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Historical perspective

An interferometric technique to study capillary waves☆

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ABSTRACT

We describe a new interferometric technique to study gas-liquid and liquid-liquid interfaces. Bubbles and drops are subjected to an alternating electric field which excites capillary oscillations at the interface, if charged. Bubble or drop deformation is detected by the change of the internal optical path of a laser beam crossing perpendicular to the oscillation axis. Due to the closed geometry, a discrete spectrum of stationary oscillation frequencies (normal modes) is excited. The interferometric nature of the measurement and the resonant nature of the oscillation modes concur in allowing for high sensitivity, in the sub-nanometric region. We present a detailed description of the experimental setup and examples of applications of the technique to the study of both gas-liquid and liquid-liquid interfaces, either naked or with adsorbed surfactant monolayers, for bubbles and drops with diameter ~ 1 mm. In particular, the resonance frequencies and the width of the resonance peaks depend on the surface tension and the viscous dampening, respectively. We show that, by this new technique, properties of the interface can be accessed with confidence at the sub-nanometer scale, and surface phenomena, like the monolayer phase transition or the peculiarities of adsorption/desorption processes, can be unraveled in concentration regimes which are too low for existing methods.

1. Introduction

The dynamic approaches provide deep insight into the peculiarities of the interfacial region between two fluids. From a theoretical point of view, non-equilibrium phenomena have been pioneered by Lord Rayleigh who developed hydrodynamic-based models to describe the dynamics of non-flat interfaces [1]. Later, Ward and Tordai [2] set forth a simple non-equilibrium model for the time evolution of the interface itself. These studies were developed later by a number of different authors who refined enormously the original oversimplified pictures and combined the geometrical variation of the interface (e.g., capillary waves) with the time-dependent structural variation of the interface [3] The shape of the interface and its structure may, or may not, change on different time scales, leading to interesting coupling phenomena (some good reviews have been periodically provided along the years, see e.g. [4]). Parallel to these theoretical studies, a lot of different experimental techniques had been suggested. The experimental tools are meanwhile on a good level and several techniques are commercially available. These techniques include the oscillating drop and bubble methods. Usually, they apply videometry and digital image processing of the drop (bubble) oscillating inside a solvent in which surface active molecules have been dissolved. This procedure yields a two-dimensional image of the cross section of the vibrating drop (bubble) resolved in space and time. From these data the shape of surface oscillations can be carefully reconstructed. A number of important effects can be extracted and the mechanisms underlying the surface dynamics can be unveiled. Among the mechanisms involved in the build-up of interfacial layers we mention, for instance, the diffusion in/from the bulk phases, the kinetic processes inside the adsorbed layer (re-orientation, aggregation etc.). In addition to the equilibrium interfacial tension, these techniques enable to measure other interesting parameters that, invariably, are frequency related, such as the interfacial tension, the surface dilational visco-elasticity and the viscous dissipation. These techniques are inherently limited by the space- and time-resolution of the images recorded by the camera. Despite the progress of the recording techniques and the excellent software programs for image analysis, very fast and/or very small deformations of the interface cannot be detected. Completely different approaches enable to extend the space and time range of interfacial phenomena. For instance, in the biophysical field, the group of Sackmann developed interferometric microscopy techniques to investigate the movement of the adhesion region between living cells (or biomimetic models) and a solid substrate (for a recent review see, e.g.

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[5].). In recent developments, these techniques reached a great sensitivity, enabling to detect oscillation amplitudes as small as a few nm [5]. As we will show later, our *differential* interferometer further improves resolution, and allow exploring also the sub-nanometric region.

2. The technique

The longingly employed technique to measure capillary waves at the gas-liquid interface is based on the study of the light scattered from their flat separation surface [6]. Capillary waves act as gratings and diffuse light in directions related to their wave-vector. Rather delicate light scattering experiments have been developed to detect the thermally excited surface oscillations. Their frequency spectrum is continuous due to the “infinite” nature of the flat interface. Instead, in the case of a finite closed interface, the spectrum is no more continuous. In fact, for a gas bubble in a liquid (or a liquid drop in another immiscible liquid), the periodic boundary conditions naturally provided by their closed geometry allow only for a discrete spectrum of stationary oscillation modes [7]. This feature, together with the idea that the bubble (or drop) itself can provide a very simple optical interferometer, gives the basis of the new technique which we are going to describe in its principles and some of its applications. The bubble (drop) stationary oscillation modes can be excited by some applied field and then analyzed in terms of their resonance behavior, namely their amplitudes, central frequencies and resonance widths. Due to the closed geometry of the bubble, some asymmetry should be introduced in the applied excitation in order to excite surface oscillations, like a solid tip where the bubble rests by adhesion or buoyancy. The oscillation amplitude is connected to the susceptibility of the bubble (drop) interface to the applied field. If excited by an electric field, the oscillation amplitude is connected to the bubble (drop) net interfacial charge. If excited by an acoustic wave, the mismatch in compressibility and density is involved. The central mode frequency is related to the forces restoring the equilibrium bubble (drop) shape while oscillating: the interfacial tension in the simplest situation. The resonance width is then determined by the energy dissipation along surface oscillations, viscosity for simple systems. The interferometric technique, we propose, is ideally suited for the bubble (drop) oscillation measurements. It provides the high sensitivity necessary to probe oscillations with very small amplitudes (in the nm range or less), much smaller than the bubble (drop) radius (in the mm range). This procedure avoids non-linear effects and ensures perfect decoupling among oscillation modes. Notably, the bubble (drop) itself provides the optical mirrors for the light beam crossing. Light is reflected at the entering and exiting air-liquid interfaces, due to the refractive index mismatch. The deformation from the equilibrium shape is then detected by the change of the optical path inside the bubble (drop) of a laser beam that traverses it in the horizontal direction.

2.1. The optical interferometer

The experimental setup is sketched in Fig. 1. A laser beam is focused at the centre of the bubble (drop). Light is reflected at the two gas-liquid interfaces (or at the two liquid-liquid interfaces, in the case of a drop in liquid). These points can be considered as two coherent light sources, CLS1 and CLS2, with finite size and divergence determined by the focusing optics of the Gaussian laser beam and the bubble radius. The laser must have a coherence length longer than the optical path inside the bubble or the drop. For mild focusing inside the bubble (drop), with waist of the order of 20–50 µm, the Rayleigh range has an extension which cannot be neglected in comparison with the bubble (drop) diameter (in the mm range). Therefore, Gaussian optics is used instead of simple geometrical optics to calculate the beam divergence at the interfaces. In the backward direction, a circular pattern of interference fringes is formed on any plane perpendicular to the beam axis, the envelope of which diverges with a much larger angle than the

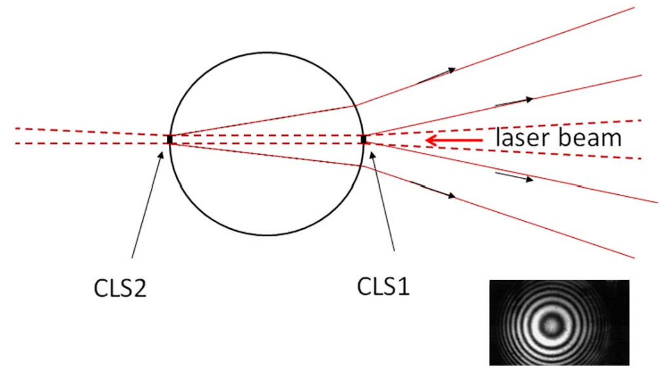

Fig. 1. The bubble as a Fabry-Perot interferometer.

incoming beam. The crucial element, determining both the fringe pattern and their divergence, is the difference between the curvatures of the wave front and the bubble at CLS1 and CLS2. In actual experiments, the divergence of the beam reflected at the second (exiting) bubble interface, CLS2, can be twice as large as the one of the beam reflected at the first (entering) bubble interface, CLS1. A change in the distance between CLS1 and CLS2 gives rise to a change in fringe pattern. A full cycle in the central fringe brightness, that is, from bright to dark to bright again, is obtained for an overall optical path variation of λ, that is, for a change in bubble radius of *λ/4*.

The optical system is designed to be compact and simple, and it is mounted on a rigid metal plate inside a sound isolating box. The laser beam (He–Ne, λ = 633 nm, 5 mW) is focused at the centre of the bubble by a lens (150 mm focal length). A portion of the fringe pattern is displaced from the laser beam axis by a beamsplitter, towards a photodetector placed on the central fringe axis, with an aperture much smaller than the central fringe width. The measured signal has the following form:

$$I(x) = A(I_1 + I_2 + 2(I_1 I_2)^{1/2}\cos(2\pi x/\lambda)) \quad (1)$$

where A is a constant (depending on the photodetection circuitry), I_1 and I_2 are the light intensities coming from CLS1 and CLS2, respectively, and x is the optical path difference.

The fringe visibility is excellent since, after Snell law of reflection, $2(I_1 I_2)^{1/2}/(I_1 + I_2) = 0.9998$ in the case of a gas bubble in water, with refractive index $n = 1.33$.

For central fringe operation, the interferometer is strictly differential since x depends on the optical path inside the bubble only ($x = 4R$, R being the bubble radius) and not, at first order, on the overall movement of the bubble relative to the laser source or the detector. The form of the response function, Eq. (1), suggests that the bubble vibrations are easily measurable for very small amplitudes, in the 10 nm range. In fact, the interferometer can operate in a region where the response function $I(x)$ is nearly linear with x, that is, around a point where $(2\pi x/\lambda)$ is equal to an odd multiple of $\pi/2$. In this case, 1% deviation from linearity is reached with a peak-to-peak vibration amplitude $\Delta R = 13.4$ nm, given the 633 nm wavelength of the He–Ne laser.

With a 5 mW He–Ne laser source, a 10^4-gain photomultiplier detector gives a typical variation ΔV = 1 V on a load resistance of 100 kΩ, for a full light span in the central fringe dictated by the intrinsic sinusoidal response of Eq. (1). Such full span ΔV corresponds to $\Delta R = \lambda/8 = 79.1$ nm, in the case of a gas bubble and to $\Delta R = \lambda/8n$ for a drop of refractive index n. Once the interferometer operates in its linear region (around the inflection point of its response), the absolute calibration of the vibration amplitude is then easily obtained by comparing the measured peak-to-peak voltage with the voltage span ΔV for the central fringe half cycle. Background ambient light is substantially reduced by means of an interference filter in front of the detector. Presence of scatterers, like for instance surfactant micelles, in the medium