Article

Nonlinear Viscoelastic Behavior of Air-Water Interface Containing Surfactant-Laden Nanoparticles

Badri VISHAL* and Pallab GHOSH

**Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati - 781039, Assam, India*

(Received : September 9, 2019)

Foams have a large number of applications in our daily life. Their stability depends on the thin liquid film, which consists of an aqueous phase bound by two air-water interfaces. During its processing, foam is exposed to a large deformation. Therefore, the study of the air-water interface under large amplitude oscillatory shear (LAOS) flow is highly relevant for foam stability. In this article, the LAOS behavior of the air-water interface was investigated. The interface was formed by 0.1 mol m^{-3} hexadecyltrimethylammonium bromide and 0.5% w/v silica nanoparticles. The LAOS study was performed by analyzing the intracycle stress waveforms and Lissajous-Bowditch curves. The Fourier transform rheology and Chebyshev polynomial approaches were used to describe the LAOS flow of the interface. The air-water interface exhibited intracycle strain-hardening and shear thickening behavior under the LAOS flow. However, at very large strain amplitude (*i.e.* 45%), the interface displayed intracycle shear thinning behavior.

Key Words: Air-water interface / Fourier-transform rheology / Interfacial shear rheology / Large amplitude oscillatory shear / Lissajous-Bowditch curve

1. INTRODUCTION

Colloidal systems, such as foams and emulsions, have high specific interfacial area. The properties of aqueous foams are usually controlled by using surfactants and sometimes by nanoparticles. Several scientists¹⁻⁴⁾ have studied the rheology of the air-water interface⁵⁻⁷⁾. These works have provided approximate mechanical properties of the interface. Additional insights into the phenomena such as film drainage⁸⁾, coarsening (Ostwald ripening)⁹⁾, and coalescence¹⁰⁾, can be obtained from interfacial rheology. It also illustrates the adsorption kinetics of surfactants and particles from the bulk phase to the interface¹¹⁾. Thus, it can be a very important tool for understanding the stability of foams¹²⁻¹⁴⁾.

The surfactants form a film by adsorbing at the interface. There are two types of film based on the way they are formed, *i.e.*, spread and adsorbed film. When small water-soluble surfactant molecules adsorb at the interface, they form a Gibbs monolayer. On the other hand, some water-insoluble materials such as inorganic nanoparticles, long-chain polymers, and proteins form a Langmuir monolayer after spreading on the interface. To characterize a Langmuir monolayer,

the Langmuir-Blodgett trough is often used, where the surface pressure is measured by compressing or/and expanding the monolayer. In many real-life situations, the interface undergoes mechanical perturbation by changing its size and shape. The response of the interface to a change in its size (at constant shape) is studied by interfacial dilatational rheology, whereas the response to a change in its shape (by keeping the size or area the same) is studied by interfacial shear rheology. The study of interfacial shear rheology is relatively less developed than the interfacial dilatational rheology.

In this article, we are interested in the response of the interface under shear deformation. The interfacial shear rheology deals with the same rheological concepts that have been developed for the bulk materials¹⁵⁾. However, this requires a few notable cautions. For instance, the shear deformation should not induce a radial flow at the interface, and the bulk effect on the interfacial flow (*i.e.*, the impact of coupling interfacial flow with the adjacent sub-phase) should be avoided. This effect can be expressed by Boussinesq number (B_0), which is the ratio of surface to bulk viscous effects, defined as

$$B_0 = \frac{\eta_s}{(\eta_1 + \eta_2)L} \quad (1)$$

where η_s is the surface viscosity, and η_1 and η_2 are the

* Corresponding author.

E-mail : badri@iitg.ernet.in

Tel: +91.361.2582253; Fax: +91.361.2690762

viscosities of the upper and lower fluids, respectively. L is a geometrical factor determined by the geometry used. Theoretically, if the value of B_0 is larger than unity, the interface shows a dominating response against shear deformation. However, the bulk flow influences the interfacial flow when B_0 is less than unity. Various geometries can be used to study interfacial shear rheology, *e.g.*, double wall ring¹⁶⁾, bicone disk¹⁷⁾, and magnetic-needle¹⁸⁾. The relationship between interfacial shear stress and the corresponding deformation (or deformation rate) was first suggested by Boussinesq¹⁹⁾, which was further improved by Scriven²⁰⁾. The Boussinesq-Scriven model gives a linear relationship between interfacial shear stress and deformation (or deformation rate)^{21, 22, 15)}. However, this model is suitable for a Newtonian interface. The presence of particles at the interface makes the interface non-Newtonian. To study the interfacial shear rheology for a particle-laden interface, the latter is allowed to flow by the rotational movement of the solid sensor on the interface. The stress response (σ_s) to the interface is directly proportional to the imposed strain (γ_s) and strain rate, which is given as

$$\sigma_s = \left(G_s + \eta_s \frac{d}{dt} \right) \gamma_s \quad (2)$$

where G_s and η_s are the shear modulus and viscosity of the interface, respectively. Equation 2 can be used to describe the viscoelastic behavior of the interface in the linear viscoelastic regime. However, under the LAOS flow, a more robust model is required. For an oscillatory shear flow in the linear viscoelastic regime, the stress response to the interface can be given by a complex interfacial shear modulus (G_s^*). This is represented by

$$G_s^*(\omega) = G_s'(\omega) + iG_s''(\omega) \quad (3)$$

where ω is the frequency of oscillation, and G_s' and G_s'' are the real and imaginary parts of the complex modulus, which represent the elastic and viscous components of the interface, respectively. These components are called the *storage* and the *loss* modulus, respectively.

Safouane *et al.*²³⁾ have studied shear rheology at the air-water interface containing fumed silica nanoparticles. They have measured the oscillatory shear moduli (*i.e.*, G_s' and G_s'') by varying the particle hydrophilicity. For particles with very high hydrophilicity, the oscillatory shear moduli were negligible, whereas for partially hydrophilic particles, G_s' was found to be greater than G_s'' . They also observed a gel point where both the moduli were same. Cicuta *et al.*²⁴⁾ have found that the interface formed by charged latex particles exhibited

predominantly viscous behavior (*i.e.* $G_s' < G_s''$) when the surface coverage was high. They also pointed out that the nature of the stress response to the interfacial deformation of hard and soft particles (*e.g.*, protein) were very similar, although they had quite different interaction potentials. The major research on interfacial rheology was made when the shear stress and strain (or strain rate) were linearly dependent²⁵⁻²⁷⁾.

Interfaces containing solid particles often show nonlinear viscoelastic behavior even at low deformation or deformation rate^{28, 29)}. In other words, the range of linear viscoelastic regime is very small. This is because the microstructure at the interface is easily destroyed by the application of even a small shear stress. However, in many practical situations (*e.g.*, during the formation and processing of foams and emulsions) they are routinely exposed to larger and faster deformation. Therefore, to deal with real life phenomena pertaining to the interface, the study of nonlinear rheological behavior of the interface is highly relevant.

The large amplitude oscillatory shear (LAOS) flow at the interface can be analyzed in many different ways. In amplitude sweep experiment, the storage modulus (G_s') and loss modulus (G_s'') are measured with strain amplitude³⁰⁾. Over the past decade, sufficient consideration has been made on the analysis of Lissajous-Bowditch curves³¹⁾. In these curves, stress responses are shown as a function of applied strain (known as *elastic Lissajous-Bowditch curve*) or strain rate (known as *viscous Lissajous-Bowditch curve*). To characterize the LAOS behavior using Lissajous-Bowditch curves, a geometrical technique to decompose the intracycle stress response (σ_s) into solid-like (σ_s') and liquid-like (σ_s'') components, has been recommended by Cho *et al.*³²⁾, which was further modified by Yu *et al.*³³⁾. The main difficulty in analyzing the Lissajous-Bowditch curves was originated due to the presence of higher harmonic terms. Previous work on the LAOS behavior has focused only on the bulk materials³⁴⁻³⁸⁾. Only a limited works have been done on the LAOS behavior of the air-water interfaces³⁹⁻⁴²⁾. Therefore, there is still a need for the advancement of this topic.

Despite the detailed study of the rheology of the interface containing surfactant-laden nanoparticles, it still poses many challenges, and the current knowledge is far from sufficient for practical applications. Therefore, in this paper, we have investigated the LAOS behavior of air-water interface on which surfactant-laden nanoparticles were adsorbed.

2. EXPERIMENTAL SECTION

The cationic surfactant (*i.e.*, HTAB) used in this study

was bought from Merck [Hohenbrunn (Germany), 97% assay]. Silicon dioxide was used as a nanoparticle, which was bought from Plasmachem. Millipore water was used to prepare all samples. All experiments were performed with a system consisting of 0.1 mol m^{-3} HTAB and 0.5% (w/v) silica nanoparticles. When the surfactant concentration was above the CMC, the entire surface was covered by the surfactant molecules only, and the nanoparticles remained either in sub-phase or in the bulk phase¹¹. Therefore, in the present work, the HTAB concentration was chosen below its CMC (*i.e.*, 1 mol m^{-3}), so that the surfactant-laden particles were able to adsorb at the air-water interface. Furthermore, it was observed that some of the nanoparticles sedimented at the bottom of the container when their concentration exceeded 0.5% (w/v)⁴³. Therefore, we did not perform experiments at the nanoparticle concentrations beyond 0.5% (w/v).

In many practical circumstances, the interface is perturbed by external mechanical forces. The perturbation may cause deformation of the interface by changing its shape or/and size. Such interfaces can be characterized by using shear rheology, where the interface is deformed in such a way that its shape changes keeping the size unchanged¹. To characterize the rheological behavior of the air-water interface, a rotational rheometer with interfacial rheology system was used. The rheometer was manufactured by Anton Paar (Germany), and its model was Physica MCR 301. This system consisted of a bicone disc (diameter = 68.28 mm, cone angle = 5°) and a measuring cell (diameter = 80 mm, height = 90 mm) as shown in Fig. 1. The rheometer had a sensitivity of detecting $0.1 \text{ } \mu\text{Nm}$ and $0.02 \text{ } \mu\text{Nm}$ of torques in the rotational and oscillatory modes, respectively, with $0.001 \text{ } \mu\text{Nm}$ of torque resolution. The temperature was set to 298 K by using a Peltier device, and it was controlled within $\pm 0.1 \text{ K}$ via a water-circulating bath.

All the experimental measurements were performed by imposing a sinusoidal strain at the air-water interface containing the surfactant-laden particles. The range of

Fig. 1 Schematic representation of the bicone geometry used for interfacial shear rheological measurements.

viscoelasticity was studied by amplitude sweep experiment. In this experiment, interfacial dynamic moduli (*i.e.*, G'_s and G''_s) were measured with strain amplitude (γ_0), which was varied from 0.01 to 100% at the constant angular frequency (ω) of 1 rad s^{-1} . The LAOS behavior of the interface was studied by analyzing the intracycle stress response. The stress analysis was performed at two ω , *i.e.*, 0.1 and 1 rad s^{-1} , and five γ_0 , *i.e.*, 1, 6.4, 10, 21 and 45%. For each ω and γ_0 , the stress response was plotted with strain and strain rate. The corresponding curve is known as *Lissajous-Bowditch curve*⁴⁴. Furthermore, under the LAOS flow, the distorted stress response was described by Fourier series. The Fourier coefficients were determined by fitting the waveform with the Fourier series. These coefficients represent the amplitudes of in- and out-of-phase stress components to the imposed strain. In order to understand the LAOS flow behavior at the air-water interface, frequency response Fourier transform rheology was used. The Chebyshev polynomials of the first kind (T_m) described the Lissajous-Bowditch curves. A sequence of physical processes approach was used to describe the LAOS flow behavior of the interface. Each experiment was repeated three times to verify the reproducibility.

The procedure employed during the rheological measurement at the interface was as follows. The dispersion containing 0.5% w/v silica nanoparticles and 0.5 mol m^{-3} HTAB, was half filled in the measuring cell. The measuring cell was left undisturbed for 15 min. The bicone disc was lowered slowly so that the tip of the disc just touched the interface. Thereafter, the disc was positioned to the interface. Then, the rheological measurements were performed by shearing the microstructure at the interface.

Two major complexities arise while performing the rheological experiment at the air-water interface. The first complexity is that a small torque is required to shear the film at the interface. However, this low value of stress response was achieved by shearing in a direct strain oscillation mode⁴⁵. The second complexity is that, during the measurement, the bulk sample may influence the flow behavior of the interface. This can be described in term of B_0 (see Equation 1). At a higher frequency of oscillation, the Boussinesq number becomes less than unity. In that case, the interfacial flow is affected by the bulk flow. Therefore, B_0 should be sufficiently high.

3. RESULTS AND DISCUSSION

The film at the air-water interface was obtained by adsorbing silica nanoparticles from the dispersion. These

nanoparticles adsorb at the interface in the present of surfactant. The film at the interface becomes complex due to the interaction between surfactant-modified particles. The LAOS study was performed on this interface having the microstructure.

3.1 Amplitude sweep experiment

Figure 2 shows the results of the amplitude sweep experiment, where the dynamic moduli (*i.e.*, G'_s and G''_s) were measured with strain amplitude. This experiment is usually conducted before the LAOS study because it provides a guideline about the strain amplitude above which the interface shows linear viscoelastic behavior. It was performed at a fixed frequency of oscillation, *i.e.*, 1 rad s^{-1} . From the figure, it can be seen that the dynamic moduli were independent of strain amplitude up to 1% of the latter (which is shown by a vertical dashed line). This region is called *linear viscoelastic regime*. It can also be observed that in this regime, G'_s was higher than G''_s by almost one order of magnitude. Therefore, the interface showed viscoelastic behavior and the elastic property of the interface dominated. The viscoelastic behavior in the linear regime was studied by using small amplitude oscillatory shear (SAOS) flow⁴⁶⁾. Deformation under the SAOS condition does not destroy the microstructure at the air-water interface. It only deforms the structure, which returns to its original state once the applied stress is removed. Therefore, the main cause of the deformation is the applied stress. The study under the SAOS condition is generally used to investigate the role of microstructure on rheology. However, in the present work, we have primarily focused on the rheological behavior of air-water interface under the LAOS condition. In the SAOS flow, the air-water interface was deformed at low strain amplitude. Upon increasing the

Fig. 2 Amplitude sweep experiment of the air-water interface. The variation of interfacial dynamic moduli (*i.e.*, G'_s and G''_s) with strain amplitude was measured at the fixed angular frequency of 1 rad s^{-1} . The film at the interface was formed by the adsorption of surfactant-laden nanoparticles from the solution, which contained 0.1 mol m^{-3} HTAB and 0.5% (w/v) silica nanoparticles. The dashed line divides the curves into two regions, *i.e.*, small amplitude oscillatory shear (SAOS) and large amplitude oscillatory shear (LAOS) flows.

strain amplitude above 1%, G'_s decreased continuously, and G''_s first increased, then approached a local maximum, and thereafter declined. The decrease in G'_s at larger strain amplitudes was due to the fact that the microstructure at the interface got destroyed. This is an indication of the *strain-softening* of the interface. The G''_s curve revealed the yielding behavior⁴⁷⁾. The strain amplitude at which G''_s started increasing is known as *critical strain*, and the strain with maximum G''_s is known as *yield strain*. This type of phenomena is called *weak strain overshoot*. From the figure, it can be observed that both the moduli cross each other at the yielding point, and thereafter, G''_s became more significant than G'_s . This indicates that the interface started showing viscoelastic behavior with the viscous property dominating. Because of the presence of higher harmonic terms under the LAOS flow, different materials often show similar LAOS behavior⁴⁸⁾. Therefore, these terms must be taken into consideration to get a complete insight into the LAOS behavior. Furthermore, interfacial shear viscosity of these interfaces was measured at various concentrations of HTAB and silica nanoparticles, as shown in the Appendix (Figures A1-A4).

3.2 Fourier series and Fourier transformation

Wilhelm *et al.*^{49, 50)} have used the Fourier series to express the contribution of higher harmonic terms, which is known as *FT-rheology*. FT-rheology is a mathematically sound approach to characterize the LAOS behavior of the air-water interface. This is highly sensitive for detecting a very small signal that arises during the LAOS flow. However, it is difficult to correlate the results obtained from the FT-rheology to their physical significance. The decomposition of the stress response into the solid-like and liquid-like components is based on the symmetrical geometry of the stress-strain curve in a complete cycle. The Fourier series is given by

$$\sigma_s(\gamma_0, \omega, t) = \sum_{n=1,3,\dots} [a_n \cos(2\pi n t) + b_n \sin(2\pi n t)], \quad 2\pi n = \omega_n \quad (4)$$

where a_n and b_n are the Fourier coefficients, ω_n is the angular frequency. The Fourier coefficients are given as follows:

$$a_n = \frac{2}{T} \int_0^T \sigma_s(t) \cos(2\pi n t) dt$$

$$b_n = \frac{2}{T} \int_0^T \sigma_s(t) \sin(2\pi n t) dt \quad (5)$$

In the linear viscoelastic regime, these Fourier coefficients reduce to the dynamic moduli. Figure 3 shows the curve fitting based on the Fourier series (Equation 4). The

stress response obtained from the experiment is shown by the solid curve, and the dashed curve shows the stress response obtained from Equation 4. When the air-water interface was sheared at a lower strain amplitude (*i.e.* 1% and 6.4%), the first harmonic term was enough to fit the experimental stress response. The stress waveforms were a perfect sinusoid. However, when the interface was sheared with a strain amplitude above 10%, the first harmonic term was not sufficient to fit the sinusoid. Therefore, to fit the waveform, the third harmonic term was added to the first harmonic term. Further increasing the strain amplitude (*i.e.*, 24 and 45%), the contribution of the fifth harmonic term can be observed. From the figure, it can be concluded that only the odd higher harmonic terms were responsible for the LAOS flow at the interface.

The impact of the higher harmonic terms on the LAOS behavior was analyzed by converting the Fourier series from time domain to frequency domain. This transformation was done by using a discrete Fourier transform (DFT) of the stress response data points, which is known as the *FT-rheology spectrum*. The DFT of the stress data points was computed by the following equation:

$$F_n = \sum_{k=0}^{N-1} \sigma_{sk} \exp(-2\pi i n k / N) \quad (6)$$

where N is the number of data points, $k = 0, 1, 2, \dots$, and i is the imaginary unit. F_n can be denoted by the corresponding magnitude (as F_n is a complex number). Figure 4 shows the magnitude of each harmonic term, which was responsible for the LAOS flow in the nonlinear viscoelastic regime. At low strain amplitudes (*i.e.*, 1% and 6.4%), the peaks corresponding to the first harmonic term can be observed. With increasing strain amplitude, peaks at higher harmonic terms are seen clearly. The magnitude of these peaks increased with strain amplitude. Furthermore, no peaks were noticed for the even harmonic terms. This may be attributed to the absence of the influence of bulk liquid to the interface.

3.3 Waveforms and Lissajous-Bowditch curves

Ewoldt *et al.*³¹⁾ have proposed a geometrical approach to analyze the LAOS behavior. In this approach, the shape of the intra-cycle stress response at larger strain amplitude is analyzed. Figure 5 shows the waveform of the intra-cycle stress response at various strain amplitudes ($\gamma_0 = 1, 6.4, 10, 21$, and 45%). The shape of the stress waveform deformed from sinusoid to the non-sinusoid. The figure clearly showed the gradual change in the flow behavior from SOAS to LAOS. Because of the non-sinusoidal waveform, the oscillatory dynamic moduli (*i.e.*, the first harmonic term in the Fourier

Fig. 3 Curve fitting of the stress response obtained at different strain amplitudes (*i.e.*, 1, 6.4, 10, 21, and 45%). These curves were fitted by using Fourier series (Equation 4), where the Fourier coefficients (*i.e.*, a_n and b_n) were computed from Equation 5. The number of harmonic terms (*i.e.*, $n = 1, 3$, and 5) was increased with increasing strain amplitude to fit the curves accurately.

series) were not sufficient to describe the LAOS behavior of the interface. At 1% strain amplitude, the stress waveform passed through the mean position, which indicated that there was no phase change between the imposed strain and the stress response. The phase shift increased gradually, and it became $\pi/2$ at 45% of γ_0 . In other words, the interface showed solid-like behavior at small γ_0 , and displayed liquid-like behavior at high γ_0 .

In Fig. 6a, the intra-cycle stress response of the interface containing surfactant-laden nanoparticles, was plotted against imposed strain. In the linear viscoelastic regime (*i.e.*, at low strain amplitudes), the Lissajous-Bowditch curves were perfectly elliptical, which was due to the perfect sinusoid of the corresponding stress response (see Fig. 5). The magnitude of G_s^* can be obtained from the slope of the elastic Lissajous-Bowditch curves, whereas the minor axis represents the phase change between applied strain and stress response. The

phase change can also be seen in Fig. 5. From Fig. 6a, it can be observed that the width of the minor axis gradually increased with increasing strain amplitude, and at very large strain amplitudes (*i.e.*, 21 and 45%), a rectangular shape was formed. Furthermore, σ'_s and σ''_s can be obtained from the elastic and viscous Lissajous-Bowditch curves, respectively, which can be represented by the following equations:³²⁾

$$\sigma_s \left(\gamma_s, \frac{\dot{\gamma}_s}{\omega} \right) = \frac{\sigma_s \left(\gamma_s, \frac{\dot{\gamma}_s}{\omega} \right) + \sigma_s \left(\gamma_s, -\frac{\dot{\gamma}_s}{\omega} \right)}{2} + \frac{\sigma_s \left(\gamma_s, \frac{\dot{\gamma}_s}{\omega} \right) - \sigma_s \left(\gamma_s, -\frac{\dot{\gamma}_s}{\omega} \right)}{2} \quad (7a)$$

$$\sigma_s = \sigma'_s + \sigma''_s \quad (7b)$$

These equations are used to decompose the stress responses into their elastic and viscous components. The elastic components of the intra-cycle stress response are shown in Fig. 6b, which were obtained from the elastic Lissajous-Bowditch curves (*i.e.* Fig. 6a) by taking the mean of the stress responses. They showed linear dependency with strain under the SAOS flow. However, the curves were bent upward under the LAOS flow. The upward lifting of the curves indicated the strain-hardening behavior of the interface. However, the overall response was strain-softening because the loss modulus (G''_s) decreased after the yield strain (see Fig. 2). A similar kind of behavior was observed by Mermet-Guyennet *et al.*⁵¹⁾.

Figure 7a shows the viscous Lissajous-Bowditch curves, where the intra-cycle stress responses are plotted against strain rate at different strain amplitudes of oscillation. At lower strain amplitudes, these curves were circular, indicating that the viscous contribution was absent. Therefore, the interface showed predominantly elastic behavior, which can be justified in Fig. 6. Nevertheless, at higher strain amplitudes, the viscous Lissajous-Bowditch curves showed a sigmoid shape. To characterize such shapes, instantaneous viscosity (η_i) can be used. Instantaneous viscosity at any point during the shearing can be obtained from the viscous Lissajous-Bowditch curve by following equation,

$$\eta_i = \frac{d\sigma_s}{d\dot{\gamma}_s} \quad (8)$$

where $\dot{\gamma}_s$ is the strain rate. The instantaneous viscosity decreased with increasing strain rate, as shown in Fig. 7. Therefore, the interface exhibited intracycle shear thinning behavior under the LAOS flow. Like the elastic component of the stress response (Fig. 6b), the viscous part can be obtained from the viscous Lissajous-Bowditch curve in a similar manner. The viscous component of the stress response for various strain amplitudes is shown in Fig. 7b.

Fig. 4 The contribution of different oscillatory harmonic terms on the LAOS behavior of the air-water interface. The Discrete Fourier Transform (DFT) of the stress data points was computed by using Equation 6. Each signal shows the magnitude of the corresponding harmonic.

Fig. 5 The variation of the intracycle waveforms of the stress response with phase angle. The stress response was obtained by imposing oscillatory shear strain at different strain amplitudes ranging from 1 to 45%.

Fig. 6 (a) Elastic Lissajous-Bowditch curves (in normalized scale) of the air-water interface. The solution contained 0.1 mol m^{-3} HTAB and 0.5% (w/v) silica nanoparticles, and (b) elastic component of the intracycle stress response as a function of strain. These curves were obtained by taking an average of the Lissajous-Bowditch curves (Fig. 6a) during the positive and negative strain rates.

3.4 Chebyshev polynomial approach

To analyze the Lissajous-Bowditch curves (Section 3.3), Ewoldt *et al.*³¹⁾ have used the Chebyshev polynomials of the first kind (T_m), which are defined as,

$$T_m(x) = \cos m\theta, \quad x = \cos \theta \quad (9)$$

The first two terms of the Chebyshev polynomials are $T_0(x) = 1$ and $T_1(x) = x$. All other terms can be obtained by using the recurrence relation, given by⁵²⁾,

$$T_m(x) = 2xT_{m-1}(x) - T_{m-2}(x), \quad m = 2, 3, \dots \quad (10)$$

Like the Fourier series approach, this approach also decomposes the LAOS stress response into σ'_s and σ''_s , given by

$$\sigma'_s = \gamma_0 \sum_{m \text{ odd}} e_m(\omega, \gamma_0) T_m(\gamma_s) \quad (11a)$$

$$\sigma''_s = \dot{\gamma}_0 \sum_{m \text{ odd}} v_m(\omega, \gamma_0) T_m\left(\frac{\dot{\gamma}_s}{\omega}\right) \quad (11b)$$

The Chebyshev polynomials are orthogonal. The elastic coefficients can be used to describe the solid-like behavior of the interface, *i.e.*, strain-hardening ($e_3 > 1$) and strain-softening ($e_3 < 1$). On the other hand, the viscous coefficients are used

Fig. 7 (a) Viscous Lissajous-Bowditch curves (in normalized scale) of the air-water interface. The solution contained 0.1 mol m^{-3} HTAB and 0.5% (w/v) silica nanoparticles. These curves were two-dimensional projections of the three-dimensional curves on the stress-strain rate plane, and (b) viscous component of the stress response as a function of strain rate in a complete cycle. These curves were obtained by taking an average of the viscous Lissajous-Bowditch curves (Fig. 7a) during the positive and negative strains.

to describe the liquid-like behavior of the interface, *i.e.*, shear-thickening ($v_3 > 1$) and shear-thinning ($v_3 < 1$). These polynomials reduce to Equation 3, when $m = 1$, and the coefficients became the dynamic moduli. Both the approaches (the Chebyshev polynomial approach and Fourier transform rheology) are based on the linear algebraic method. As discussed in Section 3.2, the FT-rheology is unable to interpret LAOS behavior for the higher harmonic terms. However, the Chebyshev coefficients can be used to describe the LAOS flow behavior.

The detailed description of the Chebyshev polynomial approach for describing the LAOS behavior of the interface can be understood from Fig. 8. The Lissajous-Bowditch curves at three strain amplitudes (*i.e.*, 1, 10, and 45%) are shown in Fig. 8. The elastic and viscous components are shown in the elastic and viscous representations, respectively. These curves were fitted by using the Chebyshev polynomials (*i.e.*, Equation 10) of different order. The elastic and viscous Chebyshev coefficients are also shown in each figure. At low strain amplitude (*i.e.*, 1%), when the air-water interface was deformed, the elastic component of the stress response increased linearly with strain; however, the viscous component was independent of the strain rate. This implies that the interface exhibited mainly elastic behavior under the SAOS flow. Only the first order Chebyshev coefficients were sufficient to fit the corresponding curves, which indicate the linear viscoelastic behavior of the interface. The third Chebyshev coefficients were almost zero. At average strain amplitude (*i.e.*, 10%), the stress components were not linearly dependent (Fig. 8b). The third Chebyshev coefficients were required to fit the σ'_s and σ''_s . Both of these components were positive implying the strain-hardening and shear-thickening behavior of the air-water interface under LAOS flow at 10% strain amplitude. A sudden rise in the elastic stress response was observed during shearing at 45% strain amplitude, which indicates hardening of the interface. The positive values of e_m at all higher orders reconfirmed the intracycle strain-hardening. However, the negative value of e_3 showed the intracycle shear-thinning of the interface under LAOS flow.

In Figs 6a, the LAOS behavior of the air-water interface (for $\gamma_0 = 45\%$) follows the sequence of physical processes approach⁵³. In the intracycle oscillatory flow at the strain reversal point, the stress response increased linearly up to the critical strain. This implies that the particle-laden interface showed an elastic behavior. After increasing the strain further, the stress reached a local maximum (*i.e.*, the yield stress) and showed an overshoot. The stress remained constant when

Fig. 8 Decomposition of the stress response into the elastic and viscous components from elastic and viscous Lissajous-Bowditch curves, respectively. These components were fitted by the Chebyshev polynomials of increasing order. The elastic (e_m) and viscous (v_m) Chebyshev coefficients are shown corresponding to the order (m) of the Chebyshev polynomial: (a) strain amplitude = 1%, (b) strain amplitude = 10%, and (c) strain amplitude = 45%.

the interface was sheared above the yield strain. This implies the elastoviscoplastic behavior of the interface⁵⁴).

4. CONCLUSIONS

The LAOS behavior of the air-water interface was investigated by using amplitude sweep, FT-rheology, analysis of the stress waveforms and Lissajous-Bowditch curves, Chebyshev polynomials, and the sequence of physical process. The amplitude sweep experiment revealed that the interface exhibited linear viscoelastic behavior up to 1% strain amplitude, and nonlinear viscoelastic behavior was observed above this strain amplitude. At 1 and 6.4% strain amplitudes, the stress waveforms were a perfect sinusoid, and the first harmonic term of the FT-rheology was sufficient to fit the waveforms. However, in the LAOS regime, higher odd harmonic terms were used to fit the non-sinusoid waveforms. The number of harmonic term increased with strain amplitude. Phase shift of the stress response also increased gradually with strain amplitude, which implies that the mechanical behavior the interface transformed from the solid-like (at low strain amplitude) to the liquid-like behavior (at large strain amplitude).

A perfect elliptical shape of the Lissajous-Bowditch curve (*i.e.* elastic component) was obtained at low strain amplitude. The shape of these curves became rectangular under the LAOS flow. The rectangular shape of the elastic Lissajous-Bowditch curve implied the elastoviscoplastic behavior. On the other hand, the viscous Lissajous-Bowditch curve showed spherical shape at small strain amplitude, and it was sigmoidal at large strain amplitude. The σ'_s and σ''_s were obtained from the corresponding Lissajous-Bowditch curves, respectively. The elastic stress showed linear dependency with strain. However, it showed intra-cycle strain-hardening under LAOS flow. The overall behavior was strain-softening. From the viscous Lissajous-Bowditch curves, it was apparent that the interface showed intra-cycle shear thickening under the LAOS flow. However, at large strain amplitude, the interface exhibited intra-cycle shear thinning.

NOMENCLATURE

a_n	Fourier cosine coefficient of the n^{th} harmonic, Pa
b_n	Fourier sine coefficient of the n^{th} harmonic, Pa
B_0	Boussinesq number
e_m	elastic Chebyshev coefficient of order m
F_n	DFT of the n^{th} harmonic
G_S	interfacial shear modulus, Pa m
G'_S	interfacial storage modulus, Pa m
G''_S	interfacial loss modulus, Pa m
G^*_S	complex interfacial shear modulus, Pa m
i	imaginary unit
L	geometrical factor, m
m	order of Chebyshev polynomial of the first kind
n	number of harmonic terms
N	total number of data points
t	time, s
T	time period, s
T_m	Chebyshev polynomial of the first kind
v_m	viscous Chebyshev coefficient of order m

GREEK LETTERS

γ_0	strain amplitude
$\dot{\gamma}_0$	amplitude of strain rate
γ_S	interfacial strain
$\dot{\gamma}_S$	interfacial strain rate, s^{-1}
η_i	instantaneous interfacial viscosity, Pa s m
η_S	interfacial shear viscosity, Pa s m
η_1	bulk viscosity of top fluid, Pa s
η_2	bulk viscosity of bottom fluid, Pa s
σ_S	interfacial shear stress, Pa m
σ'_S	elastic component of interfacial stress, Pa m
σ''_S	viscous component of interfacial stress, Pa m
ω	angular frequency, $rad\ s^{-1}$
ω_n	angular frequency of n^{th} harmonic, $rad\ s^{-1}$

ABBREVIATIONS

DFT	discrete Fourier transform
FT	Fourier transform
HTAB	hexadecyltrimethylammonium bromide
LAOS	large amplitude oscillatory shear
SAOS	small amplitude oscillatory shear

Declarations of interest: none.

APPENDIX:

Interfacial rheological data for samples with different concentrations of HTAB and silica nanoparticles

Fig. A1 Interfacial shear viscosity as a function of shear rate at two different concentrations of silica nanoparticles [i.e., 0.1 and 0.5% (w/v)]. The HTAB concentration was fixed at 0.1 mol m^{-3} .

Fig. A2 Interfacial shear viscosity as a function of shear rate at two different concentrations of silica nanoparticles [i.e., 0.1 and 0.5% (w/v)]. The HTAB concentration was fixed at 1 mol m^{-3} .

Fig. A3 Interfacial shear viscosity as a function of shear rate at three different concentrations of HTAB: below the CMC (i.e., 0.1 mol m^{-3}), around the CMC (i.e., 1 mol m^{-3}), and above the CMC (i.e., 10 mol m^{-3}). The concentration of the silica nanoparticles was fixed at 0.5% (w/v).

Fig. A4 Interfacial dynamic moduli as a function of strain amplitude at two different concentrations of HTAB (i.e., 0.1 and 1 mol m^{-3}). The concentration of the silica nanoparticles was fixed at 0.5% (w/v).

REFERENCES

- 1) Karbaschi M, Lotfi M, Krägel J, Javadi A, Bastani D, Miller R, *Curr Opin Colloid Interface Sci*, **19**, 514 (2014).
- 2) Pradilla D, Simon S, Sjöblom J, Samaniuk J, Skrzypiec M, Vermant J, *Langmuir*, **32**, 2900 (2016).
- 3) Miller R, Ferri JK, Javadi A, Krägel J, Mucic N, Wüstneck R, *Colloid Polym Sci*, **288**, 937 (2010).
- 4) Madivala B, Franssaer J, Vermant J, *Langmuir*, **25**, 2718 (2009).
- 5) Krägel J, Derkach SR, *Curr Opin Colloid Interface Sci*, **15**, 246 (2010).
- 6) Fuller GG, Vermant J, *Annu Rev Chem Biomol Eng*, **3**, 519 (2012).
- 7) Mendoza AJ, Guzman E, Martinez-Pedrero F, Ritacco H, Rubio RG, Ortega F, Starov VM, Miller R, *Adv Colloid Interface Sci*, **206**, 303 (2014).
- 8) Stocco A, Rio E, Binks BP, Langevin D, *Soft Matter*, **7**, 1260 (2011).
- 9) Meinders MB, van Vliet T, *Adv Colloid Interface Sci*, **108**, 119 (2004).
- 10) Gupta M, Van Hooghten R, Fischer P, Gunes DZ, Vermant J, *Rheol Acta*, **55**, 537 (2016).
- 11) Vishal B, Ghosh P, *J Dispersion Sci Technol*, **39**, 62 (2018).
- 12) Langevin D, *Adv Colloid Interface Sci*, **88**, 209 (2000).
- 13) Dickinson E, *Food Hydrocolloids*, **68**, 219 (2017).
- 14) Erni P, *Soft Matter*, **7**, 7586 (2011).
- 15) Edwards DA, Brenner H, Wasan DT (1991). *Interfacial Transport Processes and Rheology*. Butterworth-Heinemann, Stonham, MA.
- 16) Vandebriel S, Franck A, Fuller GG, Moldenaers P, Vermant J, *Rheol Acta*, **49**, 131 (2010).
- 17) Erni P, Fischer P, Windhab EJ, Kusnezov V, Stettin H, Laüger J, *Rev Sci Instrum*, **74**, 4916 (2003).
- 18) Brooks CF, Fuller GG, Frank CW, Robertson CR, *Langmuir*, **15**, 2450 (1999).
- 19) Boussinesq M, *Ann Chim Phys*, **29**, 349 (1913).
- 20) Scriven L, *Chem Eng Sci*, **12**, 98 (1960).
- 21) Slattery JC (1990). *Interfacial transport phenomena*. Springer-Verlag, New York.
- 22) Ghosh P (2009). *Colloid and Interface Science*. PHI Learning Pvt. Ltd., New Delhi.
- 23) Safouane M, Langevin D, Binks BP, *Langmuir*, **23**, 11546 (2007).
- 24) Cicuta P, Stancik EJ, Fuller GG, *Phys Rev Lett*, **90**, 236101 (2003).
- 25) Lexis M, Willenbacher N, *Colloids Surf, A*, **459**, 177 (2014).
- 26) Zang DY, Rio E, Langevin D, Wei B, Binks BP, *Eur Phys J E*, **31**, 125 (2010).
- 27) Sharma V, Jaishankar A, Wang Y-C, McKinley GH, *Soft Matter*, **7**, 5150 (2011).
- 28) Jung J-M, Gunes DZ, Mezzenga R, *Langmuir*, **26**, 15366

- (2010).
- 29) van Kempen SE, Schols HA, van der Linden E, Sagis LM, *Soft Matter*, **9**, 9579 (2013).
 - 30) Hyun K, Kim SH, Ahn KH, Lee SJ, *J Non-Newtonian Fluid Mech*, **107**, 51 (2002).
 - 31) Ewoldt RH, Hosoi AE, McKinley GH, *J Rheol*, **52**, 1427 (2008).
 - 32) Cho KS, Hyun K, Ahn KH, Lee SJ, *J Rheol*, **49**, 747 (2005).
 - 33) Yu W, Wang P, Zhou C, *J Rheol*, **53**, 215 (2009).
 - 34) Hyun K, Wilhelm M, Klein CO, Cho KS, Nam JG, Ahn KH, Lee SJ, Ewoldt RH, McKinley GH, *Prog Polym Sci*, **36**, 1697 (2011).
 - 35) Vishal B, Ghosh P, *Korea-Aust Rheol J*, **30**, 147 (2018).
 - 36) Poulos AS, Stellbrink J, Petekidis G, *Rheol Acta*, **52**, 785 (2013).
 - 37) Radhakrishnan R, Fielding SM, *arXiv preprint arXiv:1704.08332* (2017).
 - 38) Rogers SA, *Rheol Acta*, **56**, 501 (2017).
 - 39) Birbaum FC, Haavisto S, Koponen A, Windhab EJ, Fischer P, *Rheol Acta*, **55**, 267 (2016).
 - 40) Sagis LMC, Fischer P, *Curr Opin Colloid Interface Sci*, **19**, 520 (2014).
 - 41) Erni P, Parker A, *Langmuir*, **28**, 7757 (2012).
 - 42) Rühs PA, Affolter C, Windhab EJ, Fischer P, *J Rheol*, **57**, 1003 (2013).
 - 43) Vishal B, Ghosh P, *J Dispersion Sci Technol*, **40**, 206 (2018).
 - 44) Ewoldt RH, McKinley GH, *Rheol Acta*, **49**, 213 (2010).
 - 45) Laüger J, Wollny K, Huck S, *Rheol Acta*, **41**, 356 (2002).
 - 46) Macosko CW (1994). *Rheology: Principles, Measurements, and Applications*. Wiley-VCH, New York.
 - 47) Gorlieria F, Khidas Y, Pitois O, *J Rheol*, **61**, 919 (2017).
 - 48) Ewoldt RH, Clasen C, Hosoi AE, McKinley GH, *Soft Matter*, **3**, 634 (2007).
 - 49) Wilhelm M, Maring D, Spiess HW, *Rheol Acta*, **37**, 399 (1998).
 - 50) Wilhelm M, *Macromol Mater Eng*, **287**, 83 (2002).
 - 51) Mermet-Guyennet MRB, de Castro JG, Habibi M, Martzel N, Denn MM, Bonn D, *J Rheol*, **59**, 21 (2015).
 - 52) Mason JC, Handscomb DC (2002). *Chebyshev polynomials*. Chapman and Hall/CRC, USA.
 - 53) Rogers SA, Erwin BM, Vlassopoulos D, Cloitre M, *J Rheol*, **55**, 435 (2011a).
 - 54) Stickel JJ, Knutsen JS, Liberatore MW, *J Rheol*, **57**, 1569 (2013).