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ScienceDirect
Physica B 385–386 (2006) 722–724
PHYSICA B
www.elsevier.com/locate/physb

The 'neutron window' of collective excitations in lipid membranes

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Abstract

While most spectroscopic techniques, e.g., nuclear magnetic resonance or dielectric spectroscopy probe macroscopic responses, neutron and with some restrictions also X-ray scattering experiments give unique access to microscopic dynamics at length scales of intermolecular or atomic distances. Only recently, it has become possible to study collective dynamics of planar lipid bilayers using neutron spectroscopy techniques [M.C. Rheinstädter, et al., Phys. Rev. Lett. 93 (2004) 108107]. We determined the dispersion relation of the coherent fast picosecond density fluctuations on nearest-neighbor distances of the phospholipid acyl chains in the gel and in the fluid phases of a DMPC bilayer. The experiments shed light on the evolution of structure and dynamics, and the relation between them, in the range of the gel–fluid main phase transition. The scattering volume restriction for inelastic neutron experiments was overcome by stacking several thousand highly aligned membrane bilayers. By combining different neutron scattering techniques, namely three-axis, backscattering and spin–echo spectroscopy, we present measurements of short and long wavelength collective fluctuations in biomimetic and biological membranes in a large range in momentum and energy transfer, covering time scales from about 0.1 ps to almost 1μs and length scales from 3 Å to about 0.1 μm. The neutron backscattering technique gives information about slow molecular dynamics of lipid acyl chains and the 'membrane-water', i.e., the water molecules in between the stacked bilayers in the nanosecond time range [M.C. Rheinstädter, et al., Phys. Rev. E 71 (2005) 061908]. The dispersion relations of the long wavelength undulation modes in lipid bilayers with nanosecond relaxation times can be determined by quasielastic reflectometry on spin–echo spectrometers and give direct access to the elasticity parameters of the membranes. [M.C. Rheinstädter, et al., cond-mat/0606114].

PACS: 87.16.Dg; 83.85.Hf; 62.20.Dc; 83.10.Mj

Keywords: Collective membrane dynamics; Inelastic neutron scattering; Biomimetic membranes; Lipid bilayers

The spectrum of fluctuations in biomimetic and biological membranes covers a large range of time and length scales [1–6], ranging from the long wavelength undulation and bending modes of the bilayer with typical relaxation times of nanoseconds and lateral length scales of several hundred lipid molecules to the short wavelength density fluctuations in the picosecond range on nearest-neighbor distances of lipid molecules. Local dynamics in lipid bilayers, i.e., dynamics of individual lipid molecules as vibration, rotation, libration (hindered rotation) and diffusion, has been investigated by, e.g., incoherent neutron scattering [1,2] and nuclear magnetic resonance [7,8] to determine, e.g., the short wavelength translational and rotational diffusion constant. Collective undulation modes have been investigated using neutron spin–echo spectrometers [2,9] and dynamical light scattering [10,11]. Recently, the first coherent inelastic scattering experiments in phospholipid bilayers to determine the short wavelength dispersion relation have been performed using inelastic X-ray [12] and neutron [13] scattering techniques. Note that only scattering experiments give wave vector resolved access to dynamical properties, what is important to associate relaxation times with specific motions.

Here we report results from inelastic neutron scattering experiments in (chain) deuterated DMPC-d54 (deuterated 1,2-dimyristoyl-sn-glycero-3-phoshatidylcholine). The aim of the present paper is to review theoretical and

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doi:10.1016/j.physb.2006.06.029

experimental work of collective dynamics in lipid membranes and to show that the experimentally accessible time and length scales can be maximized by combining different (neutron) techniques. Inelastic neutron scattering thereby provides a unique method to investigate the collective dynamics (dispersion relations) of the macromolecules and the model character of the system allows to study the elementary excitations in biomimetic lipid membranes. The combination of different inelastic techniques, namely neutron three-axis, backscattering and spin–echo spectroscopy, maximizes the accessible $(q_\parallel, \omega)$ range, covering seven decades in energy and three decades in momentum transfer including spatial dimensions from intermolecular distances to about 100 nm. Note that $q_\parallel$ denotes the lateral momentum transfer in the plane of the bilayers.

The question of collective membrane motions has been addressed theoretically [14–18], but requires experimental methods covering a wide range of frequencies and length scales for validation. This discrepancy between available theoretical predictions and lacking experimental data underlines the need for new experimental approaches.

Information about fluctuations on mesoscopic length scales mainly stems from elastic scattering, i.e., from X-ray and neutron lineshape analysis and off-specular reflectivity in isotropic lipid dispersions and aligned phases [6,19–22]. In both examples, the time-averaged elastic scattering is studied, and information on, e.g., elasticity properties and interaction forces can be obtained. Contrarily, dynamical properties like transport coefficients and the validation of theoretical models can only be inferred from direct measurements of dynamical modes and the corresponding $q_\parallel$ dependence, i.e., their dispersion relation. These measurements are preferably carried out in aligned phases to preserve the unique identification of modes on the basis of the parallel and perpendicular components $q_\parallel$ and $q_\perp$ of the scattering vector Q. In the case of single membranes the scattering signal is by far not sufficient for a quantitative study of the inelastic scattering. A major achievement was the preparation of samples suitable for inelastic neutron experiments with a maximum of sample material. Multilamellar samples composed of stacks of several thousands of lipid bilayers separated by layers of water, resulting in a structure of smectic A symmetry, have been prepared. The high orientational order of the samples, which gives rise to pronounced Bragg peaks and excitations, is a prerequisite to a proper analysis of the corresponding correlation functions. Recently [13], we have demonstrated that collective supramolecular dynamics of planar lipid bilayers, notably the dispersion relation of density modes in the lipid acyl-chains, can be studied using the three-axis neutron spectroscopy technique giving access to an energy resolution of up to about 300 μeV. Neutron backscattering experiments with μeV energy resolution allowed to investigate slow motions on nanosecond time scales and to discriminate the onset of mobility at different length scales for the different molecular components, as, e.g., the lipid acyl chains and the hydration water in between the membrane stacks, respectively [23]. The accessible length and time scales are complemented by neutron spin–echo spectroscopy to cover long length scales and slow times up to almost a μs [24].

Fig. 1(a) shows the dispersion relations measured by neutron three-axis, backscattering and spin–echo

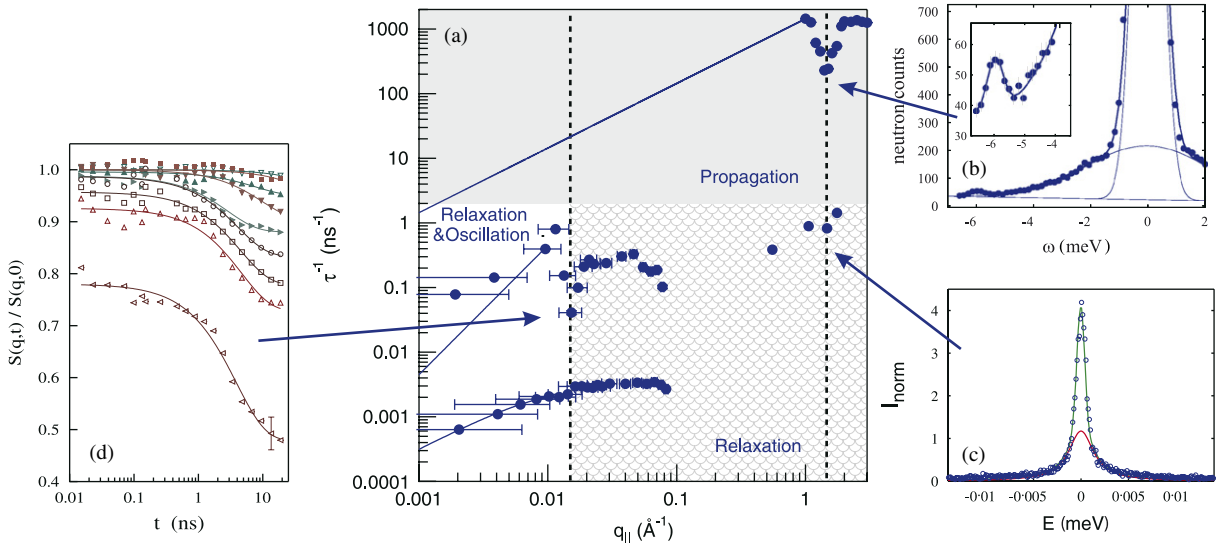

Fig. 1. (a) 'Neutron window' of collective excitations in DMPC-d54. The measurements cover a lateral $q_\parallel$ range of $0.002\,\text{Å}^{-1} < q_\parallel < 3\,\text{Å}^{-1}$ and $0.5\,\text{ps} < \tau < 1\,\mu\text{s}$. Regions assigned to propagating, relaxating (overdamped) and oscillating modes are marked in the figure. (b) The domain of three-axis spectrometry is the detection of fast propagating picosecond motions at larger $q_\parallel$ values. The inset exemplary shows an excitation of the DMPC bilayer at $q_\parallel = 1\,\text{Å}^{-1}$. Solid lines are fits of theoretical models, as explained in Ref. [13]. (c) Backscattering spectrometers are used to measure relaxations in the nanosecond time range at larger $q_\parallel$ values. The inset shows quasielastic scattering integrated over $0.4\,\text{Å}^{-1} < q_\parallel < 0.65\,\text{Å}^{-1}$. The red line is a Lorentzian line shape. It has been convoluted with the resolution function to fit the data. (d) The range at small $q_\parallel$ and long relaxation times τ is accessible on spin–echo spectrometers. Two relaxation processes are found on different time scales and both dispersion relations are shown in part (a). The inset shows selected relaxation curves of the fast ($\tau \approx 10$ ns) process (the upper dispersion curve in (a)) for $q_\parallel$-values between 0.002 and 0.05 Å^{-1}. Solid lines are fits assuming single exponential decays.

spectroscopy together. Data have been taken in the fluid phase of the deuterated DMPC bilayer. The respective type of excitation, i.e., propagating, relaxating or oscillating modes, thereby depends on length and time scale. Fast motions in the ps time range are due to sound propagation in the plane of the bilayer and can be measured on three-axis spectrometers, as e.g., IN12 and IN8 at the high flux reactor of the Institut Laue-Langevin (ILL) in Grenoble, France. Fig. 1(b) shows an energy scan at a $q_\parallel$ value of $q_\parallel = 1\,\text{Å}^{-1}$ as an example. The excitation appears as small peak at about 6 meV. Slow relaxation modes of the lipid acyl chains in the nanosecond time range can be measured by the neutron backscattering technique on, e.g., IN16. These overdamped modes appear as quasielastic broadening, as shown in Fig. 1(c). Note that three-axis and backscattering spectrometry measure $S(q_\parallel, \omega)$, i.e., in the energy domain. Spin–echo spectrometers like IN11 and IN15 extend the window to determine the slow long wavelength modes on nanosecond scales directly in the time domain. Fig. 1(d) shows the intermediate scattering function $S(q_\parallel, t)$ for selected $q_\parallel$ values, which exhibit relaxation steps that can be fitted by single-exponential decays.

These measurements for the first time offer a large window of length and time scales, ranging from about 0.1 ps to almost 1 μs and length scales from 3 Å to about 0.1 μm to test and enhance theoretical models of dynamics of biomimetic and biological membranes. Dynamics in biomimetic membranes is of particular interest in membrane biophysics to better understand the highly complex dynamics of biological membranes. An understanding of membrane dynamics can also be useful to tailor membrane properties for biotechnology applications. But the investigation of fluctuations in membrane dynamics remains an important experimental challenge of present-day biophysics, concerning in particular the biologically relevant fluid L_α state.

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