

Lipid membrane characterization with second harmonic scattering: surface potentials, ionization, membrane asymmetry and hydration

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par

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Cornelis Lütgebaucks

Abstract

Membranes, composed of a variety of lipids and other biomolecules, mediate signaling processes between cells and their aqueous environment. To fulfill this function, membranes can vary their composition leaflet-specific and thus alter their surface properties. To fully understand the impact of these processes on the molecular level, it is necessary to develop tools that can access the molecular properties of free-floating model membranes label-free. These tools are ideally surface-specific. In this thesis, we apply the nonlinear optical techniques second harmonic scattering (SHS) and vibrational sum-frequency scattering (SFS) together with electrokinetic measurements to label-free characterize the interfacial properties, hydration structure and surface potentials of liposomes in aqueous solutions.

First, we generalize the nonlinear optical theory to describe the second-order surface response from interfaces with aqueous solutions independent of the ionic strength for reflection, transmission and scattering geometries. We demonstrate that interference effects from oriented water molecules in the bulk aqueous solution alter the probing depth and the expected second-order response at low ionic strengths.

Then, we apply this theory to demonstrate that SHS patterns of liposomes and oil droplets contain all necessary information to extract the absolute surface potential of the respective particles without assuming a model for the interfacial structure. By analyzing scattering patterns that capture the orientational distribution of water around the particles, we find surface potentials of -38 mV for bare oil-droplets and -11 mV for zwitterionic liposomes in water. For anionic liposomes the surface potential varies between -150 mV and -23 mV in solutions containing different amounts of NaCl ranging from ~0 mM to 10 mM. These values are remarkably different for solutions to the Gouy-Chapman model considering a fixed surface charge density.

Next, we characterize the hydration and lipid asymmetries in binary mixed membranes using SHS and SFS. The liposomes exhibit hydration asymmetry between the inner and outer leaflet. The lipid number density between the inner and outer leaflet is the same, although geometrical packing arguments would suggest a different density. However, an asymmetric lipid distribution between the leaflets can be induced by fine tuning specific intermolecular interactions between the lipids. This is shown with dipalmitoylphosphoserine and dioleoylphosphocholine mixtures creating a membrane

structure that allows intermolecular H-bonding between the phosphate and amine groups of the lipids.

Finally, we quantify the surface properties of membranes composed of lipids containing phosphoserine and phosphocholine headgroups. Surprisingly, we find a very high degree of counterion condensation on anionic membranes in pure water: only 1 % of all lipids are ionized. This indicates a tightly packed layer of ions around the membrane that needs to be considered when modelling the interfacial structure around membranes.

Keywords: membranes, lipids, surface potential, ion condensation, hydration, non-linear optics, light scattering, soft matter, liquid/liquid interfaces, electric double layer

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