Nuclear Inst. and Methods in Physics Research, A 871 (2017) 72–76

Contents lists available at ScienceDirect

Nuclear Inst. and Methods in Physics Research, A

journal homepage: www.elsevier.com/locate/nima

New tools for grazing incidence neutron scattering experiments open perspectives to study nano-scale tribology mechanisms

H. Frielinghaus [a,*], M. Gvaramia [a], G. Mangiapia [a], S. Jaksch [a], M. Ganeva [a], A. Koutsioubas [a], S. Mattauch [a], M. Ohl [b], M. Monkenbusch [b], O. Holderer [a]

[a] Jülich Centre for Neutron Sciences at MLZ, Forschungszentrum Jülich GmbH, Lichtenbergstrasse 1, 85747 Garching, Germany

[b] Jülich Centre for Neutron Sciences JCNS-1, Forschungszentrum Jülich GmbH, Leo Brandt Straße, 52425 Jülich, Germany

ARTICLE INFO

Keywords:
Tribology
Neutron spectroscopy
Surface dynamics
Grazing incidence scattering
Enhanced waves

ABSTRACT

Using grazing incidence scattering methods allows for depth profiling near surface structures very efficiently Dosch (1986). In parallel, layered structures have been used as resonators to enhance the wave field Kozhevnikov et al. (2007), Khaydukov et al. (2011), Kozhevnikov et al. (2011) and Nesnidal and Walker (1996) that directly increases the scattered intensity too. Third, the combination of these methods with neutron spin echo spectroscopy allows for near surface studies of dynamics Jaksch et al. (2015) and Frielinghaus et al. (2012) that can be correlated to tribological effects on the molecular level. This field of science, the tribology, – so far – has been driven mainly by the surface force balance that measures the macroscopic response of the system (latest research employs also AFM) Raviv et al. (2003) [1], Chung et al. (2016) [2] and Mocny and Klok (2016) [3]. The progress of this method was to reach the nano-scale distances that were necessary to obtain information about the friction of the nano-structures. The proposed method of grazing incidence neutron spin echo spectroscopy gives access to much more detailed information of molecular response to confinement by one or two hard walls, and therefore would pave the way for very rich and precise tribological comparisons of theory with experiments.

1. Introduction

Complex fluids display a rich behavior at their interfaces to other materials that has been studied experimentally [4–12] and theoretically [13–15]. Practically, one often conducts reflectometry or grazing incidence small angle scattering experiments to obtain the structure in the normal and lateral dimensions. Close to the interface one finds an interphase of modified structure [4] compared to the bulk phase depending on the system. So for instance there can be oriented liquid crystalline order in the interphase while the bulk shows only short-range order without orientation [16] The evanescent wave in a GISANS experiment is used to highlight a certain region of depth Λ next to the interface. Varying this scattering depth Λ, allows for depth profiling in much more detail compared to simple reflectometry experiments. At this stage, the near-surface structure might support specific contact-sensitive applications of complex fluids.

The idea of highlighting different regions next to the interface was then transferred to neutron spin echo spectroscopy [17], where the dynamics of microemulsions was analyzed as a function of depth Λ. Practically, the dynamics were three times faster than the bulk, which was explained by the confinement of the lamellar membranes adjacent to the interface. The volume conservation leads to a faster feedback of the neighboring membranes and/or the solid interface. This finding, then, was connected to the lubrication effect, which means that parallel lamellae can slide off along the interface faster than the disoriented bulk structure. From this example the general topic of tribology was raised. GINSE measurements will open a new research area on friction effects that now can be analyzed on the nano-scale [18].

At this point the field of tribology that has been mainly driven by the surface force balance that measures the macroscopic response of the system [1–3] will get deeper insight from a new method.

The instrumental elements that were developed to accompany the new findings in GINSE experiments are discussed in this manuscript. On the one hand, neutron experiments need to relax the resolution in order to observe reasonable intensities on the detector. This is especially prominent for NSE experiments, because the method requires very high statistics with spin polarization analysis [17]. On the other hand, grazing incidence scattering experiments require the slit geometry

* Corresponding author.
E-mail address: h.frielinghaus@fz-juelich.de (H. Frielinghaus).

http://dx.doi.org/10.1016/j.nima.2017.07.064
Received 3 May 2017; Received in revised form 24 July 2017; Accepted 31 July 2017
Available online 5 August 2017
0168-9002/

at the entrance aperture and for the sample to define the incident angle (and the scattering depth Λ), which reduces the number of neutrons dramatically On top, the evanescent wave is only seen by the near surface structure within a distance of 40 to 100 nm, which heavily restricts the scattering volume. The first experiments sufficiently overcame the problem by huge interfaces and by samples that scatter intrinsically strong. The boundary condition at total reflection used in the grazing incidence method yields a factor of 2 for the immediate amplitude of the evanescent wave at the interface which results in an intensity gain of 4 compared to a plain illumination of the boundary layer.

Neutron waveguides have been developed to increase the scattering intensities from a highlighted zone even further [18]. In principle, two situations must be distinguished: The structure of interest lies within or outside the waveguide. The first situation limits the use of the waveguide to one specific application, while a separate waveguide with the intensity enhancement outside would be of wider interest for a whole set of samples, because the complex fluid next to the waveguide can be replaced easily. The manuscript summarizes the recent developments and highlights the waveguide as the missing part for studying tribology effects of complex fluids in contact with solids.

2. Instruments

Neutron reflectivity measurements have been performed at **MARIA** at FRM2 in Garching [19]. This instrument uses neutron velocity selector with a 10% bandwidth for highest intensities. We used wavelengths of 10 and 5 Å for higher (incident angle $\alpha_i < 1.5°$) and lower ($\alpha_i > 1°$) resolution. The vertical entrance and sample slits were of 2 mm × 5 cm size (1.5 cm at sample). The samples were kept in closed cells with a sample thickness of 0.5 mm, but large areas of ca. 13 × 5 cm at a silicon slab of 15 × 8 × 4 cm^3. The neutrons impinge through the silicon, get reflected at the solid/liquid interface and leave through the silicon. The whole cell is heated to 26 °C through a water mediated heater. The sample is aligned and positioned by a hexapod. More details of the instrument can be found in Ref. [19].

Neutron spin echo spectroscopy experiments have been performed at the **J-NSE**, Garching and the **SNS-NSE**, Oak Ridge. The first instrument used a single wavelength of 8 Å (10% velocity selector) while the second one used a wavelength band of 5 to 8 Å. The latter analyzed the actual wavelength by time of flight analysis to a resolution of ca. ±0.1 Å. Both instruments were equipped with an additional entrance aperture of 2 mm x 6 cm. Close to the sample cell (as described above) unwanted neutron paths were blocked using boron and cadmium based materials. Acquisition times for one scattering vector and the full range of Fourier times were ca. 1 day. Further details of the instruments are found in Refs. [20,21] and [22].

3. GINSES measurements

Two example measurements of relaxation curves for the systems SoyPC in D_2O [18] and a bicontinuous microemulsion, both adjacent to a hydrophilic silicon surface, are shown in Fig. 1. We used the two proposed tools, i.e. a neutron prism and the resonator simultaneously for this measurement. The lipid L-alpha-phosphatidylcholine from soybeans (SoyPC) forms well ordered lamellar bilayers close to the solid–liquid interface [23]. While the Bragg peak of this structure is well pronounced and quite sharp, the bilayer relaxations are observed much better at scattering vectors deviating from the Bragg peak, which virtually shows no dynamics (DeGennes narrowing). This implies the use of Q-values with low intensities, where, however, a reasonable fluctuation dynamics signal dominates the scattering and grazing incidence neutron spin echo experiments can be performed. Thus, the resonator was extremely important to obtain meaningful statistics. Interestingly, the asymmetry of incident and exit angles lead to a rather small in-plane scattering vector that made collective long-wavelength modes visible,

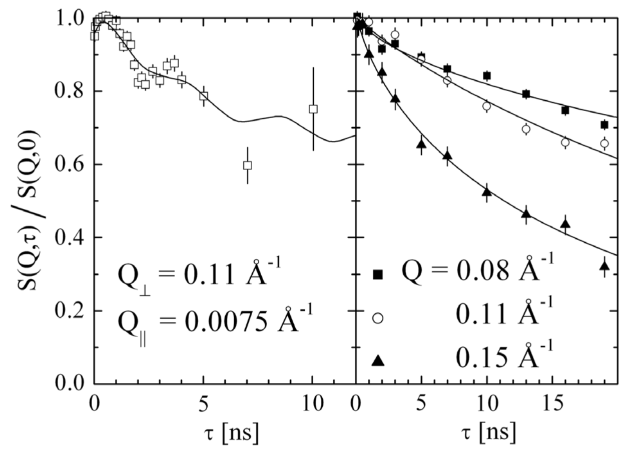

Fig. 1. The relaxation curves measured by grazing incidence neutron spin echo spectroscopy of lamellar lipid bilayer stacks (left) and of a bicontinuous microemulsion with lamellar near-surface ordering (right). The scattering depth was 200 and 240 Å. While the incidence angles were below the critical angle of total reflection, the exit angles were at considerable values according to the indicated Q (or $Q_\perp$). This asymmetry lead to in-plane $Q_\parallel$ vectors that are essential for the physics of well oriented lipid bilayers (left) but negligible in the case of microemulsions (right, where omitted).

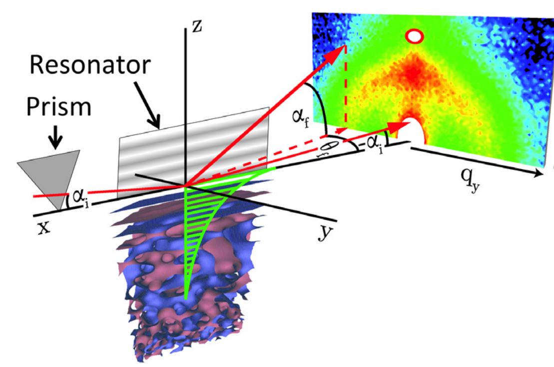

Fig. 2. The scattering geometry of a grazing incidence neutron spin echo spectroscopy (GINSES) experiment using a neutron prism and a resonator that is ideally suited for pulsed neutron sources. The sample is a microemulsion adjacent to the layered resonator structure. The green area inside the microemulsion indicates the enhanced evanescent wave. The detector plain shows a typical scattering image of a microemulsion. The red open dot indicates the typical Q-vector of the GINSES experiment.

that possessed enough elasticity to overcome the usual over-damping of soft matter systems. These modes allow for energy dissipation over large distances, and might explain the stability of cartilage in joints. The cartilage consists of proteins and lamellar lipid arrangements [24,25].

The set of the prism and resonator also allowed the strongly scattering microemulsion to be characterized at higher scattering angles, where the intensities decrease considerably (Sketch in Fig. 2). While first measurements without resonator were successfully analyzed at intermediate scattering vectors, where the collective and single-membrane modes still mix, the experiments presented here allow for analyzing smaller length scales where only single-membrane modes meet the theoretically well developed model of Zilman and Granek. The confinement conditions by the solid surface lead to an extension by the theory of Seifert [17]. The intensity gain of the microemulsion through the resonator was ca. 3.

The asymmetric setting of the GINSES experiment (Fig. 2) goes back on the condition of the incident angle α_i, which must be below the critical angle of total reflection α_c. So the exit angle α_f is much bigger than α_i. This causes a small in plane Q-vector component $Q_\parallel$ that is essential for the observation of the viscoelastic behavior of lipid bilayer stacks, but negligible for microemulsions. The normal component $Q_\perp$ is always dominating.