Exploring the collective dynamics of lipid membranes with inelastic neutron scattering

Maikel C. Rheinstädter[a] and Tilo Seydel
Institut Laue-Langevin, 6 rue Jules Horowitz, BP 156, 38042 Grenoble Cedex 9, France

Wolfgang Häußler
FRM-II, Technische Universität München, 85747 Garching, Germany

Tim Salditt
Institut für Röntgenphysik, Friedrich-Hund-Platz 1, 37077 Göttingen, Germany

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While most spectroscopic techniques, as e.g., nuclear magnetic resonance or dielectric spectroscopy, probe macroscopic responses, neutron and within some restrictions also x-ray scattering experiments give the 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. Rheinstädter, C. Ollinger, G. Fragneto, F. Demmel, and T. Salditt, Phys. Rev. Lett. **93**, 108107 (2004)]. 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 dimyristoylphoshatidylcholine 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 thousands of highly aligned membrane bilayers. By combining different neutron-scattering techniques, namely, three-axis, backscattering, and spin-echo spectroscopies, 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 1 μs 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, T. Seydel, F. Demmel, and T. Salditt, Phys. Rev. E **71**, 061908 (2005)]. 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, W. Häuβler, and T. Salditt, cond-mat/0606114]. © *2006 American Vacuum Society.*
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I. INTRODUCTION

Phospholipid membranes are intensively studied as simple model systems to understand the fundamental structural and physical aspects of their much more complex biological counterparts.[1] The lateral structure of membranes including both height and compositional fluctuations remains an important experimental challenge of present-day biophysics, concerning, in particular, the biologically relevant fluid L_α state, where the material softness compromises the use of scanning probe microscopy. Neutron scattering can contribute to the elucidation of the molecular structure, as is well documented in the literature (see, e.g., Ref. 2), as well as to the understanding of molecular and supramolecular dynamics of lipid bilayers. A unique advantage lies in the simultaneous access to both structural and dynamical properties by measuring the scattering $S(\mathbf{Q},\omega)$ as a function of wave vector $\mathbf{Q}$ and energy ω, thus linking detected motions to a corresponding length scale.

Dynamical properties are often less well understood in the biomolecular systems, but are important for many fundamental biomaterial properties, e.g., elasticity properties and interaction forces. Furthermore, lipid membrane dynamics on small molecular length scales determines or strongly affects the functional aspects, such as diffusion and parallel or perpendicular transport through a bilayer. The specific advantages of neutron scattering to study fluctuations of phospholipid membranes on lateral length scales between microns down to a few angstroms can give unique insights.

The spectrum of fluctuations in biomimetic and biological membranes covers a large range of time and length scales,[1,3–10] 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

[a]Electronic mail: rheinstaedter@ill.fr

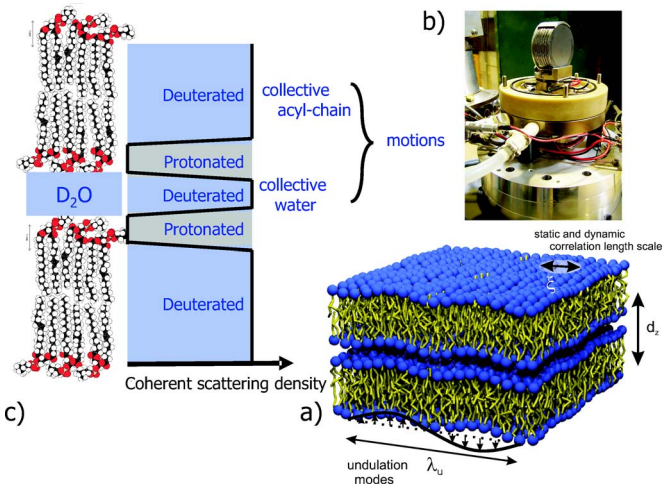

FIG. 1. (a) Collective excitations are coherent motions of several membrane molecules, as, e.g., the long wavelength bending modes of the membranes with wavelength λ_u. (b) Photograph of the sandwich sample mounted in the humidity chamber to control temperature and hydration during the experiment. (c) Sketch of a double bilayer of chain deuterated DMPC, hydrated with D_2O, together with the corresponding coherent scattering density. This type of sample preparation makes the neutron experiment basically sensitive to collective motions of lipid acyl chains and hydration water.

fluctuations in the picosecond range on the 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[3–7] and nuclear magnetic resonance[11,12] to determine the short wavelength translational and rotational diffusion constant. Collective undulation modes [see Fig. 1(a) for a sketch] have been investigated using neutron spin-echo spectrometers[6,7,13] and dynamical light scattering.[14–16] A recent study in smectic liquid-crystal membranes combined neutron spin echo and x-ray photon correlation spectroscopy (XPCS) to measure mesoscopic fluctuations over a wide time range.[17,18] Recently, the inelastic scattering experiments in phospholipid bilayers to determine the collective motions of the lipid acyl chains and, in particular, the short wavelength dispersion relation have been performed using inelastic x ray[19] and neutron[20] scattering techniques. Note that only the scattering experiments give the wave-vector-resolved access to dynamical properties, what is important to associate the relaxation times with specific motions. While in protonated samples the *incoherent* scattering is normally dominant and the time-autocorrelation function of individual scatterers is accessible in neutron-scattering experiments, (partial) deuteration emphasizes the *coherent* scattering and gives access to collective motions by probing the pair-correlation function.

The question of collective membrane motions has been addressed theoretically,[21–26] but requires experimental methods covering a wide range of frequencies and length scales for validation. This discrepancy between the available theoretical predictions and lacking of experimental data underlines the need for experimental approaches. The measurement of these motions provides not only a deeper understanding of membrane micromechanic properties down to the molecular scale but also sheds some light on the processes which are essential for the formation of contacts between cells and solid surfaces.

The information about fluctuations on mesoscopic length scales mainly stems from elastic scattering, i.e., from the x ray and neutron line-shape analysis and off-specular reflectivity in isotropic lipid dispersions and aligned phases.[10,27–31] Off-specular x ray and neutron reflectivity from the aligned phases presents the advantage that the components of the scattering vector $\mathbf{Q}$ can be projected onto the symmetry axis of the membrane.[10,29,30] 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 such as transport coefficients and the validation of theoretical models can only be inferred from the direct measurements of dynamical modes and the corresponding wave-vector dependence, i.e., their dispersion relations. Again, 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_z of the scattering vector $\mathbf{Q}$. Note that $q_\parallel$ denotes the lateral momentum transfer in the plane of the bilayers.

The aim of the present article is to review the theoretical and 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-scattering) techniques. Inelastic neutron scattering provides a unique method to study the collective dynamics (dispersion relations) of the macromolecules and the model character of the system allows to study elementary excitations in biomimetic lipid membranes. The combination of different inelastic techniques, namely, neutron three-axis, backscattering, and spin-echo spectroscopies, 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 0.1 μm, as we will discuss below. We review results from inelastic neutron scattering experiments in (chain) deuterated deuterated 1,2-dimyristoyl-sn-glycero-3-phoshatidylcholine (DMPC-d54).

The article is organized as follows. Followed by this introduction, we give experimental details in the next section. The dispersion relations of excitations and relaxations in deuterated DMPC are presented in Sec. III. We will qualitatively discuss the particular shape of the dispersion relations and illustrate their biophysical impact.

II. EXPERIMENT

In the case of single membranes the inelastic neutron-scattering signal is by far not sufficient for a quantitative study of the inelastic scattering. The major achievement was thus 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. Deuterated DMPC-d54 was obtained from Avanti Polar Lipids. We prepared highly oriented membrane stacks by spreading a solution of typically 25 mg/ml lipid in trifluoroethylene/chloroform (1:1) on 2 in. silicon wafers, followed by subsequent drying in vacuum and hydration from D_2O vapor.[32] Twenty such wafers separated by small air gaps were combined and aligned with respect to each other to create a "sandwich sample" consisting of several thousands of highly oriented lipid bilayers (total mosaicity of about 0.6°), with a total mass of about 400 mg of deuterated DMPC. Figure 1(b) shows a photograph of the neutron sample. During the experiment, the samples were kept in a closed temperature and humidity controlled aluminum chamber, as depicted also in Fig. 1(b). The hydration of the lipid membranes was achieved by separately adjusting the temperatures of the sample, the surrounding cell and heavy water reservoirs, hydrating the sample from the vapor phase. 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. We applied inelastic neutron scattering for the study of the collective dynamics of the hydrocarbon acyl chains in lipid bilayers. The main differences with respect to the inelastic x-ray scattering are related to the dispersion relation of the neutron versus the photon probe, strongly affecting energy resolution, and accessible $(q_\parallel, \omega)$ range. The energy of the incident (cold) neutrons is in the range of the excitations (some meV) resulting in a high-energy resolution, in comparison to the inelastic x-ray experiment which works with incident energies of keV. Neutrons have additional advantages when probing delicate biological samples because they are equally well scattered by light and heavy atoms and cause little or no radiation damage because of their low energy, low absorption, and the low beam intensities. H and D scatter very differently and specific parts of the sample or specific motions can be emphasized by selective deuteration. Due to the dispersion relation of the neutron itself ($\sim Q^2$), the range at low $q_\parallel$ and high ω values is difficult to access by inelastic neutron scattering. The determination of the exact speed of sound is therefore a domain of inelastic x-ray scattering.

Figure 1(c) shows a sketch two stacked bilayers with the heavy water layer in between and the corresponding coherent scattering density. By selective deuteration of the chains, the respective motions are strongly enhanced over other contributions to the inelastic scattering cross section. This particular type of sample preparation makes the neutron experiments thus basically sensitive to collective motions of the phospholipid acyl chains and the hydration water. Recently,[20] we have demonstrated that the 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.[33] 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 microsecond.[34]

III. DISPERSION RELATIONS

Figure 2(a) shows the dispersion relations measured by neutron three-axis, backscattering, and spin-echo spectroscopy. 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 scales. Propagating or oscillating modes have well-defined eigenfrequencies and lead to inelastic excitations at energy values $\hbar\omega \neq 0$. Relaxations give rise to a quasielastic broadening $\Delta\omega$, centered at $\hbar\omega=0$. The dotted vertical lines emphasize two prominent $q_\parallel$ values, i.e., intrinsic lateral length scales, of the model membranes. $q_0 \approx 1.4$ Å^{-1} is the nearest-neighbor distance of the phospholipid acyl chains $(2\pi/q_0)$; $q_{0'} \approx 0.015$ Å^{-1} marks the transition from the film to the bulk elasticity regime, as we will discuss below. At both $q_\parallel$ values, the corresponding dispersion relations show distinct anomalies as kinks or minima.

Fast motions in the picosecond time range due to sound propagation in the plane of the bilayer are best 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. By varying the three axes of the instrument, the axes of rotation of the monochromator (graphite in most cases), the sample, and the analyzer, the wave vectors $\mathbf{k}_i$ and $\mathbf{k}_f$ and the energies E_i and E_f of the incident and the scattered neutrons, respectively, can be determined. $\mathbf{Q}$, the momentum transfer to the sample, and the energy transfer, $\hbar\omega$, are then defined by the laws of momentum and energy conservation to $\mathbf{Q}=\mathbf{k}_f-\mathbf{k}_i$ and $\hbar\omega=E_i-E_f$. The accessible (Q,ω) range is just limited by the range of incident neutron energies offered by the neutron guide as well as by mechanical restrictions of the spectrometer. Figure 2(b) shows an energy scan at a $q_\parallel$ value of $q_\parallel=1$ Å^{-1}, as an example. The excitation appears as a small peak at about 6 meV. The particular shape of the corresponding dispersion relation [in Fig. 2(a)] can qualitatively be explained. The basic scenario is the following: At small $q_\parallel$, longitudinal sound waves in the plane of the bilayer are probed and give rise to a linear increase of $\tau^{-1} \propto q_\parallel$, saturating at some maximum value, before a pronounced minimum is observed at $q_0 \approx 1.4$ Å^{-1}, the first maximum in the static structure factor $S(q_\parallel)$ (the interacyl chain correlation peak). q_0 can be interpreted as the quasi-Brillouin zone of a two-dimensional liquid. Collective modes with a wavelength of the average nearest-neighbor distance $2\pi/q_0$ are energetically favorable. The static and dynamic disorder in the lipid bilayers finally leads to a minimum at finite-energy values (soft mode). A quantitative theory which predicts the absolute energy values of maximum and minimum on the basis of molecular parameters is absent so far. However, the disper-

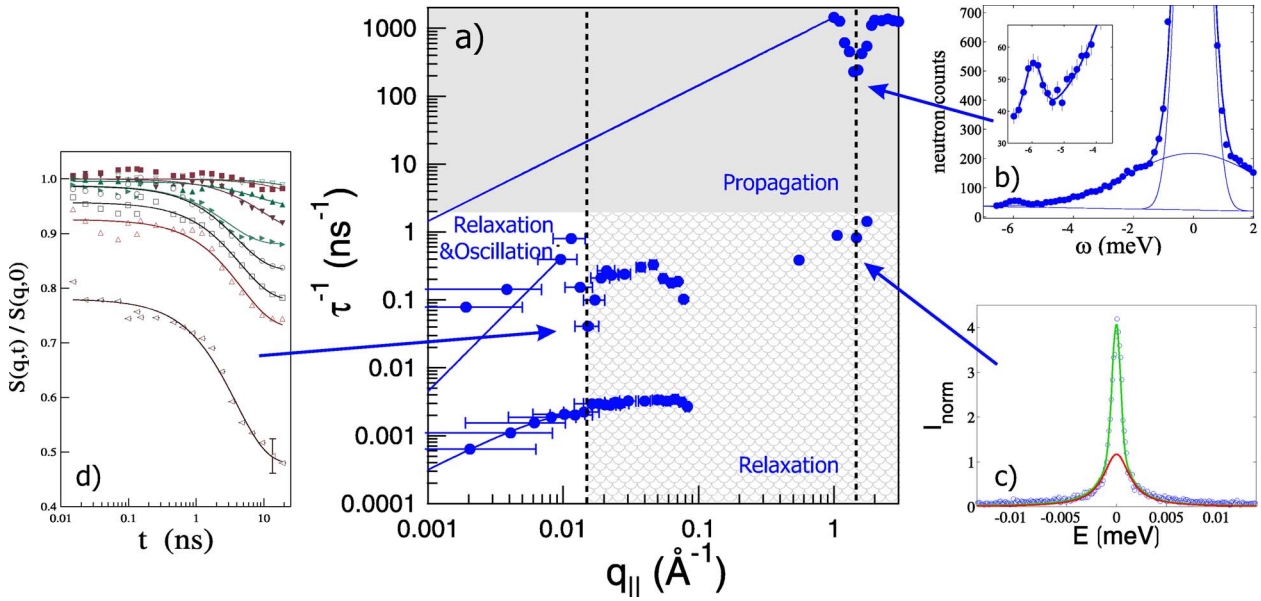

FIG. 2. (a) "Neutron Window" of collective excitations in DMPC-d54. The measurements cover a lateral $q_{\|}$-range of 0.002 Å^{-1} $< q_{\|} <$ 3 Å^{-1} and 1 μs $< \tau <$ 0.5 ps. Regions assigned to propagating, relaxating (overdamped), and oscillating modes are marked in the figure. (b) The domain of three-axes spectrometry is the detection of fast propagating picosecond motions at larger $q_{\|}$ values. The inset exemplary shows an excitation of the DMPC bilayer at $q_{\|}$ = 1 Å^{-1}. Solid lines are fits of theoretical models, as explained in Ref. 20. (c) Backscattering spectrometers are used to measure relaxations in the nanosecond time range at larger $q_{\|}$ values. The inset shows quasielastic scattering integrated over 0.4 Å^{-1} $< q_{\|} <$ 0.65 Å^{-1}. Although the Q resolution of the spectrometer is much higher, five detector tubes have been summed up here to increase the statistics of the scattering signal. 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 $q_{\|}$ 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 (a). The inset shows selected relaxation curves of the fast ($\tau \approx 10$ ns) process [the upper dispersion curve in (a)] for $q_{\|}$-values between 0.002 and 0.05 Å^{-1}. Solid lines are fits assuming single exponential decays.

sion relation can be extracted from molecular-dynamic simulations by temporal and spatial Fourier transformation of the molecular real-space coordinates[35] which shows an excellent agreement with the data. Note that the dispersion relation found is similar to those in ideal liquids, as, e.g., liquid argon,[36,37] liquid neon,[38] or liquid helium.[39] It seems that the interior of the lipid bilayer, the C atoms or C–D groups of the lipid acyl chains, behave as a *quasiliquid*. In contrast to real liquids, the chain atoms of the lipid molecules are chemically bound to each other, leading to smaller mobility and diffusion and, as a consequence, more pronounced excitations.

These experiments can be complemented by μeV energy-resolved spectra, achieved by the neutron-backscattering technique, which has been proposed by Maier-Leibnitz nearly 50 years ago. The technique is closely related to the three-axes technique, however, using constant 90° Bragg angles at monochromator and analyzer. The high resolution obtained in the exact backscattering is easily shown by computing the first derivative of Bragg's law[40] $\Delta\lambda/\lambda = \Delta d/d + \Delta\theta/\tan\theta$, where λ is the neutron wavelength, d the monochromator crystal lattice spacing, and θ the angle of incidence of the neutron beam with respect to the crystal surface. From this equation it becomes clear that the monochromaticity is maximized when the angle of incidence is 90° with respect to the monochromator and analyzer crystal surface of a spectrometer. This geometry can be realized with neutrons by using adequate deflecting disk chopper devices. Although the neutron-backscattering experiments were carried out already in 1969 at the FRM in Munich by Alefeld,[41] *exact* backscattering has been realized at the spectrometer IN16 at the ILL.[42] The energy transfer can be scanned by varying the incident energy by Doppler shifting the incident neutron energy through an adequate movement of the monochromator crystal. Hereby, an incident neutron energy shift of about -15 μeV $< \hbar\omega <$ $+15$ μeV relative to the incident neutron energy can routinely be scanned, with the energy-transfer limit only given by the mechanical limit of moving the crystal sufficiently fast. We thereby gain access to the low energetic density fluctuations corresponding to slow motions on nanosecond time scales. By analyzing the respective $q_{\|}$ dependence, we simultaneously probed internal length scales from 3 to 18 Å. Overdamped modes appear as quasielastic broadening, as shown in Fig. 2(c), integrated over 0.4 Å^{-1} $< q_{\|} <$ 0.65 Å^{-1}. Although the Q resolution of the spectrometer is much higher, five detector tubes have been summed up to increase the statistics of the scattering signal. The measurements have been performed on IN16 at the ILL. In combination with the three-axes technique, where propagating modes in the picosecond range are probed, the backscattering technique thus gives access to *relaxations* on the same length scale, but in the nanosecond time range. The minimum in the corresponding dispersion relation at q_0 might link the energy minimum in the collective short wavelength fluctuations to an enhanced diffusion of the lipids on a scale of $2\pi/q_0$, i.e., a (collective) fluctuation supported diffusion.[43] Note that three-axes and backscattering spectrometry measures $S(q_{\|}, \omega)$, i.e., in the energy domain. Spin-echo spectrometers, such as IN11 and IN15, extend the window to determine the

slow long wavelength modes on nanosecond scales directly in the time domain.

The spin-echo technique offers extremely high-energy resolution from Larmor tagging the neutrons. A neutron spin-echo measurement is in essence a measurement of neutron polarization.[44] A polarized neutron beam passes through a magnetic field perpendicular to the neutron polarization. The neutron spin precesses before arriving at the sample, acquiring a precission angle ϕ_1. At the sample, the beam is scattered before passing through a second arm, acquiring an additional precession angle ϕ_2 in the reversed sense. For elastic scattering the total precession angle is $\Delta\phi=\phi_1-\phi_2=0$ for all incoming neutron velocities. If the neutron scatters inelastically by a small energy transfer $\hbar\omega$, there will be a linear change $\Delta\phi=\tau\omega$ with τ being a real time in the case of quasielastic scattering. The spin-echo technique thus works in the time domain and measures the intermediate scattering function $S(q_\parallel,t)$ in contrast to the three-axes and backscattering techniques previously discussed. For a quasielastic response, assumed to have Lorentzian line shape with half-width Γ, the polarization will then show a single exponential decay $P_{\mathrm{NSE}}=P_s e^{-\Gamma t}$. Figure 2(d) shows the intermediate scattering function $S(q_\parallel,t)$ for selected $q_\parallel$ values for spin-echo times $0.001\ \mathrm{ns}<t<20\ \mathrm{ns}$, which exhibits distinct single-exponential relaxation steps. The use of two different neutron spin-echo spectrometers with low (IN11) and high resolution (IN15) gives access to two different relaxation processes, both shown in Fig. 2(a). Again, we can give qualitative arguments to explain the shape of the upper dispersion relation with relaxation rates between 1 and 10 ns. For $q_\parallel$ values smaller than $q_{0'}\approx 0.015\ \mathrm{Å}^{-1}$ (on length scales of several hundred lipid molecules), the lipid bilayers behave as liquid films and the corresponding dispersion relation shows a $q_\parallel^2$ dependence, basically determined by the viscosity of the water layer in between the stacked membranes.[25,26] Note that this regime does not contain microscopic information about the bilayers ("macroscopic regime" or "film regime"). With increasing $q_\parallel$, a bifurcation occurs at $q_{0'}$ where we start to probe the bulk elasticity parameters B (compressibility) and K (bending modulus) of the bilayers ("bulk elasticity regime"). Because the energy is now dissipated in the elastic degrees of freedom, the character of the motion changes from propagating or oscillating to purely overdamped relaxation. B and K can be determined from fits of theoretical models to the data. While the upper dispersion branch is well described by present theories, the slow dispersion with relaxation rates of about 100 ns [the lower dispersion curve in Fig. 2(a)] is not explained in theoretical descriptions but might result from coupling of the relaxational degrees of freedom to the propagating sound modes observed in Fig. 2(b).

IV. CONCLUSION

Because of optimized setups and sample preparation, inelastic neutron-scattering experiments supply for the time strong (coherent) inelastic signals sufficient for quantitative analysis. The measurements 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. The 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. Further investigations will address the influence of different head and tail groups to the collective dynamics. Furthermore the influence of cholesterol and membrane active proteins will be studied hopefully giving insight into the functionality of these systems. The investigation of more and more complex systems might finally lead to a better understanding of biological membranes.

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