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

Thèse n. 7626 2017
présentée le 24 Mars 2017
à la faculté des sciences et techniques de l'ingénieur
Chaire Julia Jacobi de Photomédecine - Laboratoire de biophotonique fondamentale
Programme doctoral en biotechnologie et génie biologique
École Polytechnique Fédérale de Lausanne

pour l'obtention du grade de Docteur ès Sciences
par

CORNELIS LÜTGEBAUCKS

acceptée sur proposition du jury:

Prof. Dominique Pioletti, président du jury
Prof. Sylvie Roke, directrice de thèse
Prof. Francesco Stellacci, rapporteur
Prof. Franz Geiger, rapporteur
Prof. Eric Vauthey, rapporteur

Lausanne, EPFL, 2017

Berichte aus der Biophysik

Cornelis Lütgebaucks

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

Shaker Verlag
Aachen 2017

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at http://dnb.d-nb.de.

Zugl.: École Polytechnique Fédérale de Lausanne, Diss., 2017

Printed in Germany.

ISBN 978-3-8440-5496-5
ISSN 1439-7897

Shaker Verlag GmbH • P.O. BOX 101818 • D-52018 Aachen
Phone: 0049/2407/9596-0 • Telefax: 0049/2407/9596-9
Internet: www.shaker.de • e-mail: info@shaker.de

Acknowledgements

First of all I would like to thank my supervisor Professor Sylvie Roke for giving me the opportunity to work with her and doing cutting-edge research for the last 5 years, during which I gained many new insights. I appreciate all the time she invested and the trust she placed in me. A huge thanks goes also to Grazia Gonella for very helpful discussions, her advices, and spending time in hourlong skype calls.

I would also like to thank the LBP group, past and present members, for discussions, and for creating such a kind atmosphere. Specifically, Carlos Macias-Romero, with whom I shared the 5 years in the group and who taught me a lot about optics, but more importantly became a very good friend. Also Rüdiger Scheu, who helped me getting started by answering questions already during breakfast. In addition, I also would like to thank Halil Okur and Yixing Chen for helpful discussions and proof-reading. With these four I also shared an office and that had to endure all my moods over the years.

Furthermore, a huge "thanks" to all the people, colleagues, and friends that I encountered during my stay and that helped creating awesome memories or just for feeding me: Marie Didier, Evangelia Zdrali, Jan Dedic, Orly Tarun, Nikolay Smolentsev, Filip Kovacic, Igor Nahalka, Volker Zagolla, Zahra Monemhagdoust, Enrico Chinello, Andreas Schmocker, Claudia Rodriguez, Miguel Modestino, Manon Rostykus, Clément Javercaz-Galy, Michael Reinke, Yury Kuzminykh, Christophe Moser, Samantha and Mitchell Anderson, Vitalijs Zubkovs, Mikaël Dumortier, Eric Tremblay, Clara Moldova, Matthew Blackburn, Alina Isakova, Miguel Sison, Angel Padua, and Alix D'Agostino.

Thanks to our secretary Rebecca Veselinov for being always helpful and supportive; especially for the small motivations in form of cakes and advent calendars.

Thanks to my comitee, Prof. Pioletti, Prof. Franz Geiger, Prof. Eric Vauthey, Prof. Francesco Stellacci, for taking the time to read my thesis and giving me feedback on my research. Thanks to Prof. Eric Borguet for giving me permission to use some of his data in my work.

Last, I would like to thank my parents for all the love and support they gave me and all the opportunities they provided that let me to this point.

Lausanne, January 2017 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, nonlinear optics, light scattering, soft matter, liquid/liquid interfaces, electric double layer

Contents