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Phospholipid membrane dynamics at the solid–liquid interface studied with grazing incidence neutron spin echo spectroscopy

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Abstract. Neutron spin echo spectroscopy has been used under grazing incidence conditions to study the dynamics of SoyPC phospholipid membranes at the solid-liquid interface. The use of advanced neutron optical components such as a neutron prism and a resonator structure at the interface for an increase in intensity near the interface helped to study partially elastic waves in the phospholipid membrane as well as the influence of Ibuprofen on the membrane elasticity. Previously observed phase transitions of the surface layers of SoyPC from a lamellar structure to surface crystalline phases also showed their imprint in a suppression of the phospholipid membrane dynamics.

1. Introduction
Neutron spin echo (NSE) spectroscopy provides the highest energy resolution in neutron scattering [1]. The velocity change during scattering is encoded in the degree of polarization of a polarized neutron beam. The length scales and time scales accessible by NSE spectroscopy match those of thermally activated fluctuations in soft matter systems, such as polymer chains in the melt [2] or microemulsion membranes [3, 4, 5, 6, 7]. In the last years, NSE has been applied also to surface studies at the solid liquid interface [8, 9, 10, 11, 12, 13]. One example is phospholipid membranes on a rigid substrate [10, 11]. Measuring with a highly collimated beam in one direction, the dynamics at different penetration depth can be studied with Grazing Incidence NSE spectroscopy (GINSES), using the same sample geometry as in Grazing Incidence Small Angle Neutron Scattering (GISANS). We found in phospholipid bilayers partially elastic modes with long wavelength, which agreed well to the expectation of a theoretical model by Romanov et al. [14]. The huge intensity penalty of the GINSES setup led to the development of new neutron optical components such as a neutron prism for a homogenization of the penetration depth for different wavelengths and a neutron resonator which increases the evanescent neutron field at the surface [15], which helped largely in conducting these studies of soft matter dynamics at the rigid interface.
2. Experimental Techniques

2.1. Sample materials and preparation
Phospholipid layers on top of a silicon block have been prepared first by dissolving the phospholipid (SoyPC) and eventually Ibuprofen in isopropanol, then casting the solution onto the silicon block and letting it slowly dry under reduced pressure, ensuring the production of a homogeneous film without bubble formation. Details of the preparation and the materials used can be found e.g. in Ref. [11].

2.2. Neutron scattering techniques
The structure of SoyPC layers at the interface has been investigated with neutron reflectometry and grazing incidence small angle neutron scattering at the reflectometer MARIA at MLZ (Garching) [16]. Neutron spin echo experiments have been performed at the J-NSE at MLZ (Garching) [17] and at the SNS-NSE at ORNL (Oak Ridge) [18, 19]. GISANS provides structural information of the interface near region. The neutron beam enters a silicon block from the side such that it hits the long side of the block under a very shallow angle below the critical angle, which is for typical soft matter samples and wavelengths used in such experiments of the order of 0.3-0.7°. An evanescent wave enters then the sample behind the flat surface of the silicon block and is scattered there. The 2d detector image contains then structural information in lateral and normal direction of the surface from the volume illuminated by the evanescent wave. The dynamics near the interface has been measured with GINSES, where the main difference to a “standard” NSE experiment is a strong lateral collimation of the neutron beam in the first arm of the NSE instrument. With a slit in front of the first precession coil and the sample cell used also in the GISANS experiment the incident angle on the silicon surface can be adjusted in the region below the critical angle. The penetration depth of the evanescent wave can be varied by changing the incident angle below the critical angle and by changing the contrast between the silicon block and the sample with partially deuterated material. For the broad wavelength band of the SNS-NSE (5-8 Å) a neutron prism has been used to make the penetration depth homogeneous for all λ, as described in Refs [20, 15]. The strong lateral collimation of the beam and the fact that only the interface region of the sample is probed results in long measuring times, making it very difficult to scan different q-positions (i.e. different scattering angles) during one experiment. Each single curve of S(q,τ) required approximately 2 days of beam time.

3. Results and Discussion
The ibuprofen contents in the SoyPC phospholipid layer has been varied from 0 wt% to 33 wt%. A structural investigation with GISANS, showing different phase transitions, has been reported in Ref. [11]. The phospholipid membranes form layers with a thickness of about 5-6 nm according to the reflectometry experiments. The penetration depth (approx. 40 nm) of the evanescent wave covers several phospholipid double layers. The surface near phases range from a purely lamellar phase at 0 wt% to a hexagonal phase at >25 wt% Ibuprofen contents in the membrane passing by a less ordered double hexagonal phase for medium ibuprofen contents at around 15-20 wt%. Figure 1 shows the three concentrations investigated here with GINSES, i.e. 0, 5 and 33 wt% ibuprofen. At low ibuprofen concentrations, still the original lamellar phase is preserved (only the peak of the lamellar order in qz direction is visible at qz = 2π/d, while at the highest concentration, the hexagonal ordering appears with the side peaks at qy ≠ 0.

Figure 2 shows the evolution of the phase with Ibuprofen concentration in wt%. It additionally shows the existence of a less ordered phase at medium Ibuprofen concentrations. GINSES experiments at 15 wt% showed that the dynamics at this concentration is completely frozen on the time scales of the experiment of some 10 ns [11]. GINSES experiments are shown in Figure 3 for additional concentrations from measurements at the SNS-NSE. In a previous publication we presented the existence of partially elastic surface waves, if the elastic properties
Figure 1. Structure determined with GISANS for 0wt%, 5wt% and 33wt% Ibuprofen in the SoyPC membrane (left to right). At zero and low Ibuprofen concentration, the peak from the lamellar structure is visible, at 33wt% a hexagonal surface structure is induced by the Ibuprofen of the membrane are in the right range as it is the case for pure SoyPC [10]. Here we measure a bit further away from the lamellar peak in $q_z$, between the first and second Bragg peak of the lamellar phase (at $q_z = 0.14 \, \text{Å}^{-1}$). There, the oscillatory behaviour is hardly visible any more due to a larger in-plane component $q_y$ in the geometry of the experiment.

We therefore look at the overall decay of the intermediate scattering function $S(q,\tau)$. While the fitted relaxation time for the pure and 5 wt% sample are very similar within the error...
bars (55 ± 11 and 89±25 ns repectively), the hexagonal phase showed again no decay within the time window of the GINSES experiment. The remaining difference between the two lower concentrations, if taken as real, would be an indication of a slight stiffening of the membrane. But more experiments going to larger Fourier times would be needed to answer this question, such that the relaxation times can be determined with a significantly smaller errorbar. For these rather low-q experiments a time range of up to approximately 50 ns would be desirable. The long counting times due to the low intensity prevented to go to longer Fourier times. One path to improve the situation is improved resonator structures[15, 21] , where currently the limits of different geometries and number of resonator layers are investigated.

It was reported in Ref. [13] that a spin coating preparation of a mixture of SoyPC and glycerol dioleate leads to a reverse hexagonal phase on top of a silicon block. This hexagonal phase was soft enough that also with GINSES, the membrane fluctuations were visible and could be suppressed by a different SoyPC/GDO mixture leading to a cubic phase. An interface stiffening, but not a complete elastic benaviour, has been observed in this case. The SoyPC-Ibuprofen system in its hexagonal phase has compared to the SoyPC/GDO system much stiffer, where no membrane fluctuations are visible any more.

4. Conclusion
Grazing incidence NSE spectroscopy allows to study thermal fluctuations at the difficult-to-access solid-liquid interface. Membrane fluctuations and the influence of additives on it have been studied in microemulsions and in this work in phospholipid membranes. We could see that small amounts of Ibuprofen affect the bending elasticity of the membrane to a very small extent,
while as soon as Ibuprofen introduces structural phase transitions, a complete suppression of the membrane fluctuations is observed. The disordered lamellar phase presented in [11] as well as the pure lamellar phase behave as rigid objects without dynamics in the NSE time window. It would be desirable to extend the time range of the measurements and to measure the transition to the first disordered lamellar phase in more detail to see how the membrane is affected by small amounts of ibuprofen. The GINSES technique provides access to thermal fluctuations in the vicinity of a rigid interface, while having the high resolution (relatively large Fourier time) of the NSE technique still available. Future work will be devoted to study different types of samples at the interface such as adsorbed polymers at the interface (e.g. brushes or microgel particles [22, 23]), which is highly demanding due to the even lower scattering intensity, but on the other hand relevant for a number of applications such as functional surface coatings and interesting from a fundamental point of view of polymer dynamics due to the one-sided confinement at the rigid surface.

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