

Second Harmonic Generation from Soapy Interfaces

L. Sanchez¹, E. Foret², O. Bonhomme¹, E. Benichou¹, P.F. Brevet¹

¹ Institut Lumière Matière, UMR CNRS 5306, Université Claude Bernard Lyon 1

² Laboratoire de Physique des Solides, UMR CNRS 8502, Université Paris Sud

Foams are ubiquitous in nature and as such commonly used in a large range of applications as for instance, in chemistry as well as in structure material science for example. Therefore, numerous investigations of the mechanical and rheological properties of foams have been performed. However, their macroscopic behaviour is intimately bound to the microscopic properties of soapy interfaces¹. The spatial distribution of surfactants and their dynamics remains so far poorly understood, mostly because of the lack of techniques to characterize soapy interfaces at molecular scale.

Second order nonlinear optical techniques, and in particular Second Harmonic Generation (SHG), are powerful tools to characterize interfaces as this optical phenomenon only takes place where the centrosymmetry is broken². In surface SHG experiments, a pulsed laser at a frequency ω is focused on the studied interface and the signal at the double frequency is recorded in reflection. The properties of the interface, formed by surfactants and solvent molecules, are then derived from a careful analysis of the 2ω beam intensity and polarisation analysis. Amphiphilic chromophores, designed to have a great SHG optical response, at air/liquid interfaces have extensively been studied by this method. Surface concentration, molecular organization or dynamics have thus been reported in great detail^{3,4,5}. However, very few works have considered the case of molecules which do not have particular optical features adsorbed on surfaces^{6,7}. The principal reason stems from the difficulty to establish a clear link between the non-linear optical signature of the interface and the surfactant molecule properties.

In this work, we present our recent results on non-chromophoric surfactant molecules adsorbed at the air/water interface through SHG measurements. We focus in particular on surfaces covered by standard foam surfactants of different nature, for instance positively or negatively charged surfactants, while varying the solution composition. By comparison with other surface characterization methods (for example surface tension, disjoining pressure...), we discuss the origin of the SHG signal observed and draw a picture of the surfactant behaviour at soapy interfaces.

1. M. Durand, *Contribution théorique et expérimentale à l'étude du drainage d'une mousse aqueuse*, PhD thesis, Univ Paris 11
2. Y.R. Shen et al., *Surface Second Harmonic Generation: A New Technique for Surface Studies*, Ann. Rev. Mater. Sci., 16, 69, 1986
3. K.B. Eisenthal et al., *Liquid Interfaces Probed by Second-Harmonic and Sum-Frequency Spectroscopy*, Chem. Rev., 96, 1343, 1996
4. Motschmann et al, *Phase Transition in an Adsorption Layer of a Soluble Surfactant at the Air/Water Interface*, J Coll Int Sci, 248, 462, 2002
5. P-M Gassin et al, *Tracking Molecular Aggregates at a Liquid Interface by Nonlinear Correlation Spectroscopy*, J Phys Chem C, 118, 1135, 2014
6. [Bell 1996] Bell et al, *Sum-frequency vibrational spectroscopy of soluble surfactants at the air/water interface*, J Chem Soc, Faraday Trans. 92, 515, 1996
7. O. Bonhomme et al, (en préparation)