



Dynamics of liquid interfaces under various types of external perturbations



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ABSTRACT

Dynamic interfacial parameters are the key properties of interfaces in many modern technologies and can be studied in various ways. For applications like foams and emulsions, the dynamics of adsorption and the dilational and shear rheology of liquid–fluid interfaces are investigated most frequently. This work gives an insight into recently developed new experimental approaches, such as fast capillary pressure tensiometry for growing and oscillating drops. These experiments are presented in comparison to more classical techniques like drop profile tensiometry and capillary wave damping. Progress in these experiments based on generated interfacial perturbations can be expected only by a close link to respective CFD simulations. We also present the state of the art of CFD simulations, which have reached a high level during the last decade and provide a substantial basis for dynamic interfacial experiments.

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1. Introduction

The knowledge on interfacial dynamic properties is essential for many modern technologies, such as foaming, emulsification and coatings. Whenever new interfaces are created or interfacial layers are subject to various types of perturbations (shear, compression/dilation) a high efficiency of the technology requires detailed information on the dynamic interfacial behavior [1]. The main dynamic quantity of a liquid interface is the change in adsorption with time, starting with an empty interface after its formation. The easiest way of measuring this process is interfacial tensiometry. The list of additional experimental ideas practiced in the moment further includes interfacial shear and dilational rheology, surface potential, interfacial ellipsometry, non-linear optical methods, neutron reflectivity or small angle neutron scattering [2]. From a time resolution point of view the interfacial tension and the derived methods of dilational rheology are those which give access to dynamic interfacial properties in the sub-second time range [3]. In contrast typically ellipsometry and non-linear optical methods such as Second

Harmonic Generation (SHG) are much more complex and therefore can provide a time resolution of interfacial processes on time scales of only seconds and minutes [4].

When experimental methods are used to characterize interfacial properties the theoretical background is typically based on models that assume a more or less homogeneous distribution of surfactant in the adsorption layers [5,6]. In many cases this assumption has been verified experimentally and the limits for example of the maximum frequency in oscillating drop tensiometry has been defined accordingly. New attempts have been made with CFD to describe the processes to/from and at liquid interfaces such that we can expect more detailed input. This significant support from CFD simulation can, for instance, be the analysis of the onset of Marangoni instabilities [7] which has also been experimentally verified. It is now even feasible to solve the Navier–Stokes equation for laminar liquid flows under most complex boundary conditions, including a free liquid interface under dynamic adsorption conditions. Hence, the shape of a growing or oscillating drop or bubble at low frequencies can be described quantitatively by a respective simulation and provides any changes in concentration of adsorbing species or pressure along the drop profile under corresponding dynamic conditions [8]. And also fast oscillating drops/bubbles at

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small amplitudes are the object of CFD simulations, the results of which can be verified via experimental data gained by a fast video monitoring.

This overview is focused on freshly formed static interfaces as well as under expansion and compression. Shear deformations of interfacial layers, created on purpose or as side effect in dilational experiments are not considered here. At this place we just want to mention few very recent investigations in which dilation and shear have been considered in a close connection. To this topic for example pure saponins of different origin or mixtures of Hydrophobin II with saponin are discussed [9–11]. The obtained results are discussed in terms of interfacial structure formation and possible molecular mechanisms which could have an influence on the rheological response of the adsorption layer.

The present work provides an overview of the most recent new developments and improvements of experimental methods for measuring the dynamic interfacial tension. The dilational rheology is mainly based on interfacial tension studies to follow the relaxation of interfacial layers after respective, harmonic or transient, perturbations. The slow and fast drop/bubble oscillation methods are complemented by the capillary wave damping method, which all together provide a very broad frequency range from less than a hundredth up to several hundred Hz. Experimental examples are provided to demonstrate the progress made in this field of dynamic liquid interfaces.

2. Relaxation studies with pendent drops and bubbles

The drop and bubble profile analysis tensiometry (PAT) is presently the most frequently used method for investigations of the surfactant adsorption dynamics at water/air and water/oil interfaces. The principle of PAT is based on analyzing the shape of an axisymmetric drop or bubble. The shape is mainly determined by two forces acting in opposite directions: the surface tension tends to make the drop or bubble spherical, while gravity tends to elongate the drop/bubble until it breaks off. For measurements at constant interfacial area the experimental time window ranges from about 1 s up to hours and days so that even extremely slow processes can be easily followed [12]. Another function of the instrument is the performance of harmonic perturbations of the drop/bubble surface area via sinusoidal changes of the drop/bubble volume. Such experiments give access to the surface or interfacial dilational visco-elasticity.

In general low surface active surfactants adsorb fairly quickly due to the required high bulk concentration. On the other side, highly surface active substances are used at rather low bulk concentrations and, therefore, their adsorption kinetics is slow. In both cases it is very important to select and properly apply the right experimental techniques for getting the whole adsorption kinetic curve. Similar problems arise in investigations of the frequency dependence of the interfacial tension response to small harmonic perturbations of the interfacial area, i.e. when we want to measure the dilational visco-elasticity of a surfactant adsorption layer. For a weak surfactant a method is obviously needed that works at very high frequencies as the required compressions/expansions should create a deviation of the surface layer from equilibrium fast enough such that the reestablishment of the equilibrium by desorption/adsorption can be experimentally followed. Again, on the contrary, for the very highly surface active substances a method is required with sufficiently slow compressions and expansions, i.e. measurements at low frequencies of interfacial perturbations, as it was discussed in detail in [13].

Beside the experimental peculiarities that one should be aware of when investigating surfactant adsorption dynamics, there are also some problems regarding the theoretical interpretation of the results, most of all at water/oil interfaces. During interfacial perturbations, the adsorption of surfactants is significantly affected by the attractive forces of the hydrophobic oil molecules, despite the ionic repulsion of the surfactants' polar heads. On the other side, desorption of the surfactant molecules from the water/oil interfaces is hindered by the same

attractive hydrophobic forces with oil molecules. The result of these processes can be an asymmetry of the adsorption and desorption fluxes upon interfacial area oscillations when measuring the dilational rheology. The current theoretical models (Langmuir and Frumkin) still used for interpretation of the water/oil experimental results have been primarily developed for the water/air interface. The development of a new model requires a clear picture of the mechanism of the additional hydrophobic interaction impact on the adsorption dynamics, starting from a recently developed theory where the surfactant and the oil molecules adsorb in competition at the water/oil interface [14].

Here we will discuss as a first example the dilational rheology of β -lactoglobulin (β -LG) at the water/air interface. In [15] the influence of the adsorption layer age on the visco-elastic properties of β -LG was studied. In Fig. 1 the dilational elasticity of β -LG versus bulk concentration is shown for the oscillating frequency of 0.1 Hz.

The thermodynamic model used for the description of the experimental data consists mainly of the equation of state for the surface pressure Π as a function of surface coverage θ [15]

$$-\frac{\Pi\omega_0}{RT} = \ln(1-\theta) + \theta(1-\omega_0/\omega) + a\theta^2 \quad (1)$$

and the respective adsorption isotherm

$$b_j c = \frac{\Gamma_j \omega \exp\left[-\frac{\omega_j}{\omega}(2a\theta)\right]}{(\omega_j/\omega_{\min})^\alpha (1-\theta)^{\omega_j/\omega}} \quad (2)$$

where c is the bulk concentration and a is the interaction between adsorbed molecules. The other parameters are: ω and ω_0 are the molar area of the surfactant and a water molecule, respectively, Γ_j is the adsorption of component j and α is a model parameter discussed in [16].

For the calculation of the different curves, all model parameters were kept constant except the adsorption constant b_j . Its value was varied in order to estimate the effect of the surface age on the adsorption activity, represented mainly by the parameter b , under constant conditions like molar area distribution, interaction constant, aggregation number, secondary layer formation, etc. The model parameters are summarized in [16].

As another example for studies of the dilational rheology, the visco-elastic modulus $|\varepsilon| = \sqrt{\varepsilon'^2 + \varepsilon''^2}$ of $C_{14}TAB$ adsorption layers at the water/hexane interface versus its bulk concentration is shown in Fig. 2 [16] (ε' and ε'' are the real and imaginary parts of E). Fig. 2a contains

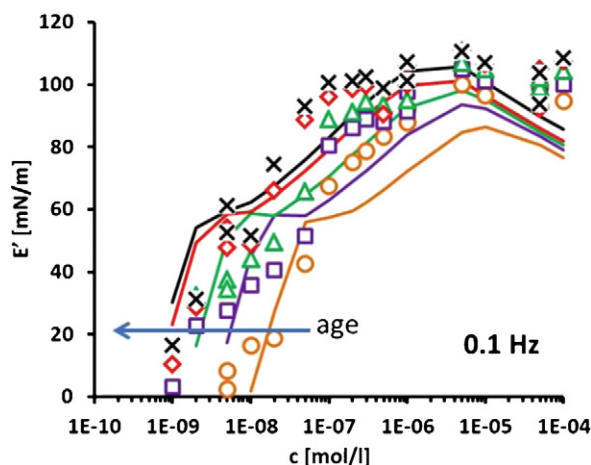


Fig. 1. Experimental 'quasi-equilibrium' isotherms of elasticity at different surface ages: 10,000 s (circles), 18,000 s (squares), 30,000 s (triangles), 60,000 s (diamonds) and 80,000 s (x); solid lines follow the best fit to the experimental data as calculated with the model given above; the arrows point into the direction of increased age.

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