Supporting Information: Enzymatic Hydrolysis of Triglycerides at Water–Oil Interface Studied via Interfacial Rheology Analysis of Lipase Adsorption Layers

Aliyar Javadi[1, 2, 3, 4, *], Saeid Dowlati[1, 2], Sara Shourni[2], Sherly Rusli[1], *Kerstin Eckert*[3, 4], *Reinhard Miller*[5] *and Matthias Kraume*[1]

1. *Technische Universität Berlin, Chair of Chemical and Process Engineering, Straße des 17. Juni135,10623 Berlin, Germany*
2. *Chemical Engineering Department, College of Engineering, University of Tehran, 14395-515, Tehran, Iran.*
3. *Institute of Fluid Dynamics, Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Bautzner Landstraße 400, 01328 Dresden, Javadi.aliyar@hzdr.de*
4. *Institute of Process Engineering and Environmental Technology, Technical University Dresden, D-01069 Dresden, Germany.*
5. *Technical University Darmstadt, Hochschulstraße 12, D-64289 Darmstadt, Germany*

* Corresponding Author: Javadi.aliyar@hzdr.de, javadi.aliyar@ut.ac.ir

Table of Contents

Fourier Series

Using the Fourier series, a periodic function can be decomposed into an infinite number of sine and cosine waves, representing the response as a fundamental wave with some higher harmonics. The mathematical formulation of the IFT response in terms of a Fourier series is as follows:

$$\gamma(t)-\gamma_0 \equiv \Delta\gamma(t) = a_0 + \sum_{n=1}^{\infty} a_n cos(\frac{2n\pi}{T}t) + b_n sin(\frac{2n\pi}{T}t) \quad \text{S1}$$

where a_0, a_n, and b_n are the Fourier coefficients, $\gamma(t)$ is the interfacial tension, γ_0 is the equilibrium interfacial tension, $T = 2\pi/\omega$ is the oscillation period, and ω is the angular frequency. Here, we use the Fourier analysis to analytically decompose an asymmetric IFT response to calculate the compressive and expansive elasticities separately.

The Fourier Series of Asymmetric IFT Responses

A period of IFT response for a 2.5 mg·mL^{-1} lipase solution between 3050–3100 s, smoothed with a Savitzky–Golay filter, is redrawn in Figure . The response can be adequately assumed as a combination of two sinusoidal half-cycles with different amplitudes (A_1 and A_2) and frequencies (ω_1 and ω_2) to make analytical calculations possible. The angular frequencies of the two half-cycles are not the same as a result of the nonlinear interfacial behavior, while their harmonic average remains ω. So, the IFT response takes the following form:

$$\Delta\gamma(t) = \begin{cases} A_1 sin(\omega_1 t) & \gamma(t) \geq \gamma_0;\ 0 \leq t \leq \frac{\pi}{\omega_1} \\ A_2 sin\left(\omega_2(t-(\frac{\pi}{\omega_1}-\frac{\pi}{\omega_2}))\right) = A_2 sin(\frac{\pi\omega_2}{\omega_1}-\omega_2 t) & \gamma(t) < \gamma_0;\ \frac{\pi}{\omega_1} < t < \frac{\pi}{\omega_1}+\frac{\pi}{\omega_2} \end{cases} \quad \text{S2}$$

The coefficients of decomposing this signal into a Fourier series are as follows:

$$a_0 = \frac{1}{T}\int_0^T \Delta\gamma(t)dt = \frac{2}{T}\left\{\frac{A_1}{\omega_1}-\frac{A_2}{\omega_2}\right\} \quad \text{S3}$$

$$a_n = \frac{2}{T}\int_0^T \Delta\gamma(t)\cdot cos(n\omega t)dt = \frac{1}{T}\left\{A_1\left(cos(\frac{n\omega\pi}{\omega_1})+1\right)\left[\frac{1}{\omega_1+n\omega}+\frac{1}{\omega_1-n\omega}\right] - A_2\left(cos(n\omega T)+cos(\frac{n\omega\pi}{\omega_1})\right)\left[\frac{1}{\omega_2-n\omega}+\frac{1}{\omega_2+n\omega}\right]\right\} \quad \text{S4}$$

$$b_n = \frac{2}{T}\int_0^T \Delta\gamma(t)\cdot sin(n\omega t)dt == \frac{1}{T}\left\{A_1 sin\left(\frac{n\omega\pi}{\omega_1}\right)\left[\frac{1}{\omega_1-n\omega}+\frac{1}{\omega_1+n\omega}\right] - A_2\left[\frac{sin(n\omega T)-sin\left(\frac{\pi n\omega}{\omega_1}\right)}{\omega_2+n\omega}+\frac{sin(n\omega T)+sin\left(\frac{\pi n\omega}{\omega_1}\right)}{\omega_2-n\omega}\right]\right\} \quad \text{S5}$$

The first to fourth order Fourier polynomials of the response signal are also drawn in Figure , suggesting that the second-order Fourier polynomial fits the experimental results sufficiently well:

$$\Delta\gamma_2(t) = a_0 + a_1 cos(\omega t) + b_1 sin(\omega t) + a_2 cos(2\omega t) + b_2 sin(2\omega t) \quad \text{S6}$$

Calculating Expansive and Compressive Elasticities

To calculate the expansive and compressive elasticities, we should know the maximum and minimum points of $\Delta\gamma_2(t)$:

$$\varepsilon'_{exp} = \frac{\gamma_{amp,exp}}{A_{amp}/A_0} = \frac{\Delta\gamma_2(t = {}^{T}/_{4})}{A_{amp}/A_0} = \frac{a_0 + b_1 - a_2}{A_{amp}/A_0} \quad \text{S7}$$

$$\varepsilon'_{com} = \frac{\gamma_{amp,com}}{A_{amp}/A_0} = \frac{\Delta\gamma_2(t = {}^{3T}/_{4})}{A_{amp}/A_0} = \frac{a_0 - b_1 - a_2}{A_{amp}/A_0} \quad \text{S8}$$

where ε'_{exp} and ε'_{com} are the expansive and compressive elasticities, $\gamma_{amp,exp}$ and $\gamma_{amp,com}$ are the maximum and minimum of the second-order Fourier polynomial, A_{amp} is the amplitude of the interfacial area oscillation, and A_0 is the average interfacial area before the oscillation.

The total harmonic distortion (THD) is the ratio of the amplitudes of higher harmonics to the amplitude of the fundamental frequency and a parameter to characterize the order of nonlinearity [45]:

$$THD = \frac{(a_2^2 + a_3^2 + \dots + a_n^2)^{\frac{1}{2}}}{a_1} \quad \text{S9}$$

In analogy to the THD, the ratio of the higher harmonics to the first and second-order amplitudes for the studied signal is less than 5%, making the approximation sufficiently accurate.

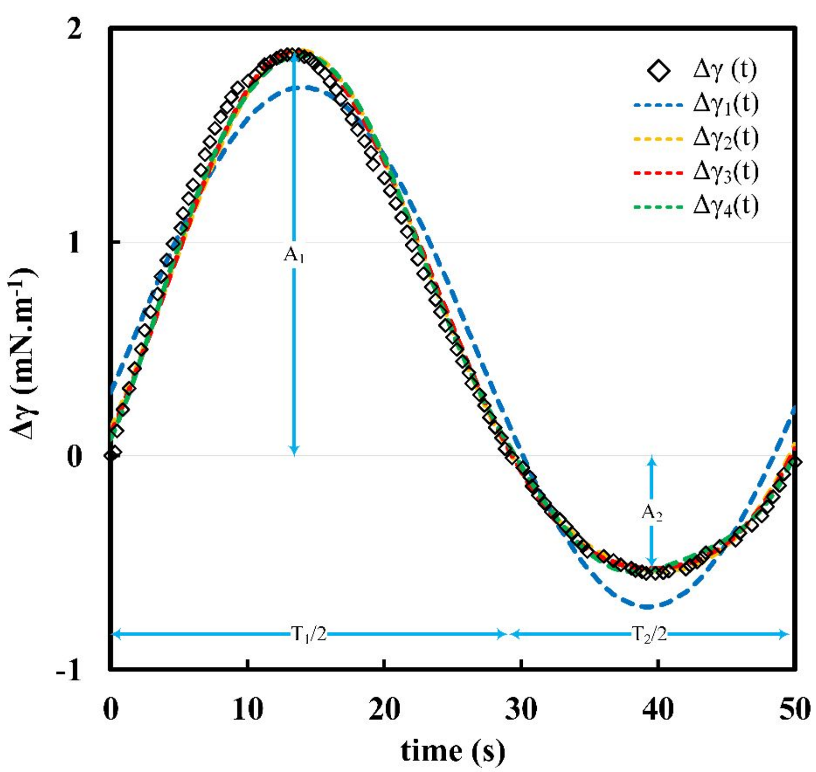

Figure S1- IFT response to a sinusoidal perturbation of the interfacial area with 0.5 mm3 volumetric amplitude (~1 *mm2 area amplitude) for a 2.5 mg·mL-1 lipase aqueous solution droplet formed in sunflower oil at a frequency of 0.02 Hz versus aging time between 3000–3050 s and its Fourier polynomials of first to fourth-order.*