3 Δf_7 Δf_{13}). While shown, the fundamental Δf and Δd responses were not used to fit due to their sensitivity to mounting. The responses are coloured from darkest to lightest in order of increasing harmonic number. Experimental conditions same as Figure 5 in the main text. Model parameters same as Figure 3 in the main text.

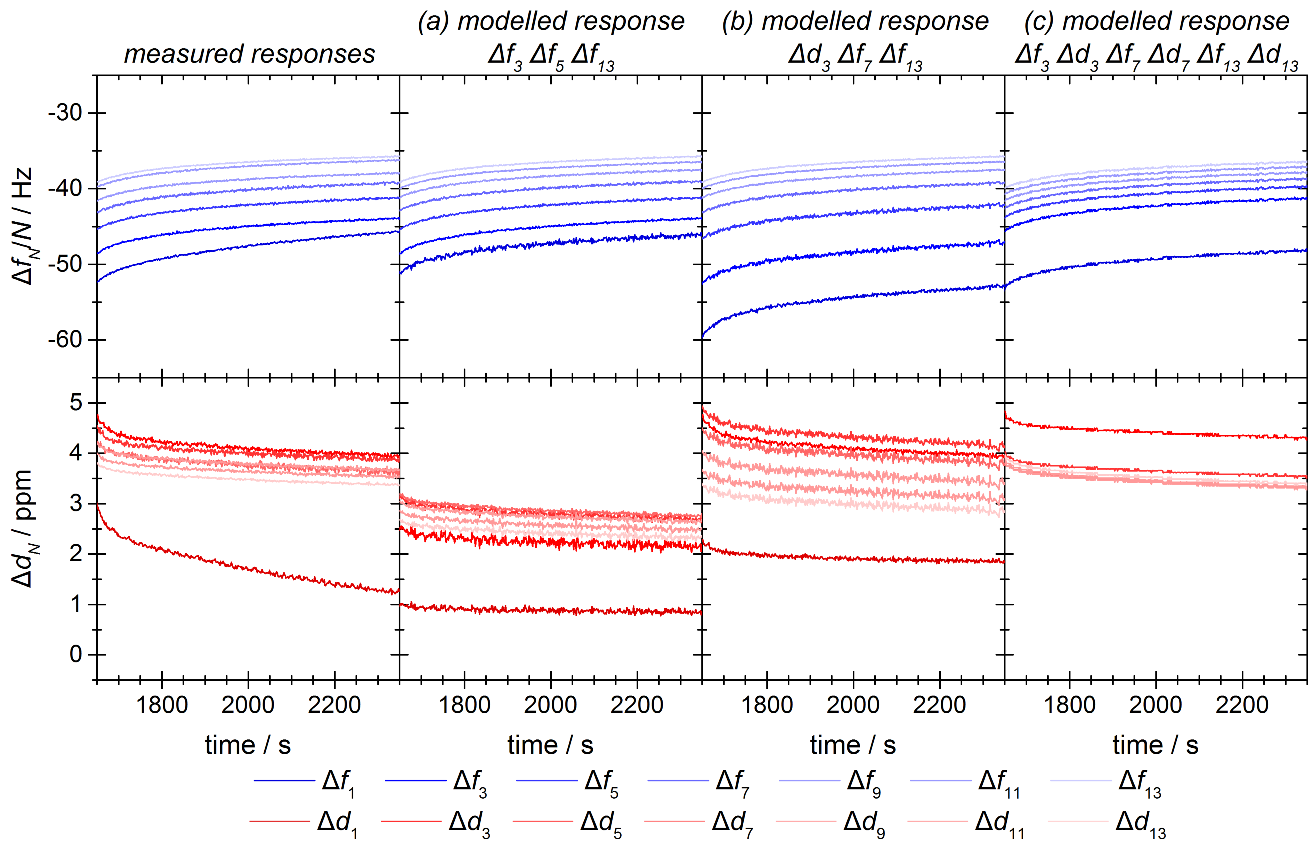


Figure S7. The fit to the measured responses from three alternative response combinations noted in Table S2 using the settings shown in Figure S4.

S8. Effect of Different Initial Estimates of Film Properties on TPM-sensitivity

Table S3 shows the effect of changing the initial estimates of an adlayer's properties on the optimum harmonic combination and the associated TPM-sensitivity score of these calculations. A change in an order of magnitude of some of the film property values does not always change the optimal harmonic combination. Although the selection of responses varies in each case, all these alternative harmonic combinations yield similar TPM-sensitivity scores. This illustrates the utility of using these algorithms to guide the selection of harmonics for investigations into poorly characterised materials due to their high tolerance for incorrect initial film estimates.

Table S3. The initial estimates of the films properties with the resultant optimal harmonic combinations grouped by row.

Film thickness (nm)	Film viscosity (mPa s)	Film shear (kPa)	Optimal response combination	TPM-sensitivity
5	3.16	316	$\Delta d_3\ \Delta f_5\ \Delta f_{13}$	4.1×10^{16}
10	3.16	316	$\Delta d_3\ \Delta f_5\ \Delta f_{13}$	1.9×10^{17}
1	3.16	316	$\Delta f_3\ \Delta f_7\ \Delta f_{13}$	1.5×10^{15}
10	31.6	316	$\Delta d_3\ \Delta f_7\ \Delta f_{13}$	6.9×10^{13}
10	31.6	1	$\Delta d_3\ \Delta f_5\ \Delta f_{13}$	2.6×10^{11}
10	31.6	1000	$\Delta f_3\ \Delta f_7\ \Delta f_{13}$	2.6×10^{14}
10	316	1000	$\Delta d_3\ \Delta f_7\ \Delta f_{13}$	2.5×10^{11}

Fixed model parameters: $\rho_{film} = 1.45 \times 10^3$ kg m^{-3}, $\rho_{bulk} = 1.0 \times 10^3$ kg m^{-3}, $\eta_{bulk} = 0.89$ mPa s, $f_0 = 4.95$ MHz, $\sigma_{\Delta f} = 0.053$ Hz, $\sigma_{\Delta d} = 0.021$ ppm.

S9. References

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