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Solid-supported multilayers of surfactant bilayers give a strong speckle pattern in coherent x-ray reflectivity

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Abstract

Charged surfactant bilayers deposited in thick multilayer films and swollen in vapor or in solution have been studied by coherent x-ray reflectivity. We report a pronounced static speckle pattern which persists under conditions of full hydration, despite the fact that the bilayers are fluid, relatively soft, and consisting of soluble amphiphiles (DDABr). Characteristic of the macroscopic domains size, the speckle pattern is observed in the plane of incidence (rocking curves) but not in out-of-plane scans, where smaller distances are probed and diffuse scattering from thermal fluctuations is seen.

Many phospholipids and synthetic surfactant bilayers spontaneously form lamellar phases in water. These stacks with a microstructure characteristic of smectic-A lyotropic liquid crystals are model systems for studying structure, interactions and elasticity of membranes, which are of intense interest in soft matter and biophysical research. One central issue here is the role of thermal fluctuations, and more generally of collective motions in fluid membrane assemblies. In the past, elastic x-ray scattering has been used extensively to study the collective motions such as bilayer undulations, assuming that the diffuse scattering around the lamellar Bragg peaks (on the diffuse sheets) reflects thermal diffuse scattering. Here we use coherent reflectivity [1] as a sensitive test to whether the diffuse scattering measured in a given range of wave vectors can be fully understood in terms of fluctuating membranes.

For the scattering experiments on membrane multilayers, we have recently presented a new

approach [2] illustrated in Fig.1, which combines highly oriented surfactant lamellar phases on a flat solid support, interface sensitive scattering techniques and the control of the osmotic pressure. High pressures (dehydrated membranes) are obtained by vapor of controlled humidity, while low pressures (fully hydrated bilayers) are imposed by direct contact with a polyelectrolyte solution of the same sign as the membranes, so it does not penetrate into the multilayer. We used the synthetic cationic surfactant DDA^+Br^- with bilayer thickness of 23\AA at imposed osmotic pressures corresponding to swellings in the range of a few layers of water molecules up to of a few hundred \AA . Under these conditions, specular, non-specular and grazing incidence diffuse scattering x-ray reflectivity measurements can be carried out along the different symmetry axes of the oriented membranes.

All measurements were carried out at the European Synchrotron Radiation Facility (ESRF). The

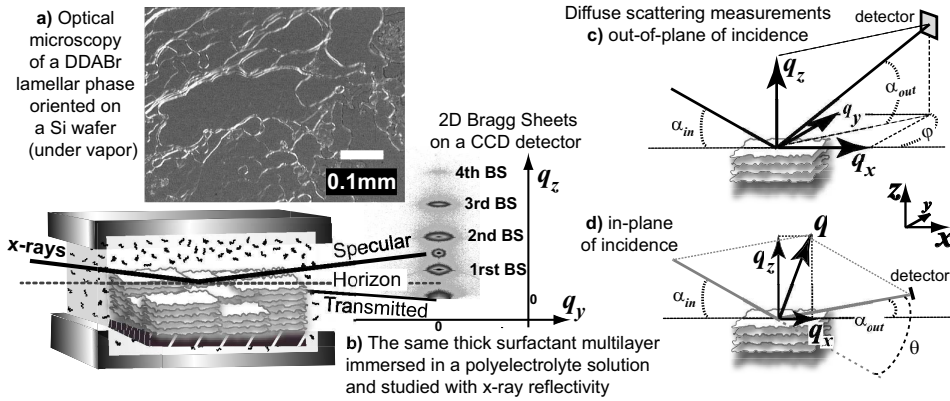


Fig. 1. a) Optical micrograph of a DDABr surfactant multilayer (several hundred parallel bilayers) equilibrated with vapor that shows terraced domains. b) Sketch of the environment used for measuring x-ray reflectivity of oriented charged lamellar phases through a polyelectrolyte solution (osmotic stressor), with a typical out-of-plane diffuse scattering pattern recorded on a CCD detector (ID1, ESRF). c) An illustration of out-of-plane of incidence and (d) in plane reflectivity scans.

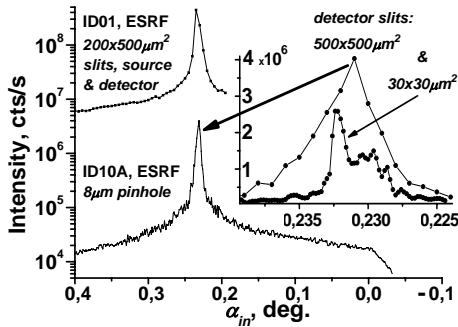


Fig. 2. Rocking curves on the 1st Bragg peak of a swollen DDABr multilayer ($d = 116\text{\AA}$) in solution. Top curve is measured with relatively incoherent beam at ID1 while the bottom one is measured with coherent illumination at ID10A. It evolves to a strong speckle pattern when measured with high detector resolution (see inset).

intense rocking curve plotted on Fig.2 was measured at the ID1 beamline, on the first Bragg peak (1BP) of a swollen DDABr film immersed in a polyelectrolyte solution giving a period of $d = 116\text{\AA}$. The very sharp specular peak (with a width of a few thousands of degree around $\alpha_{in} = \alpha_{1BP} = 0.232^\circ$) is characteristic of macroscopic flatness of the membranes since it is well separated from the diffuse [3]. The lower curve of Fig.2 is the same scan performed with higher spatial coherence of the impinging x-rays obtained at ID10A with a $8\mu\text{m}$ pinhole set at 130mm in front of the sample. The pinhole diameter defines the beam and

is comparable to the spatial coherence of the undulator beam (ξ_{trans} , transverse to the beam direction) estimated as $\xi_{trans} = 0.5\lambda R/d_s \sim 11\mu\text{m}$ (for an effective source size of $d_s = 200\mu\text{m}$, obtained by horizontal collimation at $R = 46\text{m}$ and a wavelength of $\lambda = 0.955\text{\AA}$ at $E = 13\text{keV}$). The temporal (longitudinal) coherence is given by the energy bandwidth set by Si(111) monochromators ($\Delta E/E \sim 10^{-4}$ at $E = 13\text{keV}$ on ID10A and $E = 13.4\text{keV}$ at ID1), at both beamlines of $\xi_{long} = \lambda E/\Delta E \sim 1\mu\text{m}$. The two rocking curves look similar in shape when measured with a large detector aperture ($150\mu\text{rad}$ along z and y at 851mm from the sample for ID1 and $375\mu\text{rad}$ at 1340mm for ID10A), except that the coherent measurement shows some additional sharp features precursor of a speckle pattern, probed at low contrast due to detector resolution. These speckle structures become very pronounced close to the specular position ($\alpha_{in} \sim \alpha_{out}$), in particular when the detector slits are closed to $30 \times 30\mu\text{m}^2$ (*i.e.* $22\mu\text{rad}$ angular acceptance), as it can be seen on linear scale in the inset.

A yet more pronounced speckle pattern is observed at lower swellings, *i.e.* less hydrated samples (period $d = 31.2\text{\AA}$) (Fig.3). We attribute the speckle pattern to the interference of waves reflected from different domains over the elongated beam footprint. No bare substrate areas are seen,

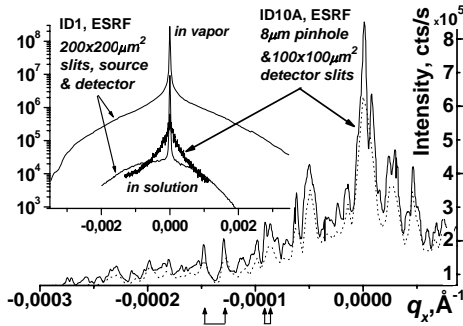


Fig. 3. Rocking curves on the 1BP at low swellings obtained by immersion: a) in a concentrated polyelectrolyte solution ($d = 31.2 \text{ \AA}$) or, b) in a vapor phase ($d = 29.7 \text{ \AA}$). The coherent measurement (ID10A) of the speckle pattern in conditions a) was repeated (solid and dotted line). In the inset, it is compared to less coherent measurements (ID1) on the same conditions a) and b).

but macroscopic domains are evidenced optically in vapor (Fig. 1, a rocking curve of the sample is shown in Fig. 3); they extend from a few microns to several hundred microns in the plane. Terrace structures can be seen at higher magnifications, and create corresponding x-ray optical path length differences. If the patches sit on top of a perfect smectic crystal extending laterally over the full coherent footprint, they should be of comparable thickness or thicker than the underlying stack in order to give such a strong speckle pattern. On the other hand, the speckle can also come from buried lateral domains reflecting x-rays with a phase shift from that of their neighbors. In that case, the path length difference from one domain to another must be smaller than ξ_{long} and must be larger than $\Delta h = \pi/q_z = d/2 = 58 \text{ \AA}$ in order to give a noticeable phase shift (π). Within both hypotheses (thick surface patches or buried lateral domains) we can estimate an average lateral distance L characteristic of the domains from the extension of the speckle in reciprocal space. At large swellings ($d = 116 \text{ \AA}$ at $\alpha_{1BP} = 0.232^\circ$, see Fig.2) we estimate this size to $\sim 0.0014^\circ$ or equivalently $\Delta q_x \sim 1.3 \cdot 10^{-6} \text{ \AA}^{-1}$ from which we obtain a lateral length scale $L \simeq 0.48 \text{ mm}$. Also in full hydration but at low swelling ($d = 31.2 \text{ \AA}$ at $\alpha_{1BP} = 0.875^\circ$) the sample of Fig.3 gives a speckle pattern with characteristic sizes indicated by arrows: (0.0014° and 0.0053° or equivalently $\Delta q_x \sim 4.9 \cdot 10^{-6} \text{ \AA}^{-1}$ and $\Delta q_x \sim 1.85 \cdot$

10^{-5} \AA^{-1}). These give domain sizes in the range of $L \simeq 0.03 \text{ mm}$ to 0.13 mm showing that the lateral domain size increases upon swelling (larger membranes d-spacing). The number of domains which are coherently illuminated can also be estimated since it scales as $4\pi\xi_t/L\lambda nq_{z,1BP}$, where n is the order of the Bragg peak scanned. At low swelling ($q_{z,1BP} = 0.2 \text{ \AA}^{-1}$) we obtain in the beam footprint (when measuring the 1BP) ~ 18 domains, considering a domain size of 0.03 mm and ~ 4 domains, considering a domain size of 0.13 mm . At larger swelling ($q_{z,1BP} = 0.054 \text{ \AA}^{-1}$), a domain size of 0.48 mm gives ~ 4 domains in the footprint so few domains would be needed to give such speckle pattern. Moving the beam footprint in the y direction for more than its size gave a different speckle pattern showing that the phase shifts depend on the particular domain configuration probed. At the same position repeated scans evidenced similar but slightly different speckle configurations (see Fig.3) and this might evidence the permanent reconstruction of the domains. At the same time the contrast in the peaks and valleys remained the same.

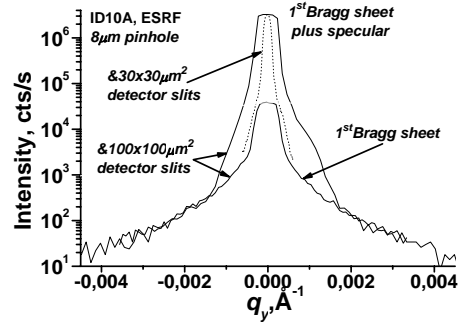


Fig. 4. Out-of-plane of incidence reflectivity scans across the first Bragg sheet of the sample in Fig.2.

We then measure the diffuse scattering out-of-plane of incidence in order to reach higher components in q_y . As is well known, in the plane of incidence, q_x is limited by the sample horizon. The (θ) angle was fixed defining q_z to the 1BP position. Then the angle φ was scanned at fixed α_{in} . Two curves obtained at high swelling with the pinhole set-up and $100 \times 100 \mu\text{m}^2$ detector slits, are shown in Fig. 4 for comparison. They overlap at large q_y but differ in the peak since one is measured at $\alpha_{in} = 2\alpha_{1BP}$, which brings the specular reflection

on the detector in the center of the scan, while the second was measured at $\alpha_{in} = 0.75 \cdot \alpha_{1BP}$ below the specular spot, and only shows the diffuse component of the Bragg sheet. The distances probed along y go here from the footprint size (the pinhole size $\sim 8\mu m$) down to $\sim 0.32\mu m$ (for largest plotted $q_y = \pm 0.004\text{\AA}^{-1}$) which is much smaller than the domain size evidenced above. Interestingly, the curves measured along q_y are smooth and do not show any speckle even when the slits are closed to $30 \times 30\mu m^2$ which only reduces the width of the Bragg sheet (dotted curve normalized to previous one). The absence of x-ray speckle in out-of-plane scans while they were present in rocking scans was reported on very different solid state systems such as a GaAs/AlAs multilayer by Robinson and coworkers [1], and explained in terms of projected spatial coherence and footprint anisotropy at grazing incidence (here around 2mm along x and $8\mu m$ along y). While speckles are also observed on Si(111) surfaces [4] they occur here on the diffuse Bragg sheet where the multilamellar stack dominates the signal. Speckles are observed only at small q_{\perp} , while the curves at high q_{\perp} are smooth. This finding can be explained if we assume that in the small q_{\perp} regime the diffuse signal is predominantly due to large scales domains, while at higher q_{\perp} probed out of the plane of incidence, the signal stems predominantly from thermal fluctuations which average out to a smooth curve. In both ranges of $q_{\perp} = \sqrt{q_x^2 + q_y^2}$, (i) the small q_x range probed in the plane of incidence, and (ii) the high q_y range probed out of the plane of incidence, we performed autocorrelation measurements of the temporal photon statistics, i.e. X-ray Photon Correlation Spectroscopy (XPCS) measurements. In both cases, no signal from the sample was found. The accessible time window defined by the synchrotron ring structure ($2 \times 1/3$ filling mode) and by photon statistics was extending from $10\mu s$ to 1 s, under beam conditions where standard calibration samples (colloidal suspensions) showed sufficient contrast and dynamical signal. We have estimated the relaxation frequencies using the Romanov and Ul'yanov model [5]; If the stack is thinner than ~ 1000 DDABr bilayers, the lowest frequency is above $\omega \sim 10^{+4}s^{-1}$, which is too fast for

our set-up.

In summary, we have shown that dehydrated and highly swollen fluid amphiphilic films can give a strong speckle pattern in the diffuse scattering when measured with coherent x-ray beams probing large lateral scales (rocking scans at small q_x). These explanations are in line with the XPCS measurements at high q_{\perp} , where the time scale of the fluctuations probed is certainly too fast for our set-up. At low q_{\perp} where a lower frequency was expected, no signal from the sample was seen either and this could be due to stacks with less than 1000 bilayers with dynamics that are still too fast. If the lateral domains have a depth extension in the film, the thermal fluctuations could be subject to an effective spatial cut-off, since domains walls or other defects might suppress the propagation of collective motions. In the literature to date, the diffuse scattering is commonly attributed to thermal fluctuations from which the membrane elasticity is deduced. The present work points out a caveat for the x-ray lineshape analysis of smectic systems since incoherent measurements are not able to distinguish the source and nature of scatters (static or dynamic). The presence of terrace structures and buried domains, as well as the dimensions and time scale over which the membranes fluctuate collectively, have to be further investigated in such films.

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