

COMPENDIUM

Principles and application of Brewster angle microscopy

INTRODUCTION

Reflection of light from surfaces is part of our daily experience. However, an amazing property of optics is the possibility of having zero reflection. In more detail no reflection occurs from a clean and perfect interface illuminated under a unique angle of incidence with p-polarized light. This well-understood phenomenon is described by Brewster's law providing the so called Brewster's angle for the involved optical media. Any subsequent changes of the optical properties at the interface will lead to reflection. This fact is the basis of Brewster angle microscopy, a recent technique for the study of nanofilms at the water/air interface or at the surface of other transparent nonadsorbing dielectric substrates.

Even just with a monolayer on an interface Brewster's law is not fulfilled and the covered part of the surface reflects light although with very low intensity. By increasing the intensity of the illumination the contrast between the covered and the clean part of the surface can be enhanced. By using a microscope optic and a CCD-detector high contrast images of the lateral morphology of the layer can be taken. Typical fields of application are life sciences, colloid and surface chemistry and materials research.

BREWSTER'S LAW

When a light beam passes the boundary between two media of differing refractive index generally some of it is reflected. The Brewster's angle (θ_B) is a particular angle of incidence where light with one particular polarization state cannot be reflected. The state that cannot be reflected is parallel to the the plane of incidence. Light with this polarization is said to be p-polarized.

$$(1) \quad \tan \Theta_B = \frac{n_2}{n_1}$$

Note that, since all p-polarized light is refracted (i.e. transmitted), any light reflected from the interface at this angle must be s-polarized. A glass plate or a stack of plates placed in a light beam under Brewster's angle can thus be used as a polarizer.

For glass as a medium ($n_2 \approx 1.5$) in an ambient of air ($n_1 \approx 1$), Brewster's angle for visible light is approximately 56° to the normal while for an air-water interface ($n_2 \approx 1.33$) it reaches approximately 53° . Since the refractive index for a given medium is a function of the wavelength of light Brewster's angle will also vary with wavelength.

BREWSTER ANGLE MICROSCOPY

Brewster angle microscopy was introduced in 1991 [1],[2]. No light is reflected from the air-water interface under Brewster's angle incidence if p-polarized light is used. With constant angle of incidence the formation of a monolayer on the water surface modifies the Brewster's angle condition and light reflection is observed [1]. *Figure 2* illustrates the principle of obtaining the contrast for a surface covered with a nanofilm by Brewster angle microscopy.



Figure 1: Sir David Brewster was a Scottish physicist, mathematician, astronomer, inventor, and writer. (11 December 1781 – 10 February 1868) (image: Wikipedia)

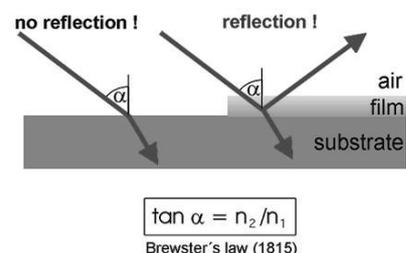


Figure 2: Principle of Brewster angle microscopy: making use of Brewster's Law for imaging ultra thin films with high contrast.

Brewster angle microscopy is an effective visualisation method for substructures with long range orientational order [3]. To obtain a contrast between subdomains of different molecule orientations an analyzer is positioned in the reflected beam path.

INSTRUMENTATION

The origin of commercial Brewster angle microscopes was the instrument developed by Dirk Hönig in his diploma-thesis [3] (figure 3). Since the first presentation at the LB6 in Paris Brewster angle microscopy has been established as a worldwide standard technique for the investigation of ultra thin films. Nanofilm's BAM1 (figure 4) was the first commercial instrument available followed by different versions of the BAM2 (figure 5). Currently we offer two different Brewster angle microscopes. The nanofilm_ep3bam (figure 6) is based on the ellipsometric platform nanofilm_ep3 and can be upgraded to an imaging ellipsometer.

The new nanofilm_ultrabam (figure 7) is based on a complete new optical pathway of light. The unique imaging optic provides fully focused images at max. 35 frames per second. Thus for the first time in a commercial instrument high resolution AND overall focused real time imaging of monolayers becomes possible. It enables the visualization of Langmuir monolayers or adsorbed films in real time (movie at <http://nanofilm.de/bam>).

APPLICATION

- Morphological features of monolayers during compression/decompression

The morphological study of monolayers has led to more detailed understanding of the two-dimensional condensed phase structure of monolayers. Brewster angle microscopy is the most informative method for such study [5]. Brewster angle microscopy can be used for direct observations during compression of monolayers in a Langmuir trough. The advantage against epi fluorescence and AFM is that no markers are required and that the film not needs to be transferred to a solid substrate.

A number of papers report BAM images at characteristic points of the π -A compression-decompression isotherm (for example: [5],[6],[7]...). For such investigation a software integration of the LB-system is essential.

- Inner structure of 2D condensed phase domains

Optical anisotropy induced by regions of different molecular orientations of alkyl chains within monolayers have been the subject of recent investigation. As mentioned, Brewster angle microscopy is an effective method to visualize the substructure with longrange orientational order by using an analyzer. Typical examples are methyl esters of fatty acids [8].

- Formation dynamics, non equilibrium structures

The formation of condensed phase in a fluid monolayer can occur far from equilibrium and growth kinetics can be so fast that the stable phase does not have time to reach its lowest energy state on the microscopic level. Metastable microstructures are formed under non-equilibrium conditions and the growth patterns of these structures are mainly affected by the complex interplay of microscopic interfacial dynamics and external driving forces.

Flores et al. [9] study how patterns formed by Langmuir monolayer domains of a stable phase, usually solid or liquid condensed, propagate into a metastable one, usually liquid expanded. During this propagation the interface between the two phases moves as the metastable phase is transformed into the more stable

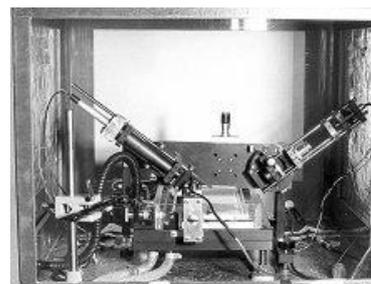


Figure 3: Prototype, Diploma Thesis, Dirk Hönig [3].



Figure 4: BAM1 (1991) – first commercial Brewster Angle microscope.

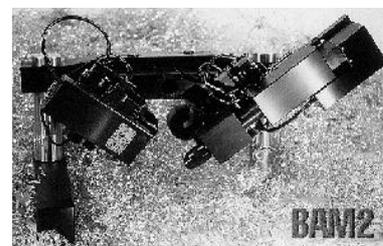


Figure 5: BAM2 (1995)

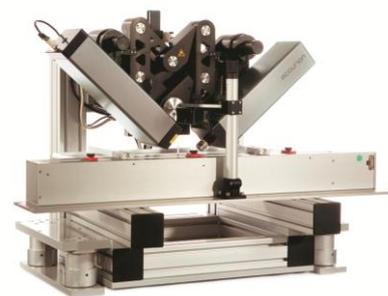


Figure 6: nanofilm_ep3bam (since 2003)

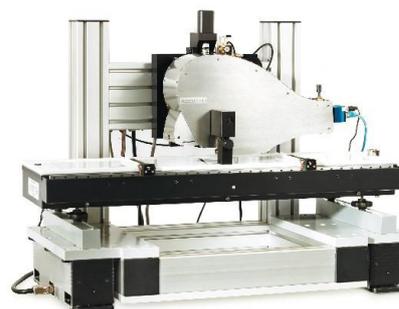


Figure 7: nanofilm_ultrabam (since 2010)

one. The interface becomes unstable and forms patterns as a result of the competition between a chemical potential gradient that destabilizes the interface. During domain growth they found a morphology transition from tip splitting to side branching and doublons were also found. These morphological features were observed with Brewster angle microscopy in three different monolayers at the air/water interface: dioctadecylamine, ethyl palmitate, and ethyl stearate.

▪ Monolayers & chirality

Monolayers of enantiomers of amphiphilic molecules can differ. The interaction of enantiomers and diastereomer pairs can be investigated for specific monolayer states. *Figure 10* shows domains of D-Dipalmitoylphosphatidylcholin (D-DPPC), L-DPPC and the racemate [10].

▪ Monitoring 2D-structures

Langmuir blottget techniques also offer the promising possibility of “bottom-up” self-assembly methods to realize new 2D-structures. Current examples are using self-assembled monolayers at the air/water interface. Chen and Berman [11] used Langmuir monolayers of diacetylene lipids with a cytosinyl head-group (PDC) mixed with an alcohol derivative of the same lipid (PDOH). They used for example different film compositions and a guanosine-containing subphase. A specific base-pair formation at the air–solution interface between the diacetylene monolayer and the free complementary nucleoside in the solution is suggested. At the end the complexe and very beautiful structures were fixed by *in situ* UV polimerization.

Currently nanoparticles at the air/water interface are used in an increasing number of applications for example to produce 2D colloidal crystals or nanowires. Gil et al. monitored the formation of 2D colloidal crystals by the Langmuir–Blodgett technique by Brewster angle microscopy [12]. In addition to Brewster angle microscopy (BAM), the monolayers have been characterized by surface pressure–area and surface potential–area isotherms at the air/water interface. After being transferred to a substrate the morphologies of the Langmuir–Blodgett films were analyzed by imaging ellipsometry and by scanning electron microscopy (SEM). Volinsky and Jalinek demonstrate the formation of a network of elongated Au “wires”. The laser-induced structured films exhibited high stability and could be transferred from water onto solid substrates without disrupting the Au organization [13].

▪ Biofluids

Currently Brewster angle microscopy is used in a wide range of applications. One class of applications is related to biological liquids like tear fluids or more in detail Meibomian gland secretion lung surfactants in/from pulmonary fluid. Kärcher et al. [14] observed the spreading process of Meibomian gland secretions in a Langmuir trough with a Brewster Angle Microscope (BAM). The secretion was characterized by an extremely rapid continuous spreading suggesting that enough material would be available to recover the superficial lipid layer of the tears between the blinks of the eye. Winsel et al. [15] investigated the morphology, thickness and surface pressure of the surfactant film of broncho-alveolar lavage (BAL) fluid from patients with sarcoidosis. The surface films were investigated during spontaneous adsorption of the BAL’s surface active material at the air/aqueous buffer interface. During the spontaneous adsorption of the pulmonary surfactant the surface pressure increased from initially 26 mN/m to 44 mN/m in the equilibrium state. Simultaneously to the increase of the surface pressure a continuous increase of the reflectivity signal was observed by quantitative Brewster angle microscopy (BAM). The film thickness is calculated from the reflectivity values using an optical model. The BAM images show the inhomogeneous nature of the

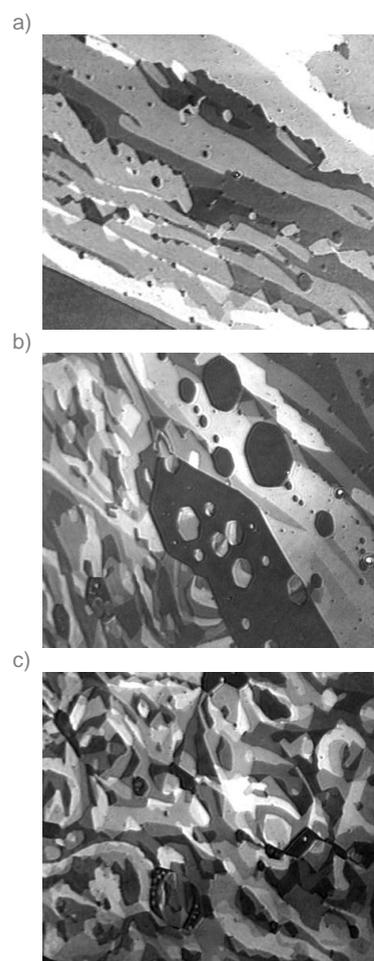


Figure 8: Ethyl stearate monolayer at $\pi < 1 \text{mN/m}$, Field of view ca. $600 \mu\text{m}$ (nanofilm_ultrabam)

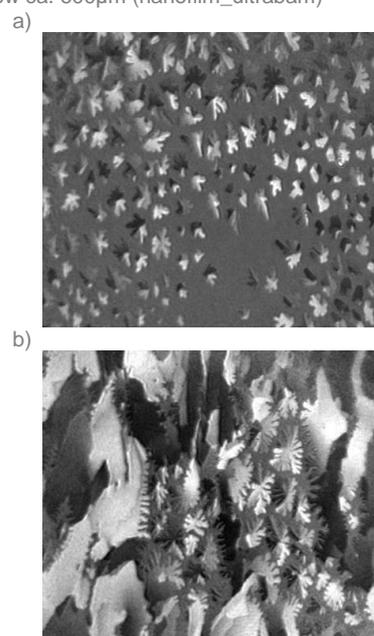


Figure 9: Monolayer of DMPE during first-order phase transition, contrast in domains caused by long range orientation order (nanofilm_ultrabam).

surfactant film with three distinct phases of different reflectivity even at relatively low surface pressures.

INTEGRATION OF OTHER TECHNIQUES

- Nanosecond pulsed lasers

Time-resolved Brewster Angle Microscopy for photochemical and photothermal studies on thin-films and monolayers transient events in thin films and interfaces have been studied using time resolved pump-probe nanosecond Brewster angle microscopy. Based on a Brewster angle microscope EP³-BAM, Hobley et al. [16] used two synchronized nanosecond pulsed lasers in the pump-probe configuration. The time-resolved BAM has been shown to be a versatile tool in studying dynamics of changes in monolayers and interfaces. Both morphological changes and photochemical transformations can be studied through the manifold of changes in both real and imaginary part of the refractive index at the interface. Different effects like increased rates of domain growth due to interfacial effects or unique domain morphologies are hints for cooperative domain growth in molecular monolayers. We are looking forward that the method will have wide applications in the study of membranes, lipid bi-layers or ultra thin layers during materials processing.

- Imaging ellipsometry and UV/VIS reflection spectroscopy

Pérez-Morales et al. [17] used imaging ellipsometry at the air–water interface to determine the optical parameters of a mixed monolayer containing an anionic phospholipid matrix (DMPA), and a cationic porphyrin (Ni-TMPyP, Ni(II)-tetrakis(4-methylpyridyl) porphyrin) as large counter ion. The nulling ellipsometric measurements were done on two phases observed directly by Brewster angle microscopy over specific regions with a size of few microns. Therefore values of the ellipsometric angles for the different regions at the interface (domains and surrounding areas) have been obtained. The difference in reflectivity of the monolayer-covered water surface and the bare water surface under normal incidence was determined with a reflection spectroscope at normal incidence.

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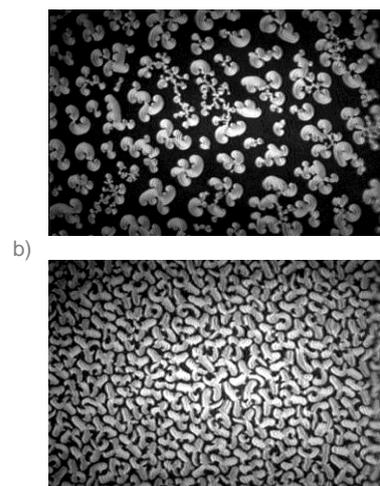


Figure 10: Brewster angle micrograph of of D-Dipalmitoylphosphatidylcholin and the racemate [9]

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