

Interfacial Rheometry - An Introduction

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SCOPE

An interface can be defined as the boundary between two immiscible phases, whether they are a gas, a liquid or a solid. Interfaces are extremely important in colloid systems such as emulsions (liquid in a liquid) or foams (gas in a liquid). A characteristic feature of many colloidal dispersions is the large area-to-volume ratio of the dispersed phase. At the interface between the dispersed and the continuous phase, phenomena such as adsorption of molecules take place. These effects dominate in most systems and determine the physical properties of a colloidal system as a whole.

Despite the large area to volume ratio, the amount of material to modify an interface can be quite small and sufficient to change the flow properties of dispersions considerably.

INTERFACIAL (SURFACE) TENSION

The most important physical parameter characterizing an interface or surface is the interfacial (surface) tension. What gives rise to the surface or interfacial tension?

Let's consider a gas-liquid interface. In the liquid phase the molecules are attracted by short-range forces (Figure 1), the Van der Waals attraction forces and in particular the London dispersion forces.

The phenomenon of the surface tension can be explained in terms of these attraction forces. The molecules in the bulk of the liquid are on average surrounded by equal attraction forces in all directions. The molecules at the liquid-air interface however experience an unbalance of these forces, which results in a net inwards pull at the surface. Molecules at the surface will leave the surface as

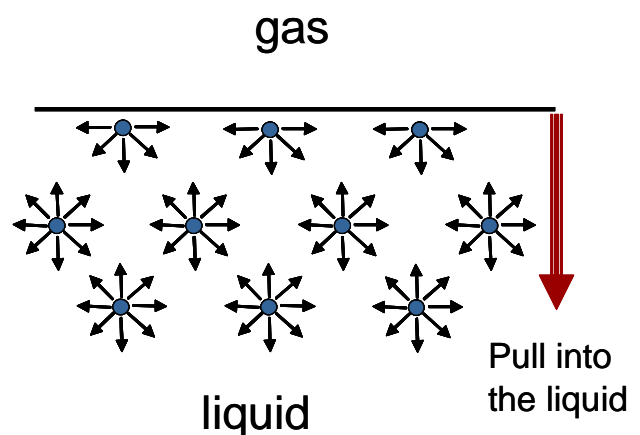


Figure 1: Origin of the surface tension of a liquid at the liquid-air interface

fast as possible for the interior of the liquid. As a consequence the surface will contract spontaneously to adopt a minimum surface arrangement. Bubbles of gas and droplets of liquid therefore tend towards a spherical shape. Interfaces are dynamic, that means at equilibrium an equal amount of molecules go to the interface and leave the interface for the fluid or the gas phase. The average residence time of a molecule at the surface of a liquid is in the order of microseconds.

The surface tension can be defined as the force acting in right angle to any line of unit length on the liquid surface⁽¹⁾. A more convenient description of the surface energy is the work required to increase and reverse the surface area by a unit amount at isothermal conditions

There is no fundamental difference between the terms surface and interface. Typically the term surface is used to describe the boundary between two phases, one of which is gaseous. The boundary between two non-gaseous phases is an interface.

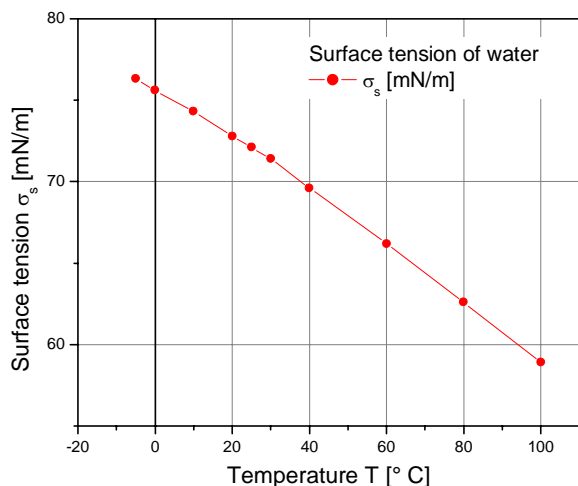


Figure 2: Variation of the surface tension of water with the temperature

At the interface between two liquids, there is also an imbalance of the intermolecular forces, however of much lesser magnitude than the imbalance at a surface. Interfacial tension values lie in-between the individual surface tensions of the two liquids.

The high surface tension for water is due to the fact, that in addition to the van der Waals forces, hydrogen bonding contributes significantly to the imbalance of forces at the liquid surface (Table 1). In case of hydrocarbons, the surface tension is the result of the London dispersion forces only. The contribution of hydrogen bonding to the surface tension of water is approx. $51 \text{ mN}\cdot\text{m}^{-1}$, the contribution of the dispersion forces is $21.8 \text{ mN}\cdot\text{m}^{-1}$. The surface tension decreases for most liquids linearly with temperature, as shown in figure 2.

Measurement of interfacial tension

A number of methods are available to measure surface i.e. interfacial tension, both static and dynamic. Static measurements are usually more

| Surface tension and Interfacial tension against water at 20° C | | | |
|--|------|------|-------------------|
| Water | 72.8 | - | mNm^{-1} |
| Benzene | 28.9 | 35.0 | mNm^{-1} |
| Acetone | 23.7 | | mNm^{-1} |
| CCl_4 | 26.8 | 45.1 | mNm^{-1} |
| n-Hexane | 18.4 | 51.1 | mNm^{-1} |
| n-Octanol | 27.5 | 8.5 | mNm^{-1} |

Table 1: Surface and interfacial tension for different fluids

accurate and it is possible to measure the surface tension to an accuracy of 0.01 to $0.1 \text{ mN}\cdot\text{m}^{-1}$. The two most common static methods are based on the Du Noüy ring and the Wilhelmy plate.

The Ring method measures the force required to detach a ring from a surface or interface (Figure 3). The detachment force is related to the surface (interfacial) tension σ_s by the expression:

$$\sigma_s = \frac{\beta F}{4\pi R} \cos \theta$$

β is a correction factor for the non vertical direction of the tension force at the detachment point. β depends on the dimensions of the ring and the nature of the interface. Values for β can be calculated according to Zuidema and Waters⁽²⁾. To ensure, that the contact angle θ is zero (complete wetting) and constant, all residues have to be carefully removed from the platinum ring by flaming before the measurement.

The Wilhelmy plate method is less bound to errors and probably the most frequently used method. A mica plate is suspended from a balance as shown in figure 4. Similar to the Du Noüy ring, the plate can be pulled out of the fluid and the weight W_{det} at the detachment is recorded. The surface tension can be calculated according to:

$$W_{det} - W = 2(x + y)\sigma_s$$

W is the weight of the plate; x, y the length and breath respectively. The Wilhelmy plate can also be operated in a static mode, continuously measuring changes of the surface tension. In this mode, changes in force required to maintain the plate at constant

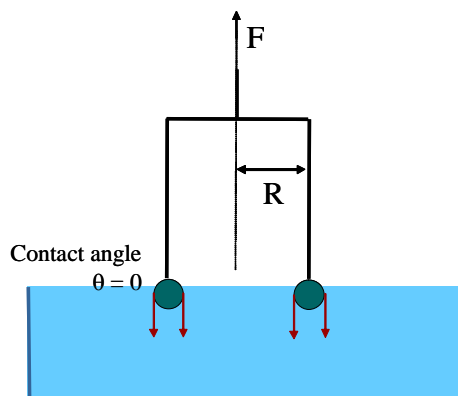


Figure 3: Measurement of the interfacial tension using the Du Noüy ring

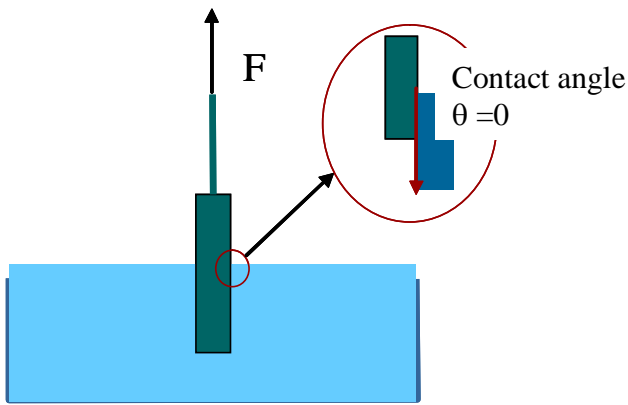


Figure 4: Wilhelmy plate method

immersion depth as the surface tension varies is measured. Note that for a mica plate a zero contact angle is assumed. Any contamination of the mica plate has to be removed by flaming before the experiment

The pendant drop method is based on the measurement of the weight or volume of a drop, detaching at the tip of a hollow needle. At the point of detachment:

$$\sigma_s = \frac{\beta mg}{2\pi r}$$

with m the mass of the drop of the liquid under investigation and β a correction factor. The drop can be photographed and the interfacial tension computed from the dimensions of the drop (figure 5). The dynamic pendant drop method or oscillating jet method looks at the change of the cross section of a drop emerging from a nozzle. Surface tension measurements at very short time intervals can be performed in order to monitor the change of the surface tension with time.

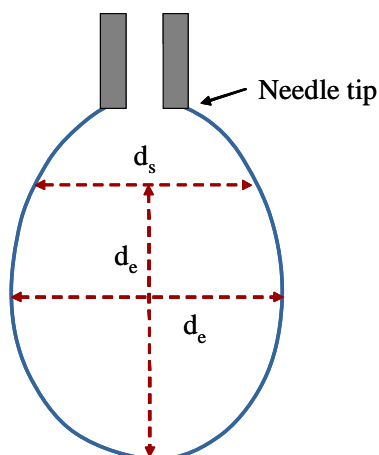


Figure 5: Pendant drop method

SURFACE ACTIVITY

Amphiphilic materials

A main characteristic of interfaces is the adsorption of amphiphilic molecules. Amphiphilic molecules have a strong affinity to the interface because of their hydrophilic head groups and hydrophobic tail. Surface active materials such as low MW surfactants, lipids, and emulsifier have both a hydrophilic and a lipophilic region and have a preference for water-oil interfaces. Proteins are amphiphilic because they are partly hydrophobic (hydrocarbon regions) and partly hydrophilic (amino and carboxyl groups, peptide linkages)

Adsorption and orientation

Amphiphilic materials are adsorbed at the interface to form an orientated monomolecular layer structure. This behavior is referred to as „surface activity”. The adsorption at the interface is not immediate and is controlled by the diffusion of the amphiphilic molecules to the interface. Molecules such as short-chain fatty acids or alcohols are soluble in both water and oil. The hydrocarbon part of the molecule is responsible for the solubility in the oil, the polar $-(COOH)$ and $-OH$ groups have enough affinity to the water to drag along the small non-polar hydrocarbon tail. These molecules love to locate at the water-oil interface and they orient themselves with the hydrocarbon tail in contact with the oil and the polar head group oriented towards the water. This is energetically speaking a more favorable situation compared to the complete solution in either the oil or the water (Figure 6). The adsorption is a dynamic process, which means that molecules are continuously adsorbed at the interface due to their affinity to the interface and mixed in the fluid phase again due to the thermal (Brownian) motion.

The tendency of surface active molecules to locate at the interface favors the expansion of the interface. This expansion process is balanced against the tendency of the interface to contract under the normal surface (interfacial) tension. Surface active materials, when adsorbed at the interface reduce the interfacial tension. The expansion or surface pressure π of the adsorbed layer is the difference between the surface tension without monolayer and the resulting surface tension when a monolayer is

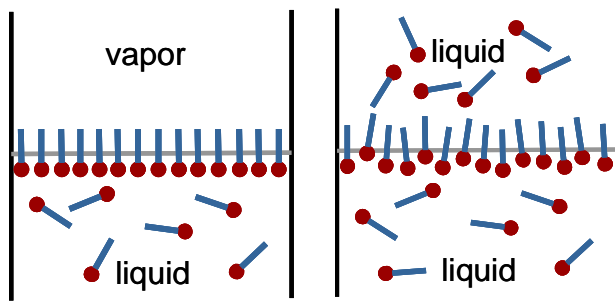


Figure 6: Adsorption of surface active materials at the water-gas and water-oil interface

present:

$$\sigma = \sigma_{so} - \pi$$

The longer the hydrocarbon tail for the fatty acids for example, the stronger the tendency to locate at the interface, the higher the surface pressure i.e. the lower the resulting interfacial tension.

Monolayer films

With increasing length of the hydrocarbon tail, fatty acids or alcohols become insoluble in water; nevertheless they can be deposited with the aid of a suitable solvent on top of the water surface and form a monolayer film, the polar groups oriented to the water and the hydrophobic hydrocarbon chain oriented away from the water phase. These insoluble monomolecular films represent an extreme case of adsorption at a liquid surface.

Since for insoluble molecules the concentration of surfactant molecules in a monolayer at the surface is directly known from the amount of material deposited, the surface pressure π of the monolayer can be determined as a function of the area per molecule in a Langmuir trough (Figure 7). In the Langmuir Adam⁽³⁾ trough (also referred to as surface balance), the insoluble monolayer is contained

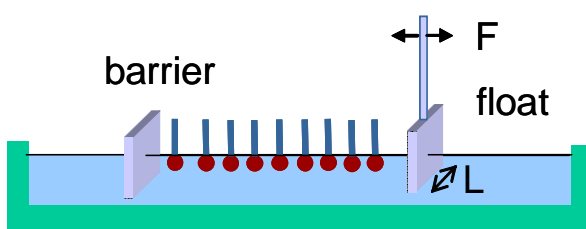


Figure 7: Langmuir trough (Langmuir Adam surface balance) to measure the surface pressure π

between Teflon barriers, one movable, the other floating and attached to a force detector. The surface pressure of the film is the recorded force divided by the float length. The area of the film is varied by means of the movable barrier. It is essential for the float and barrier to allow no leakage. The trough walls, the barrier and the float must be hydrophobic and the liquid (water) level must be slightly higher than the bottom of the barrier. Teflon is an ideal material in this respect.

The graph in figure 8 shows the development of the excess surface pressure as a function of the area per adsorbed molecule⁽¹⁾ at the water-air and the water-oil interface. The adsorbed molecule used is cetyl trimethyl ammonium bromide. π -area curves can be considered to be the equivalent of the PVT diagrams in the bulk. In the aqueous phase, the molecules are ionized to $C_{16}H_{33}N(CH_3)_3^+$ and Br^- and therefore repel one another. The film pressure is greater for a given area at the oil-water interface than at the air-water interface, because the oil penetrates between the hydrocarbon chains of the film molecules and removes most of the inter chain interaction. The $\pi \cdot A = kT$ relation holds for the liquid gas interface, because electrical repulsion and inter-chain attractions are of the same order of magnitude, whereas at the water-oil interface, the electrical repulsion forces outweigh the inter-chain attraction forces⁽¹⁾.

Today most surface balances operate with a Wilhelmy plate measuring the surface pressure continuously. The surface pressure is the difference between the recorded surface tension and the surface tension of the pure liquid.

INTERFACIAL RHEOMETRY

There are two types of deformations that can be applied to an interfacial film in order to study the rheological properties: - Dilatational, which corresponds to extensional testing in the bulk, and - Shear. In order to study the interfacial properties, rheological experiments, dilatational or shear, are conducted on artificially prepared flat surfaces rather than on the complex colloidal systems themselves

Dilatational interfacial rheometry

Dilatational rheometry measures the change in the interfacial tension due to a specific change in interfacial area. This is a measure of the resistance

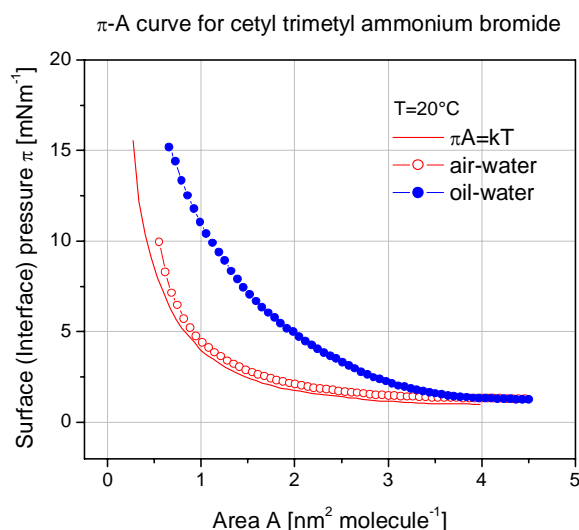


Figure 8: Surface pressure as a function of surface area for cetyl trimethyl ammonium bromide adsorbed at the water air and the water oil interface

to compression and expansion of the adsorbed film at the interface. Dilatational measurements can be done using the Langmuir trough and varying the surface area as a function of time or applying an oscillatory deformation using the Teflon barriers.

The most commonly used technique today is the pendant drop method. The interfacial tension is calculated from the size and shape of a liquid drop suspended from a capillary in a less dense fluid. The interfacial area is changed by controlling the flow rate of the liquid through the capillary. The problem with the dilatational method is, that while changing the surface area, adsorption and de-adsorption effects change the interfacial tension. For freely soluble surfactants at high concentrations this can result in no change of the interfacial tension at all.

Shear interfacial rheometry

In contrast to dilatational interfacial rheometry, interfacial shear rheometry provides a direct measurement of the mechanical strength or shear viscosity of the absorbed layer. Most interfacial shear measurements are based on three dimensional bulk measurement techniques adapted to two dimensions. Standard rheometers, as long as the torque sensitivity is available, can be used for the measurements.

For testing at a liquid-air interface, a circular knife-edge geometry can be used. The knife edge touches the surface and the surface film between the outer circular wall of the container and the ring is sheared. Contributions of the liquid and gas phase

are neglected.

The bi-cone geometry is typically used for water-oil interfaces. As the cone makes contact with both phases, the individual components contribute to the measured result also. Because of the increased size of the bi-cone, the measured torque is higher. The disadvantage is that the contributions of the pure liquid phase need to be measured separately and corrected for.

The Du Noüy ring, commonly used for interfacial tension measurements, can be applied to shear testing also. Like the knife-edged ring and the bi-cone, the ring is located at the interface between two liquids or a liquid and a gas. The surface between the inner ring and the circular wall of the container is sheared and the torque is recorded. The light construction of the ring permits very sensitive measurements. For oscillation measurements, similar to the bulk rheometry, a free oscillation and a forced oscillation technique are possible.

The free oscillation technique relies on the evaluation of the logarithmic decrement (ratio of successive strain amplitudes), determined from the damped oscillation at resonance frequency. The forced oscillation technique measures the in-phase and out of phase component of the torque (deformation) in an oscillatory test at a selected frequency (AAPN012).

CONCLUSION

The performance of multiphase systems depends strongly on the properties at the interface. Understanding the contributions of interfaces to the overall behavior is important for the formulation of materials with specific properties. The interfacial tension is an important parameter characterizing simple interfaces; however for more complex interfaces dilatational and shear measurements need to be performed to provide a more complete characterization.

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