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Interfacial Shear Rheology of Films Formed by Coffee

Patrick Heyer, Jörg Läuger

Anton Paar Germany GmbH, Helmuth-Hirth-Strasse 6, 73760 Ostfildern, Germany,
Phone: +49-711-72091-0, Fax: +49-711-72091-50
info.de@anton-paar.com, www.anton-paar.com

ABSTRACT

Coffee is a complex dispersion, which for many coffee drinks is topped by a foam structure of tiny bubbles, e.g. the espresso foam - also called espresso cream or "crema". Interfacial shear rheology does not probe the foam itself, but measures the adsorption of the amphiphilic ingredients and their network formation at the liquid surface. Higher values of the interfacial properties and a faster film formation are expected to correlate with a better foam stability.

INTRODUCTION

The scope of the paper is twofold: First, to show that interfacial rheology is a valuable tool to get information on the film formation and therefore the foam stability of coffee, and second, to compare the results obtained by a biconical disc geometry and a Du Nuöy ring.

BACKGROUND

The two-dimensional interfacial shear stress is defined as:

$$\tau_i = \eta_i \cdot \dot{\gamma} \qquad (1)$$

with η_i being the interfacial shear viscosity. ($[\eta_i]$ = Pa·s·m = N·s/m), and $\dot{\gamma}$ being the shear rate, respectively. Other interfacial shear properties like the interfacial shear storage modulus G_i' and the interfacial shear loss modulus G_i'' can be defined accordingly.

Often when disks, rings, bicones, or similar geometries are used as interfacial rheometers, the interfacial flow is assumed to be completely decoupled from the bulk phase flow, i.e., dissipation of interfacial stresses into the bulk phases is considered negligible. In that case, such a rheometer may be treated as a two-dimensional Couette device, and the interfacial shear viscosity is easily calculated from the torque with standard procedures. In general, however, a more comprehensive analysis of the flow field in the rheometer geometry is desirable, yielding an interfacial velocity distribution that accounts for bulk contributions to the interfacial shear stress.

Biconical Disc

The biconical geometry is depicted in Fig. 1. The edge of the bicone bob is located in the interfacial region between two immiscible liquids or at the surface of a single liquid. With the biconical bob being the rotor located at the interface and the stationary outer cup the biconical geometry acts as a "two-dimensional concentric cylinder geometry".

Based on a mathematical treatment of the biconical disc rheometer a software analysis package with a solution of the full flow field for the bicone was developed, thus allowing the calculation of the absolute interfacial rheological properties for steady and dynamic shear conditions. All details about the instrumental setup of the bicone rheometer and a detailed description of the analysis of the flow field can be found in the article of Erni et al. [1].

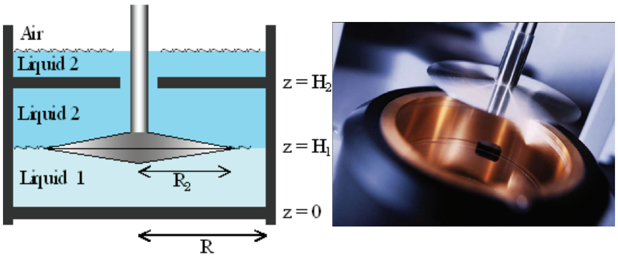

Figure 1. Biconical geometry. H_1= 22,5mm, H_2=45mm, R=40mm, R_2=34,14mm, 2α=10°.

The bicone can be positioned very accurately at the interface position by a normal force assisted surface detection of the liquid/air interface.

Du Noüy Ring

The Du Noüy ring was designed to measure interfacial tension between two liquids or the surface tension of a liquid. In a tensiometer the ring is pulled vertically through the interface and the respective force is measured. The Du Noüy ring was also used to measure interfacial properties [2]. The motivation to use this measuring system was to have a very light geometry with a small moment of inertia, which would allow to measure film properties with the employed instrument. The Du Noüy ring is shown in Fig. 2. It is basically a Platin-Iridium (Pt-Ir) wire with a thickness of 0.36mm. The outer diameter of the ring is 20mm.

For the Du Noüy ring no flow field analysis exists. Therefore the film flow can not be separated from the coupling to the subphase. Instead a simple concentric cylinder geometry analogy is made. In this work the ring is treated as a two-dimensional cylinder geometry with a large gap. The formulas for the three-dimensional large gap cylinder are used [3] and modified by leaving out the gap length L. This approach gives new relations for the shear rate (C_{CSR}) and shear stress (C_{CSS}) factors of the geometry, which are needed to calculate the shear rate ($\dot{\gamma}$) from the rotational speed (n) and the shear stress (τ) from the torque signal (M), respectively.

$$\dot{\gamma} = C_{CSR} \cdot n \tag{2}$$

$$\tau = C_{CSS} \cdot M \tag{3}$$

As discussed before, this simple approach neglects the subphase contributions to the torque signal. For strong films (large Boussinesq numbers) this rough approximation might be sufficient. In this case bulk viscous effects are neglected and the interface is considered as an isolated two-dimensional fluid. The interfacial shear properties can be calculated with the respective geometry factors. In addition the values for the uncovered interface must be measured separately and subtracted from the values obtained with the interfacial film.

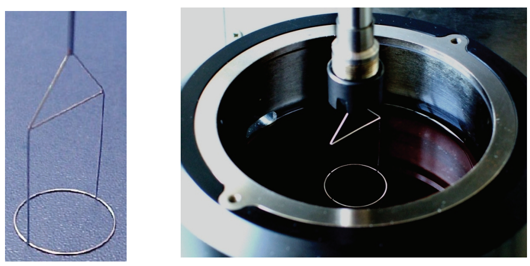

Figure 2. The Du Noüy ring geometry.

However, in most cases bulk phase contributions to the interfacial shear properties are relevant and in order to get real absolute interfacial properties a full flow field analysis, like it is available for the biconical geometry, would be needed. Such an analysis is not available for the Du Noüy ring.

The approximation only takes into account the film located outside of the ring, which is true for the low molecular surfactants. These surfactants are solved in a solvent and spread onto the liquid surface.

However, in case of a protein solution with proteins solved in the liquid phase the proteins adsorb at the interface with time and form a film outside and inside the ring.

The positioning of the Du Noüy ring at the liquid surface is not so easily possible compared to the biconical geometry. A reproducible positioning by eye is almost impossible and even more challenging for the Du Noüy ring compared to the biconical disc. As with the biconical geometry the positioning of the Du Noüy ring can be done by a normal force assisted surface detection of the liquid/air interface. However, in the case of the bicone the change in normal force at the touching of the interface is of the order of 0.08N, whereas for the Du Noüy ring the values are around 0.008N or 0.8g and therefore one decade lower. Since the fragile ring might not be perfectly parallel to the water surface and the wetting of the ring is not reproducible the exact positioning remains difficult. A better approach is to measure the normal force while the ring is submerged in the bulk phase and moved up. As soon as the surface level is reached the ring starts to be pulled back by the surface tension of the liquid indicated by an increasing negative normal force of the order of 1mN. This technique is the most reproducible way to position the ring at the surface of the liquid and at the same time ensuring a good wetting of the ring.

For measurements on films between two liquids the lower density liquid can be poured on top of the first liquid after positioning of the geometry at the liquid / air interface. This procedure is possible for both the biconical geometry and the Du Noüy ring.

SAMPLE, INTRUMENT AND METHODS

An MCR 301 rheometer from Anton Paar with the interfacial rheology accessory and a bicone geometry as depicted in Fig. 1 was used. The temperature was set to 23°C.

For film formation measurements the bicone was first positioned by a normal force assisted surface detection to the water/air interface. After that the geometry was lifted up and a soluble coffee powder was mixed into distilled water. Then the geometry was moved back to the interface position. A special software analysis is used to take into account the film subphase coupling and to calculate the absolute interfacial properties. For comparison measurements a Du Noüy ring with a diameter of 0.36mm was attached to the rheometer instead of the bicone.

RESULT AND DISCUSSION

Fig. 3 shows the film formation for the same coffee sample at 3 different concentrations. Measured at constant strain and frequency it is possible to follow the adsorption and network formation of the surface active ingredients at the liquid/air interface. For higher concentrations the film shows elasticity already after a shorter time. In the case of the lowest concentration the moduli are increasing over a longer time. Within the first 100min no elasticity is detected at all and G'' is starting from very low values of about 10^{-5}Pa·m.

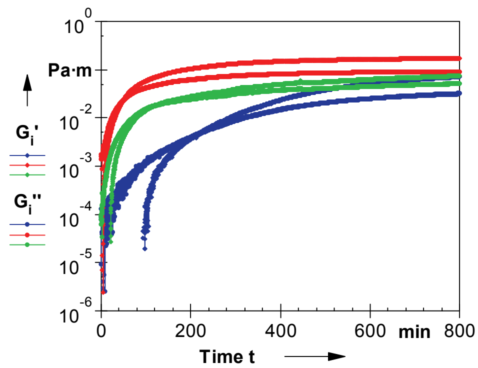

Figure 3. Film formation measurement at a constant strain (0.1%) and a constant frequency (1Hz) for 3 concentrations (0.05g, 0.15g, and 0.3g coffee powder / 114ml water)

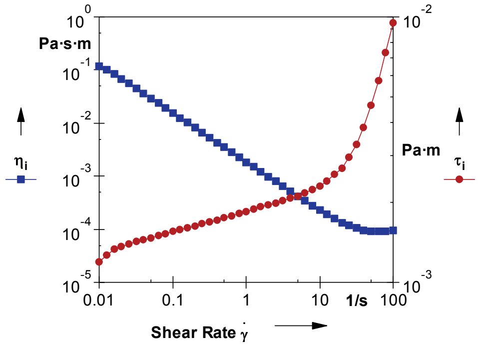

Fig 4. Interfacial shear viscosity and interfacial shear stress as a function of shear rate of a coffee film (0.15g /114ml) 14h after the start of the film formation.

The interfacial shear viscosity and the interfacial shear stress as a function of the applied shear rates of a coffee (0.15g/114ml) film measured 14h after the onset of the film formation is depicted in Fig. 4. A strong shear thinning behavior is observed. The interfacial viscosity increases towards lower shear rates indicating a typical behavior for a fluid with an apparent yield stress. At shear rates higher than $30 s^{-1}$ turbulence of the subphase starts to influence the results leading to a constant or even slightly increasing viscosity reading.

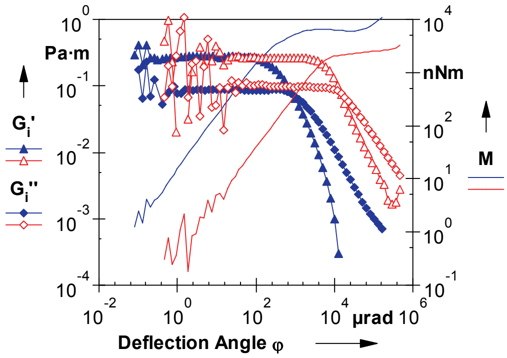

Figure 5. Strain sweep (f = 1Hz) of a coffee film (0.3g /114ml) for bicone (closed symbols) and Du Noüy ring (open symbols). G_i', G_i'' and torque M versus the deflection angle

In Fig. 5 strain sweeps for the bicone and the Du Noüy ring are depicted. At low strains or deflection angles the interfacial shear storage modulus G_i' is higher than the interfacial shear loss modulus G_i'' indicating a gel-like structure at rest. The absolute values for G' and G'' are similar, but there are some differences: For the bicone the end of the linear visco-elastic (LVE) range is reached at strains about 5 times lower compared to the Du Noüy ring. One possible reasons is that due to the undefined geometry of the ring only part of the applied strain is transferred into the sample. For both geometries reliable measurements starting from torques of about 5nNm are possible. The corresponding deflection angles are 0.3µrad for the bicone and 20µrad for the ring, respectively, i.e. with the bicone it is possible to work at much lower strains and also much lower stresses due to the much larger geometry.

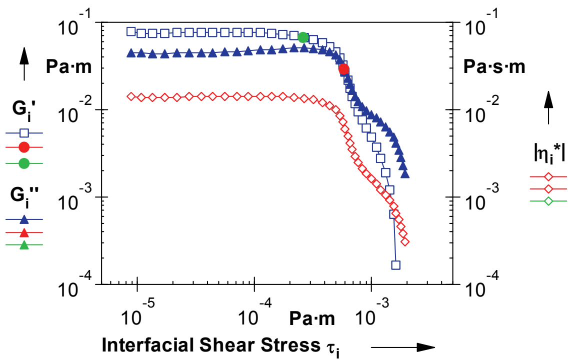

Figure 6. Bicone data versus interfacial shear stress. The yield (end of LVE-range) and flow point (crossover point) are indicated as points on the G_i' curve.

In order to evaluate the behavior of the interfacial film it is useful to look at the moduli as a function of the interfacial shear stress. In Fig. 6 the bicone data are shown versus the interfacial shear stress. The stress value at which the interfacial storage modulus is starting to decrease can be attributed as the apparent yield point. At strains higher than the crossover point between G_i' and G_i'' the viscous part, i.e. G_i'', is higher compared to the elastic part, i.e. G_i'. Therefore the crossover point is also called flow point.

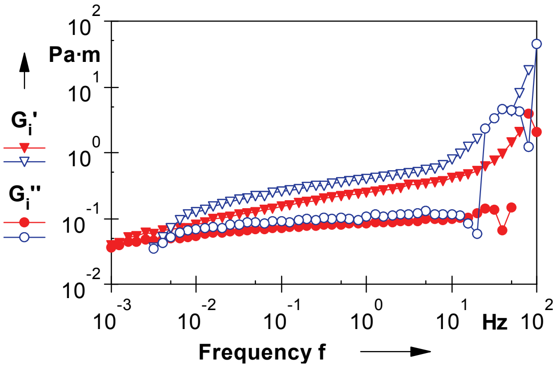

Figure 7. Frequency sweeps of a coffee film (0.3g/114ml) for bicone (closed symbols) and Du Noüy ring (open symbols).

Frequency sweep tests with the bicone and the ring as depicted in Fig. 7 illustrate that G_i' is higher than G_i'' over a frequency range from 0.005Hz up to 50Hz. At frequencies higher than 20Hz the data might be influenced by turbulence as well as by sample and instrument inertia effects. The strain was kept constant, but was set higher (0.1%) in the case of the Du Noüy ring compared to the bicone (0.01%) in order to have a similar sample strain as for the bicone. For both geometries the moduli increase slightly towards larger frequencies with G_i' showing a stronger increase. At a certain frequency G_i' deviates from a straight line showing a steeper increase. At larger frequencies inertial effects dominate, i.e. the ratio of sample torque to electrical torque is getting too small. The limiting frequency is substantially larger for the biconical geometry (20Hz) compared to the Du Noüy ring (5Hz) indicating the overcompensation of the larger moment of inertia by the larger dimensions of the bicone, i.e. with the bicone larger frequencies are possible compared to the Du Noüy ring.

Beside the initial film formation and the stability of the final film, it is worth to look at the time dependence after a mechanical distortion of the film, i.e. the structure recovery or thixotropic behavior. Fig. 8 shows results of a so-called 3 Interval Thixotropy Test (3ITT). In the first and third interval a small amplitude oscillation with constant strain and constant frequency was applied, whereas in the second interval a rotation with a constant shear rate was preset. The structure of the interfacial film breaks up during the constant shear rate interval, but it recovers fully in about 300s to the initial values.

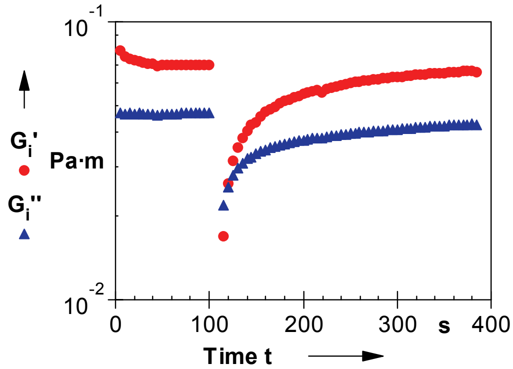

Figure 8. Structure recovery with a 3ITT-Test of a coffee film (0.3g/114ml): Interval 1+3: Oscillation with 0.1% strain at 1Hz. Interval 2: 10s rotation with a shear rate of $10s^{-1}$.

CONCLUSIONS

An interfacial rheology system based on a biconical geometry in combination with a rheometer allows all kinds of test methods including steady flow and dynamic measurements. The flow field analysis reveals absolute values for the interfacial properties.

The system allows the investigation of coffee films formed at the water/air interface. Viscosity curves are describing the shear rate dependence of the films. Amplitude and frequency sweeps are used to characterize the rest structure of the films. Structure recovery tests allow the description of the thixotropic behavior of the interfacial film. The coffee films are fully recoverable after distortion by a steady shear flow, and the time dependence of this process can be illustrated exactly.

Interfacial shear rheology with a biconical geometry is a sensitive tool for the investigation of interfacial films formed at the liquid’s surfaces. Although with a Du Noüy ring it is possible to measure the qualitative behavior and relative differences only the bicone geometry is sensitive enough to test weak films and to reveal real absolute values for the interfacial shear rheological quantities.

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