Swelling of DOPC multilayers in water

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EMBL Hamburg outstation beam line: muscle

The swelling of PC multilayer systems was found to proceed in two stages and to end with the complete loss of the initial lamellar order [1,2]. The experiments were performed in the system DOPC/H_2O, (~1% lipid); the results were obtained for a temperature range between 15°C and 65°C by complementary X-ray and optical microscopy experiments. The lipid was prepared as an open ring deposited from its chloroform solution onto the inner walls of an X-

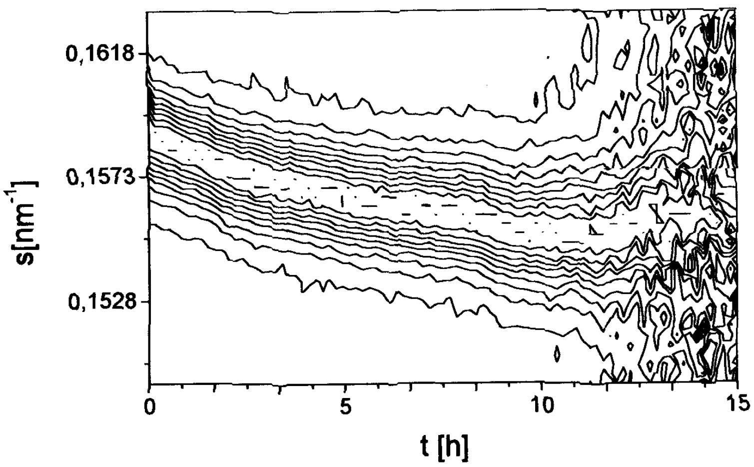

Figure 1: Loss of lamellar order, measured in a DOPC sample swelling at 15°C.The 1st order peak contours are depicted, normalized at any instant to their respective maximum. The increase of the repeat distance into its final value is reflected in the change of the maximum position (contour center). The peak intensity starts to drop after approx. 10h, at constant final spacing d_1 (scattering angle). The second order peaks exhibit the same characteristic.

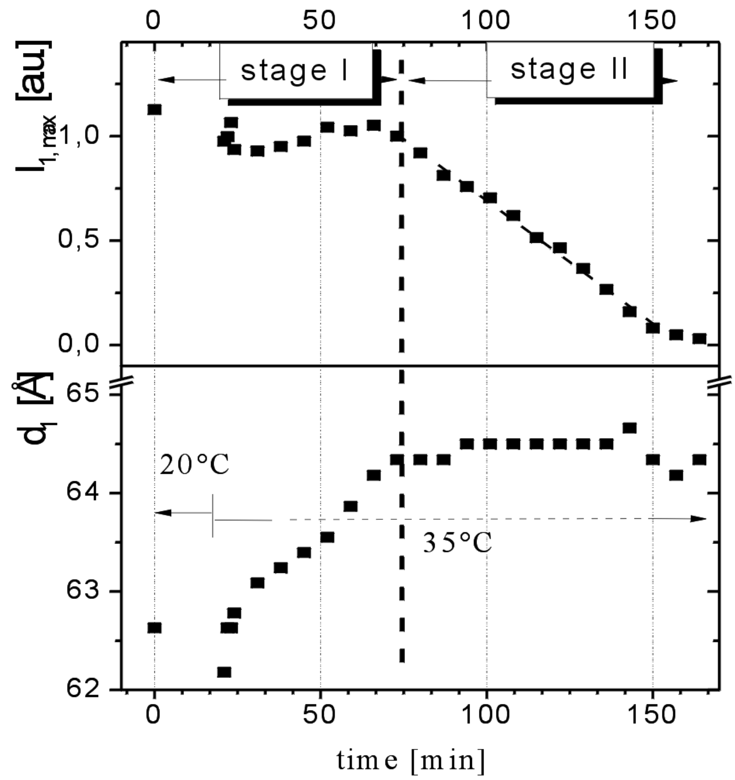

Figure 2: Analysis of a series of spectra showing the two stages observed during the swelling of PCs in water, measured with a DOPC sample at 35°C. Top: maximal intensities of the 1st order vs. time. The decrease of the intensity in the second interval can be linearly approximated. Low: repeat distance of the L_α phase vs. time.

During stage I, the 1st order intensity $I_{1,max}$ is essentially constant but the membrane separation changes. Stage II starts about the time when the spacing d_1 is close to its maximal value. Thereafter, I_1 continuously drops until no order is left. The correlation between the onset of order loss and the assumption of the maximal spacing is a hint that fully developed fluctuations may be a precondition of the order decay.

ray glass capillary. Water was added at 20°C; the capillary was sealed and heated to the final swelling temperature within 3 min. Time dependent diffraction spectra were taken and analyzed for the development and stability of the order in the bilayer system. The results were compared to the mesoscopic morphologies as seen in the microscope [1].

The first stage of swelling consists of the build-up of a lamellar order, often in a highly oriented (>90%) stack of bilayers. It was observed to be followed by a complete loss of this initial order during stage II. The main features of this swelling behavior are shown in fig.1,2. Immediately after water addition to the initially dry sample the lamellar order of the L_α-phase is established, characterized by a repeat distance value d. The values found in our experiments for d_{max} slightly exceed the ones reported by others as an 'equilibrium distance' [3,4] for the lamellar spacing at the same temperature. Thereafter, the lamellar signal changes in that the peak intensities $I_{1,2}$ of the two diffraction orders continuously decrease and finally disappear whereas the peak position remains constant. No new structure was seen to develop instead, down to a low angle limit corresponding to 700Å.The behavior was the same for all temperatures investigated and in many samples, without any exception. The experiments thus reveal two clearly distinguishable stages of the swelling process.
The observations suggest that the lamellar order is not an equilibrium structure but characteristic of an intermediate state [1,5] . From this temporary bound state the membranes undergo a continuous transition into a released state. The onset of intensity decrease and order loss seems to start almost when the full hydration repeat distance d_{hyd} and the related development of pronounced undulations is reached [1,3,5]. No indications for an unbinding transition were found. The peak profiles could not be reproduced within a fluctuation model as described by Caillé.
Our preliminary model to describe the swelling of PC membranes is presented in fig.3. It explains the observations by a peeling off of the outer membranes from a stack that still remains ordered. Such a process can be induced by the formation of localized, highly curved hats that are excited by normal membrane fluctuations. Such an explanation was recently proposed as one effect that might be evoked from non-quadratic elasticity contributions of Gaussian curvature terms in the bending Hamiltonian [5].
The equilibrium state of fully hydrated PC membranes is still left to be found.

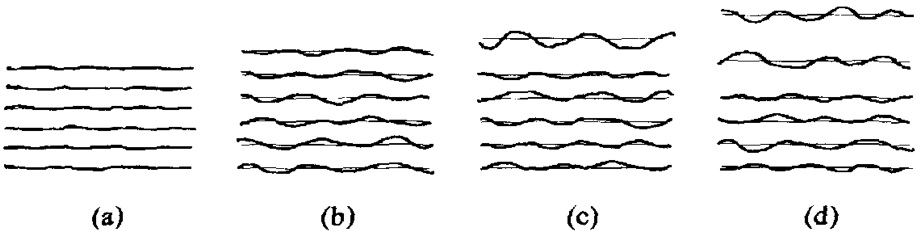

Figure 3: Schematics of the proposed model for the swelling process. a) lamellar order immediately after water addition; b) thermal fluctuations develop as the spacing approaches d_{max}; c) the outermost membrane starts to separate while most bilayers still maintain the common spacing; d) more and more membranes successively peel off from the initially (a,b) ordered stack.

References

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