

## Charge Redistribution in Lipid Films under Varying Electric Potential: Insights from Monte Carlo Simulations

Andrey V. Brukhno

*Centre for Molecular Nanoscience – A.Brukhno@leeds.ac.uk*

### Abstract

Supported lipid mono- and bilayers are significantly easier to manipulate in experiment than biological membranes and, therefore, provide a convenient model for those. One way of characterising supported nanoscopic films and their interactions with the surrounding electrolyte solution is via electrochemical experiments, such as cyclic voltammetry. The reported numerical calculations elucidate the physical principles of the molecular phenomena indirectly registered in voltammetry of supported lipid films.

We present a Monte Carlo study on the charge redistribution within the interface of lipid mono- and bilayers supported on an atomically smooth (mercury) electrode to which a varying electric potential is applied. Our coarse-grained simulations closely mimic voltammetry experiments where a non-trivial dependence of the capacitance on the applied voltage,  $C(V)$ , is observed. [1,2] Self-consistent field calculations and Monte Carlo simulations unveiled the following rearrangements in hydrophobically adsorbed lipid films [3]:

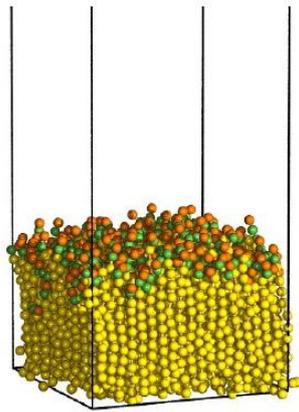
i) desorption of the lipid monolayer from the electrode driven by the accumulation of salt ions (the counterions) at its surface, resulting in a narrow electric double layer beneath the lipid film;

(ii) subsequent transformation of the monolayer into a bilayer as the surface charge is raised further;

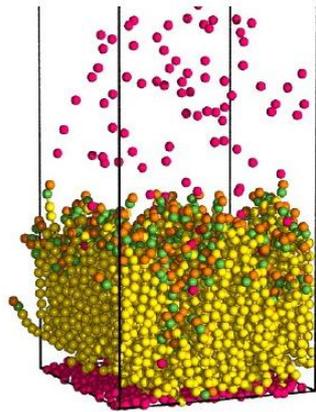
(iii) in the case of zwitterionic (or strongly polar) lipid head groups, the desorption is followed by the bilayer readsorption via interaction with the electric double layer and release of the excess counterions.

We argue that the voltammetry peaks are associated with a stepwise process of formation of layers of alternating charge: an inner electric double layer – upon monolayer desorption; triple or multi-layer – upon bilayer readsorption. The obtained dependence of the surface potential (voltage) on the surface charge density,  $\varphi_0(\sigma)$ , exhibits a characteristic hysteresis feature. The back and forth going level of  $\varphi_0$  in a narrow range of  $\sigma$ -variation is rationalised as a simulation evidence of the primary peaks in  $C(V)$ . The voltage hysteresis loop detected in simulation is replaced in voltammetry experiments by a stepwise raises in the surface charge. [2]

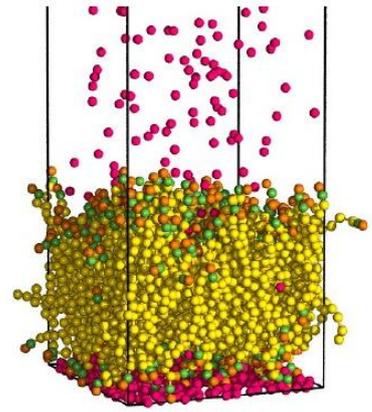
1. F. A. M. Leermakers and A. Nelson, *J. Electroanal. Chem.* 278, 53 (1990).
2. D. Bizzotto and A. Nelson, *Langmuir* 14, 6269 (1998).
3. A. V. Brukhno et al., *Soft Matter* 7, 1006 (2011), [arXiv:1007.3004v2](https://arxiv.org/abs/1007.3004v2).



SCD = 0,  
neutral surface



SCD =  $-0.05 e/\text{\AA}^2$   
1:1 salt  $\approx 0.3$  M



SCD =  $-0.1 e/\text{\AA}^2$   
1:1 salt  $\approx 0.3$  M

1. F. A. M. Leermakers and A. Nelson, J. Electroanal. Chem. 278, 53 (1990).
2. D. Bizzotto and A. Nelson, Langmuir 14, 6269 (1998).
3. A. V. Brukhno et al., Soft Matter 7, 1006 (2011), [arXiv:1007.3004v2](https://arxiv.org/abs/1007.3004v2).