Fluctuation dynamics in smectic liquid crystal membranes

I. Sikharulidze and W.H. de Jeu *(FOM-Institute AMOLF, Amsterdam)*
B. Farago *(ILL)*

Smectic liquid crystal membranes represent an example of a system with low-dimensional ordering. They consist of stack of liquid layers, formed by elongated molecules with their long axis perpendicular to the layer surface. The fluctuations diverge in such a system preventing the formation of long-range order (Landau-Peierls instability). Long-wavelength fluctuations in smectic membranes exhibit oscillatory damping and exponential decay. These regimes have been investigated with x-ray photon correlation spectroscopy (XPCS) experiments. In both cases the relaxation times are determined by macroscopic properties of the liquid crystal like surface tension and viscosity. Using neutron-spin echo (NSE) we have measured fluctuations of shorter wavelengths. On this scale the relaxation times are defined by the elastic properties of the liquid crystal. Combining XPCS and NSE we achieved a full coverage of the different timescales of the relaxation phenomena in smectic membranes.

Low-dimensional ordering and the associated fluctuation behaviour are of considerable general interest and have been studied for a wide variety of systems comprising smectic membranes (free-standing smectic films), Langmuir films, Newtonian black films, and surfactant and lipid membranes. In this context, smectic membranes provide unique, substrate-free and almost perfectly oriented model systems [1]. In these systems, the thermal fluctuations increase along with the size of the sample and eventually destroy the ordering of the liquid layers (Landau-Peierls instability).

Smectic membranes with a thickness varying from two layers (about 5 nm) up to thousands of layers (microns) can be suspended over an opening in a solid frame. At ESRF we studied the dynamics of the layer fluctuations by x-ray photon correlation spectroscopy (XPCS) [1-3]. In this context we have extended the accessible range of XPCS down to 20 ns, potentially allowing overlap with the time range typical for neutron-spin-echo methods. We observed a crossover between an oscillatory and an exponential regime of fluctuation damping with the wavelength of the fluctuation. These results are in a good agreement with present theories. However, they are so far still rather restricted compared to the rich theoretical predictions [1,4]. For example, the observed fluctuation regime was limited to surface-tension dominated damping. A crossover to bulk elastic damping has been predicted for the fluctuations with shorter wavelenghts.

Neutron-spin-echo measurements were performed at IN15 in order to check additional possibilities to be compared with XPCS. We used wavelengths of 9 and 15 Å, giving timescales up to about 40 and 100 ns, respectively, and the compound 4-octyl-4'-cyanobiphenyl (8CB) at room temperature in the smectic-A phase. Phenyl-deuterated 8CB had been custom synthesized for optimum contrast. Large-size membranes of 50x50 mm^2 were prepared on an aluminium frame. The thickness varied in several discrete regions from about 0.5 µm up to a few µm.

The NSE results of figure 1 show fluctuations with a much larger wave vector then obtained with XPCS. As the neutron beam is three orders of magnitude larger than the x-ray beam used in XPCS, significant intensity is still found at far off-specular positions. Moreover NSE is less demanding from the intensity point of view as the results are extracted from single scattering events. Using a large 2D detector for the data collection we integrated out the contributions from fluctuations with different wavelength and hence with different relaxation times. As a consequence the experimental curves have the form of a stretched exponential. The interpretation of the data follows by solving the equation of motion for a fluctuation with wavevector $q_\perp$ with appropriate boundary conditions [4]. This leads to two relaxation times τ_1 and τ_2. For small values of $q_\perp$ they are complex conjugate numbers, for large values of $q_\perp$ they become real. In the latter regime the relevant 'slow mode' behaves approximately as:

$\tau_1 \approx \eta_3 L / (2\gamma + KLq_\perp^2)$. (1)

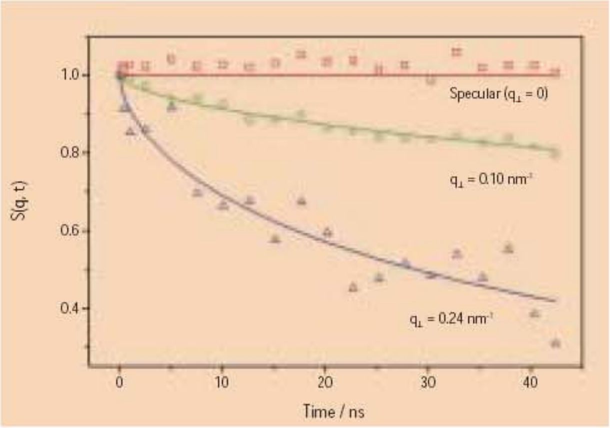


Figure 1: Relaxation curves for fluctuations with different wave vector $q_\perp$ obtained from the neutron spin echo experiments. Full lines are fits to a stretched exponential.

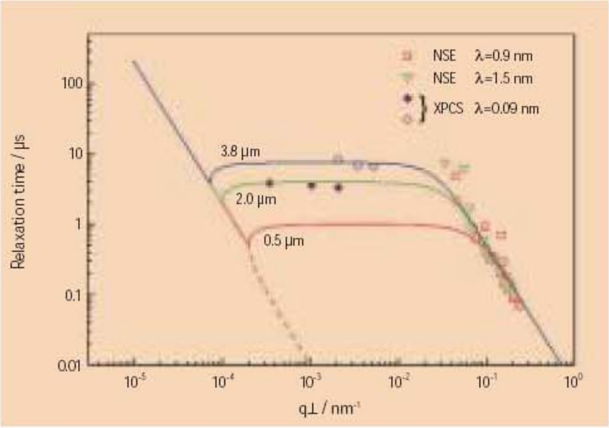
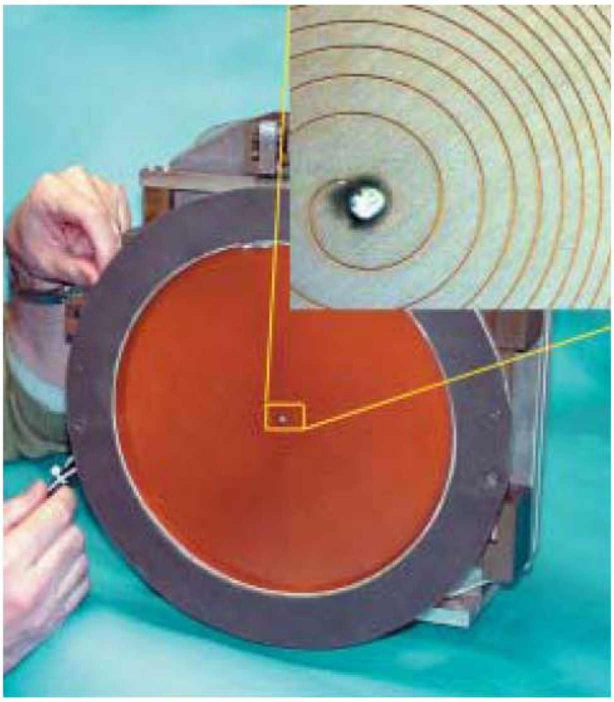


Figure 2: Theoretical dispersion curves and experimental results from both NSE and XPCS for smectic membranes with various thicknesses.

Here η_3 is the sliding viscosity of the smectic layers, L the membrane thickness, γ the surface tension and K the elastic constant for layer bending. The dispersion curves are plotted in figure 2 for different membrane thicknesses. For small values of $q_\perp$ we can omit the second term in the denominator in (1). As a result the relaxation becomes surface-tension dominated ($\tau_1 \sim \eta_3 L \ / \ 2\gamma$), which leads to a plateau value proportional to L.



IN15 Fresnel Coil.

Around $q_\perp \approx \sqrt{2\gamma / KL}$ both terms in the denominator in (1) are of the same order of magnitude. For larger values of $q_\perp$ the second term in the denominator in (1) becomes dominant. Here a transition occurs to bulk-elasticity determined damping. In this case relaxation time can be expressed as $\tau_1 \approx \eta_3 / KLq_\perp^2$. The NSE data at large $q_\perp$ and the XPCS results at lower values are nicely in agreement with theory. In the region of large $q_\perp$ the relaxation time does not depend on L, which is a lucky coincidence in the light of the multiple thickness regions in the large membranes needed for NSE.

In conclusion, we have shown that the combination of NSE and XPCS gives access to two different regimes of surface-tension and bulk-elasticity dominated damping of the fluctuations in smectic membranes.

References:
[1] W.H. de Jeu, B.I. Ostrovskii and A.N. Shalaginov, Rev. Mod. Phys. 75 (2003) 181
[2] I. Sikharulidze, B. Farago, I.P.Dolbnya, A. Madsen and W.H. de Jeu, Phys. Rev. Lett. 91 (2003) 165504
[3] I. Sikharulidze, I.P.Dolbnya, A. Fera, A. Madsen, B.I. Ostrovskii and W.H. de Jeu, Phys. Rev. Lett. 88 (2002) 115503
[4] A.N. Shalaginov and D.E. Sullivan, Phys. Rev. E 62 (2000) 699