INTERFACIAL RHEOLOGY

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Summary

There are a number of applications in both technology and nature where interfaces between two liquids or between a liquid and a gas play an important role. Often, complex molecular species or particulates will accumulate at the interface and render the interface in itself a complex two dimensional (2D) viscoelastic fluid. This chapter starts off with a review of methods to characterize the rheological properties of interfaces. Secondly, some applications of interfacial rheology will be discussed, including the use of rheologically complex fluid interfaces to stabilize emulsions and the properties of lung surfactants. It will also be shown how 2D interfaces can be used to efficiently visualize flow phenomena in certain classes of rheologically complex fluids, which remain difficult in 3D.

1. Introduction
Amphiphilic molecules and particles that have an affinity to interfaces will collect in these regions, possibly even crowd the interface, and give the latter all the structural and rheological properties of an – albeit two-dimensional - complex fluid. Such interfaces are encountered and their properties exploited in various areas, such as food science or chemical technology, in biomedical applications and in medicine. Some material classes are characterized by a substantial amount of internal interfaces, such as emulsions, foams and polymer-polymer blends, where the dynamics of the interface play an important role on the morphological processes that in turn control the bulk materials microstructure. Complex fluid interfaces are also omnipresent in many biological systems, including cell membranes and the lung surfactants that are present in e.g. human lungs. Lung surfactant is a complex mixture of lipids and proteins which lowers the surface tension in the lung alveoli to facilitate breathing, the rheological properties of the monolayer are important in keeping it in place. Also, current research tries to understand if certain respiratory diseases can be linked to lung surfactant composition and rheology. It is hence important to be able to measure the rheological properties of thin fluid layers to predict the behavior in technological or natural processes. However, like bulk rheology, measuring the surface viscoelastic properties can also be used as an analytical technique, for example to probe interactions between adsorbed molecules in monolayers composed of different polymers or polymer-surfactant mixtures, or to measure the interactions between particles.

The existence of a surface viscosity was first proposed by the Belgian mathematician and physicist Joseph Antoine Ferdinand Plateau (1801-1883). By using the magnetic field of the earth as an external source, and using a compass needle he studied the
damping on bare and surfactant laden interfaces. He concluded that the needle tended to damp more when surfactant was present. As a result, Plateau attributed this to the existence of a ‘surface viscosity’. However, his experiment was plagued by the existence of gradients in surfactant concentration, which led to extra, so-called “Marangoni” stresses. Hence he was not able to determine the interfacial viscosity quantitatively, only qualitatively. It took until the beginning of the 20th century before a French mathematician and physicist Joseph Valentin Boussinesq (1842-1929) described theoretically the deformation of 2D liquids. He intended to connect the hydrodynamic equations of two fluid phases discontinuously and to develop a 2D rheological theory for fluid-fluid interfaces. Moreover, Boussinesq was the first who proposed a linear model to describe the interfacial stress tensor based on the surface rheological properties. In the 1960’s, a chemical engineer, Prof. L.E. “Skip” Scriven (1931-2007) presented an approach where the mobile interface presents itself in problems of fluid mechanics through the boundary conditions and he developed a constitutive model for Newtonian interfaces. Compared to bulk liquids, where the dilational viscosity of the fluids can typically be neglected and only a Newtonian shear viscosity needs to be considered, this is not the case for interfaces. Figure 1 shows the two fundamental deformations taking place at the interface. With each of them a viscosity can be associated. For more complex fluid interfaces, rheological material functions can be defined for both types of deformations, along similar lines as has been done for bulk liquids.

Current research is trying to establish a rigorous approach for more complex structured interfaces. Several devices and measuring probes have been suggested to study efficiently interfacial rheological properties. Therefore in this chapter, we will start with an overview concerning the present state of our understanding of both shear and dilatational deformations in surface rheometry.

Complex fluid interfaces also provide us with an advantage to visualize the interfacial flow phenomena. A direct visualization of the relation ship between flow and structure can bring some useful insights to rheologists. Probing the integral system in three dimensions (by using for example confocal laser scanning microscopy) is difficult, especially if one is interested in the dynamics under flow or processing conditions. Therefore the three dimensional case is converted to a two dimensional problem. This can be done in various ways: pinning particles at a liquid-liquid interface by capillary forces, study dynamics in confined conditions, or use the adhesion onto solid substrates. However these two dimensional systems can be used to understand three dimensional phenomena; they can also be used to understand real-life interfacial issues. For example, the coarsening of an emulsion with micron sized droplets results from the coalescence of the droplets. To suppress the coalescence, additives (particles, surfactants, proteins) are adsorbed at the interface between droplet and bulk medium in order to lower the interfacial tension and/or increase the interfacial elasticity. It is clear that a good understanding of the dynamics and interactions of the additives at the interface can result in a better design of stable emulsions, as was first discussed in the early 1980’s by van de Tempel and Lucassen-Reynders, and for example nicely demonstrated in the recent work of Georgieva et al. (2009). Fischer and Enri (2007) recently reviewed the role of interfacial processes in drop deformation. Also, colloidal particles at a flat interface can mimic the properties of atomic systems. Brownian
motion studies and collective rearrangements under flow can for example be used for a better understanding of mixing processes.

In the present chapter we will first review the measurement methods, subsequently discuss some examples of applications and of flow visualization studies.

2. Interfacial Rheometry

The measurement of the interfacial properties is challenging, not only because the forces and torques associated with the deformation of an interface will be small, but also and more fundamentally because the flow and deformation of an interface will entail deformation and flow in the surrounding bulk phases. The intimate coupling between the flow in bulk and at the interface is often complex to analyze. Mathematically speaking, the rheological properties of the interface appear as a boundary condition in the fluids mechanics problem and hence knowledge of the entire bulk velocity field is required when analyzing the response of the interface to the resulting interfacial deformation. It is possible that the entire response of a measurement device is dominated by the bulk – for example a pristine water-air interface - or dominated by the interface for densely packed systems. A dimensionless ratio of the two components of the drag experienced by a rheological probe can be written as dimensionless group:

\[
Bo = \frac{\text{surface drag}}{\text{subphase drag}} = \frac{\eta_{\text{surface}}}{\eta_{\text{subphase}} \times G}
\]

where \( Bo \) is the dimensionless Boussinesq number, \( \eta_{\text{surface}} \) is the surface viscosity (Pa.s.m), \( \eta_{\text{subphase}} \) is the subphase viscosity (Pa.s) and \( G \) is a typical length scale of the measuring probe (m) being related to the ratio of area of the measurement probe relative to the perimeter in contact with the interface. When \( Bo \) is much larger than 1, the drag experienced by the measuring probe dominates; when \( Bo \) is much smaller than 1, the properties of the surrounding phases are measured. The main goal in surface rheometry is to provide adequate sensitivity to detect the interface alone in the presence of these lower and upper fluids. When designing an instrument to study sensitive surface rheological properties, a small value of \( G \) is thus recommended. In the next sections different devices (direct and indirect viscometers) with various measuring probes will be discussed, resulting in a variety of sensitivity ranges due to the variety of measuring probes. Further information can be found in the textbooks of Slattery (1990), Edwards, Brenner and Wasan (1991) and reviews and progress reports in journals from Miller et al. (1996), Bos and Van Vliet (2001), Murray (2007) and Krägel et al. (2008)

2.1. Indirect Interfacial Shear Viscometers

A wide range of techniques and instruments has been proposed. A first category consists of experimental techniques based on the displacement of tracer particles at a fluid-fluid interface, which must be evaluated using image analysis. The flow type in these systems is either a drag flow or a surface pressure driven flow. Although for these setups inertia effects at high Reynolds numbers can be taken into account, the necessity to introduce and observe tracer particles makes measurements experimentally time
consuming. The most known viscometers in this category are the canal surface viscometer, the deep-channel surface viscometer, the rotating wall knife-edge surface viscometer and the transient rotating cylinder device. For example, the canal surface viscometer is based on the determination of the surface film flow rate through a very narrow canal under a surface pressure difference, analogous to the Hagen-Poiseuille method to study bulk viscosity of fluids. The value of the surface viscosity can be calculated by the following equation:

\[
\eta_{\text{surface}} = \frac{\Delta P \times \pi \times a^3}{12 \times L \times Q} - \frac{a \times \eta_{\text{subphase}}}{\pi}
\]  

(2)

where \( Q \) is the film flow rate through the canal of width \( a \) and length \( L \) and \( \Delta P \) the pressure difference over the canal. In this formula, the subphase drag is taken into account. A disadvantage of this setup is that various conditions (smooth walls, no wall slip, Newtonian flow, dilational motion at the end of the canal) must be achieved for the above formula to be valid. Stone (1995) nicely showed how the Boussinesq number affects the flow profile, and how even for Newtonian interfaces, the velocity profile can deviate dramatically from a parabolic one at low \( Bo \). A modern variant of this device is a deep-channel surface viscometer, which consists of two concentric, stationary vertical cylinders with smooth walls. This setup is shown in Figure 2.

Figure 2. Scheme of a deep-channel surface viscometer

The cylinders are placed in such a way that they almost touch a rotating flat-bottomed dish. By its rotation with a known angular velocity \( \Omega \), the fluid between the channel walls will be deformed, and a shear deformation is obtained. When tracer particles are placed in the fluid interface in the centerline of the channel they can easily monitored.
by a camera. The surface viscosity can then be calculated using the experimentally measured centerline surface viscosity:

$$\eta_{\text{surface}} = \frac{\eta_{\text{subphase}} \times a}{\pi} \times \left( \frac{V^*}{V} - 1 \right)$$  \hspace{1cm} (3)

where $a$ is the channel width, $V^*$ is the centerline surface velocity in the absence of a film and $V$ the surface velocity in the presence of a monolayer.

Microrheological measurements, in which the Brownian movement of a submicron diameter sphere is used to study the rheology of Langmuir monolayers, have been a subject of debate. Yet, given a careful analysis of the Boussinesq problem, microrheology provides a sensitive method for measuring the surface rheological properties as, for example, shown by Sickert et al. (2007) and Peng et al. (2009).

2.2. Direct Interfacial Shear Rheometers

In contrast to indirect measurement techniques, the category of direct interfacial shear rheometers consists of experimental techniques that measure the torque on a probe located within the interface to deform it directly. The oldest direct experimental techniques to study interfacial properties were based on a measuring probe coupled to a torsion wire such that the probe touches the fluid-fluid interface of a system in a cylindrical dish. However these measurements are particularly cumbersome. Most rheometers consist of a stationary dish and a rigid coupling between a rotating or oscillating measuring probe and motor that detects both torque and displacement, for example a standard rheometer for rotational bulk measurements. This setup scheme will also be used in the figures below. According to the interfacial probe or geometry, different surface viscometer names are used: knife-edge viscometer, blunt knife surface viscometer, disk surface viscometer, bicone surface viscometer, double wall-ring surface viscometer and magnetic needle surface viscometer.

2.2.1. Knife-edge Surface Viscometer
The first direct interfacial rheometer was based on a single knife-edge probe with a circular knife just touching the interface of a solution or dispersion in a dish. This setup is shown in Figure 3. For this experimental technique, the knife has to be non-wetting, such that it touches the interface, without breaking it. A double knife-edge as well as a blunt knife viscometer have also been suggested. However, placing the knife precisely at the interface remains a cumbersome manipulation. Also a detailed analysis of the fluid mechanics seems to be lacking.

In more recent setups, the knife-edge is replaced by a Pt/Ir Du Noüy ring, a readily available geometry typically used to measure interfacial tensions, with a circular cross section, as a measuring probe. This can be mounted onto commercial rotational rheometers for bulk measurements. The working equations used to analyze the data are taken to be equivalent to a Couette geometry. This assumption may however not be valid. The gap is wide, causing problems with shear wave propagation and non-homogeneous stress profiles at the interface, and the flow field in the subphase can be very complicated. For the Du Noüy ring, this effect has not been clearly analyzed. For rheologically complex fluids this geometry should be used as an indexer, rather than as a rheometer.

**2.2.2. Disk Surface Geometry**

The classical disk surface apparatus is widely used in literature and is commercially available. It is similar to the geometry depicted in Figure 3, except for the fact that now a flat disc is touching the interface. This thin, flat circular disk is forced to rotate or oscillate within the plane of the interface, by application of a small torque. To facilitate the calculation of the surface properties, the exerted torque should again be decomposed...
in a surface torque due to the interfacial viscosity and a subphase torque due to the deformation of the subphase. However, this simple decomposition of the torque only holds at large \( Bo \) numbers and does not take into account the intimate coupling between flow at the interface and in the subphase. In the simplified case, the viscometer can be treated as a 2D Couette device and the interfacial shear viscosity can easily be calculated from the applied torque with the following proportionality:

\[
\eta_{\text{surface}} = \frac{T \times 8 \times R_{\text{disk}}^3 \times \eta_{\text{subphase}} \times \Omega}{4 \times \pi \times R_{\text{disk}}^3 \times \Omega} \tag{4}
\]

where \( T \) is the applied torque and \( R_{\text{disk}} \) the radius of the disk. For lower \( Bo \) numbers, theoretical results for fluid-fluid interfaces are available in literature, based on the calculation of the interfacial and subphase velocity distributions. A variation on the viscometer above is the location of a thin, flat disk just below or above the interface. The disk can be driven by a rheometer, a torsion wire or a magnet embedded in the disk. These devices do suffer of an incomplete analysis of the flow field. These geometries are also typically limited to the use at air water interfaces.

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**Biographical Sketches**

**Kasper Masschaele** was born on May 19th, 1982 in Hasselt, Belgium. He attended K.U Leuven from 2000 till 2005, from which he obtained a masters degree in chemical engineering. His graduation work was carried out in the rheology group of prof. J. Vermant. The subject of his thesis was “The interaction between titanium dioxide, associative polymer and surfactants”. In October 2005 he started his research ‘The influence of external fields on colloidal particles at an interface’ as a PhD-student in the same group.

**Steven Vandebril** was born on July 26th, 1982 in Lier, Belgium. He attended K.U. Leuven from 2000 till 2005 from which he obtained a masters degree in chemical engineering. His graduated work was carried out in the applied rheology group of Prof. Jan Vermant. The subject of his thesis was “The thermodynamic and rheological properties of natural lung surfactant”. In October 2005 he started his research on “Control of morphology and properties of immiscible polymer blends by nanoparticles” as a PhD student in the same applied rheology group.

**Basavaraj Madivala** was born on April 4th 1976 in Turuvanur, India. He obtained a Bachelor’s degree in Chemical Engineering from Bangalore University in 1998, followed by a masters of science by research in 2003 from the Materials engineering department from the Indian Institute of Science. He obtained his PhD degree at K.U. Leuven on Tailoring the gel rheology in bulk and at interfaces under the supervision of Professor Jan Vermant. In December 2008 he started working as a postdoctoral researcher at the University of Delaware in the group of Prof. Wagner in the Chemical Engineering Department.

**Jan Vermant** is a Professor of Chemical Engineering at K.U, Leuven. He was born on august 20th 1968. He studied Chemical Engineering at K.U. Leuven and obtained his PhD in 1996 under the supervision of Prof. Jan Mewis and Paula Moldenaers. After a period of postdoctoral research at Stanford, Ecole des Mines and the CNRS and K.U. Leuven, he joined the faculty at K.U. Leuven in 1999. He has held visiting appointments at the University of Delaware, Stanford University and Princeton University. His research focuses on the relation between structure and rheology in complex fluids, both in bulk and at interfaces. Honors and awards include a Dupont Young Faculty Award and the 2007 Exxon-Mobil Chemical Science and Engineering Award Europe.