Complex Dynamic Behavior of Fluctuating Smectic-*A* Films as Studied by Scattering with Coherent X-Rays

Andrea Fera,[1] Igor P. Dolbnya,[2] Gerhard Grübel,[3] Harm Geert Muller,[1]
Boris I. Ostrovskii,[1,4] Arcadi N. Shalaginov,[5] and Wim H. de Jeu[1,*]

[1]*FOM-Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands*
[2]*DUBBLE CRG, ESRF, BP 220, 38043 Grenoble Cedex, France*
and Budker Institute of Nuclear Physics, Novosibirsk, Russia
[3]*ID10, ESRF, BP 220, 38043 Grenoble Cedex, France*
[4]*Institute of Crystallography, Academy of Sciences of Russia, Leninsky prospekt 59, 117333 Moscow, Russia*
[5]*Department of Physics and Guelph-Waterloo Physics Institute, University of Guelph, Guelph, Ontario N1G 2W1, Canada*

(Received 5 June 2000)

Coherent dynamic x-ray scattering has been used to study the thermally excited layer fluctuations in freely suspended smectic films of the compound 4O.8. Using 8-keV x rays and films with a thickness around 0.3 μm we resolve relaxation times down to a few μs. A combination of damped and oscillatory behavior is observed for the layer undulations, which can be attributed to inertial effects. These are due to the surface contribution to the free energy which cannot be disregarded for thin films.

PACS numbers: 61.10.Kw, 42.25.Kb, 61.30.–v

If the dimensionality of a physical system is below the so-called marginal dimensionality, fluctuations can prevent the onset of true long-range order. Smectic-*A* (Sm-*A*) ordering, which consists of stacks of liquid layers, provides a nice example of such behavior. The reduced translational order leads to strong thermal fluctuations of the smectic layers, and the mean-square layer displacement $\langle u^2(\mathbf{r})\rangle$ diverges logarithmically with the sample size (Landau-Peierls instability) [1]. As a result the static density-density correlation function decays algebraically with distance ("quasi-long-range order"). These effects have been well documented experimentally. However, some of the fundamental questions regarding the dynamics of smectic systems have been addressed only recently. This concerns the behavior of the time-dependent layer displacement correlation function in the thermodynamic limit and the effects of finite sizes in freely suspended smectic films, including nonzero surface tension and viscous dissipation [2,3]. This has been triggered off by new possibilities to study the dynamics of these fluctuations experimentally with coherent x rays. If coherent radiation is incident on a random medium, the scattered intensity shows a speckle pattern that reflects the instantaneous arrangement of the scattering centers. Movement of the scatterers causes a corresponding change in this pattern and thus contains information on the dynamics of the system. Photon correlation spectroscopy or dynamic light scattering (DLS) measures the time dependent intensity autocorrelation function of the speckle pattern. With visible light this is a well-established technique, while coherent dynamic x-ray scattering (DXS) has been developed only recently at third generation high-brilliance synchrotron sources [4]. In contrast to DLS, however, DXS can give access to dynamic processes on an atomic or molecular length scale. So far, the feasibility of DXS has been shown on various hard and soft condensed systems [5], with some emphasis on relatively slow dynamics (ms range) like those of colloidal particles in various liquids.

Smectic liquid crystals can be suspended over an opening in a solid frame. Because of the controlled thickness (from two to over hundreds of layers) and the uniform ordering of the smectic layers parallel to the surfaces, these films provide perfect model systems [6]. From the dynamic point of view, the finite film thickness changes the continuous bulk response spectrum into discrete response modes that depend also on the surface parameters. DXS in the soft x-ray region has recently been applied to thick freely suspended smectic films [7]. Decay times typically in the range of tens of μs were reported to scale linearly with the film thickness (tens of μm). In this Letter we report DXS with hard x rays of thin smectic films. We observe an "oscillatory" behavior of the correlation function, which cannot be described by a simple exponential time dependence. This can be attributed to a complex behavior of the relaxation time originating from the inertial contribution to the dynamic response of thin films, in agreement with recent theory.

Freely suspended smectic films of N-(4-*n*-butoxybenzilidene)-4-*n*-octylaniline, abbreviated as 4O.8, were spanned over a 10×23 mm^2 hole in a stainless steel frame and equilibrated as described earlier [8]. The films were mounted in a two-stage oven and evacuated in order to prevent possible sample degradation, to reduce air scattering, and to avoid acoustic low frequency dynamics. 4O.8 was obtained from Frinton Laboratories Inc., and has the following phase transitions (in °C): K 33 Cr-*B* 48.5 Sm-*A* 63.5 N 78 I.

DXS was performed at undulator beam line ID10A (Troika I) at the European Synchrotron Radiation Facility (ESRF, Grenoble) [4]. The sample was mounted vertically and illuminated with 7.98 keV radiation selected by a Si(111) monochromator. The longitudinal coherence

 0031-9007/00/85(11)/2316(4)$15.00

length $\xi_l = \lambda^2/\Delta\lambda \approx 1.5\ \mu$m was determined by the bandpass $\Delta\lambda/\lambda \approx 10^{-4}$ of the monochromator. The source size of width $s = 928\ \mu$m at a distance $R = 46$ m from the sample leads to a transverse coherence length $\xi_t = \lambda R/(2s) \approx 4\ \mu$m in the horizontal (scattering) plane. The transverse coherence length in the vertical direction was about 100 μm. A circular pinhole of 12 μm diameter was placed about 0.25 m upstream of the sample to provide a collimated and partially coherent beam (see Fig. 1). A set of guard slits of $20 \times 20\ \mu$m^2 in front of the sample was used to remove the parasitic incoherent scattering from the pinhole. An analyzing aperture of 40 μm was placed in front of the detector at 1.2 m from the sample. These dimensions are chosen such that the slit is roughly of the size of a single speckle. The photon flux was about 2×10^8 photons/s at 100 mA ring current. The degree of coherence was determined to be of the order of 15% by measuring the contrast of the Fraunhofer diffraction pattern produced by the collimating aperture in the absence of a sample. The resolution of our setup was given by $\Delta q_z = \Delta q_y \approx 10^{-3}$ nm^{-1} and $\Delta q_x \approx 10^{-4}$ nm^{-1}. The thickness L of each film was determined from the Kiessig fringes in the specular reflectivity. From rocking curves the mosaicity of the films (determined by the residual curvature of the supporting frame) was found to be typically of the order of 0.002° (FWHM).

The intensity-intensity time correlation function $G^{(2)}(q,t) = \langle I(q,0)I(q,t)\rangle$ was recorded at the first Bragg peak, corresponding to a wave vector transfer $q_z = 2\pi/d = 2.2$ nm^{-1}, where d is the smectic layer periodicity. The reflected radiation was measured with a fast scintillation counter based on yttrium-aluminium-perovskite (YAP) doped with Ce. The YAP detector was coupled to a charge-sensitive amplifier followed by a low-level threshold discriminator, which finally resulted in a time resolution of approximately 120 ns. To determine the autocorrelation function the arrival times of all individual pulses from the detector were stored in a buffer memory and subsequently transferred to a hard disc via a micro-Enable card (Silicon Software GmbH). These times were digitized to the accuracy of the clock frequency (100 MHz). The stored data were used to construct the autocorrelation function using appropriate software. More fundamentally, the time resolution of our measurements was limited by the 16 bunch mode of the synchrotron source, in which electron bunches are equally spaced in the storage ring at 176 ns intervals. Using the method described, the bunch structure of the incoming photons could be well resolved and integrated out. In spite of the high time resolution, data at times faster than about 700 ns are considered to be less reliable due to various limitations in the detection electronics. The mean counting rate $\langle I\rangle$ was typically 5–10 kHz. The correlation function from the film was normalized via division by a reference correlation function. In this way residual correlations in the beam could be eliminated. As reference, a NiC multilayer was used with a periodicity of 3.6 nm, comparable to the smectic layer spacing of 4O.8. The correlation function from the multilayer did not display any dynamic effects and could not be distinguished from the behavior recorded for the direct beam at different stages of the experiment. The statistical error has been calculated from the photon counting statistics, which gives at low count rates: $\Delta G^{(2)}(t) = \sqrt{G^{(2)}(t)}[\langle I\rangle\sqrt{T\Delta t}\,]^{-1}$, where T is the total counting time and Δt the sampling interval. For our experiments typically $\langle I\rangle \approx 5$ kHz, $T \approx 3600$ s, and $\Delta t = 180$ ns, which leads to about 1% accuracy. It should be realized that this error is still considerable in relation to the variations in $G^{(2)}(t)$ to be considered. For larger times the accuracy could be improved by integrating over larger time intervals.

Figure 2a displays the intensity autocorrelation function $G^{(2)}(t)$ of a freely suspended 4O.8 film in the Sm-A phase and a reference correlation function; Fig. 2b gives the resulting normalized correlation function. The correlation function shows a decay of the layer fluctuations in the time

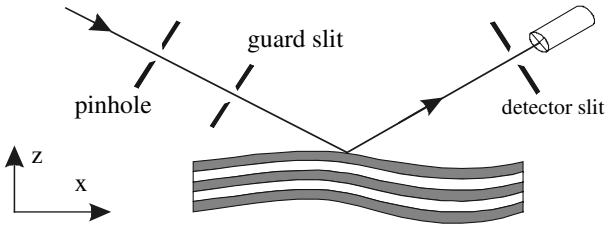

FIG. 1. Scheme of the experimental setup.

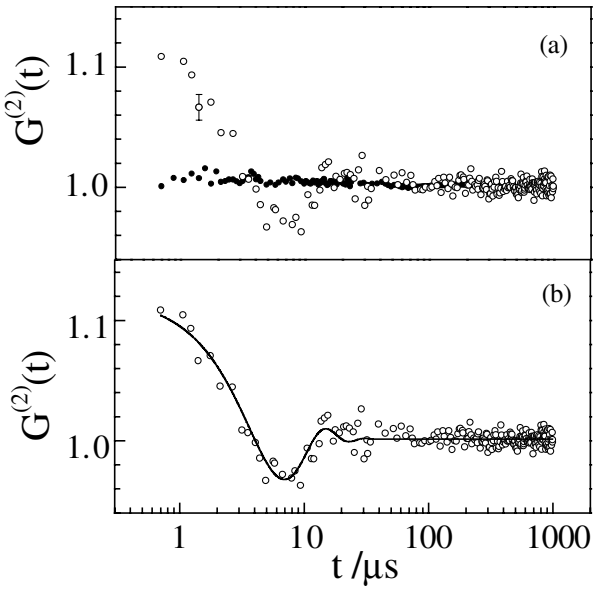

FIG. 2. Autocorrelation function for a 95 layer film (thickness 0.27 μm) in the Sm-A phase at 50.1 °C. (a) Raw data (open dots) and reference signal from the NiC multilayer (filled dots). (b) Normalized correlation function obtained by dividing the raw data by the NiC reference signal; solid line is a fit to Eq. (1). For error bars, see text.

scale of microseconds and oscillatory behavior in the range of tens of microseconds. We fitted the results to the simplest form of an oscillating exponential decay:

$$G^{(2)}(t) = 1 + A\cos(\omega t)\exp(-t/\tau), \qquad (1)$$

where the amplitude A is determined by the degree of coherence. Fitting of the experimental data to Eq. (1) gives $A = 0.120 \pm 0.005$, $\tau = 5.8 \pm 0.5$ μs, and $2\pi/\omega = 15.9 \pm 0.3$ μs. Similar values were obtained at other temperatures in the Sm-A phase.

The results can be understood within the framework of the Landau-De Gennes smectic free energy extended with a surface term for $\mathbf{r} = (\mathbf{r}_\perp, z = L/2)$ [9]:

$$F = \tfrac{1}{2}\int d^3r \left\{B\left[\frac{\partial u(\mathbf{r})}{\partial z}\right]^2 + K[\Delta_\perp u(\mathbf{r})]^2\right\} + \tfrac{1}{2}\gamma\int d^2r\,[\nabla_\perp u(\mathbf{r}_\perp, z = \pm\tfrac{1}{2}L)]^2. \qquad (2)$$

Here the perpendicular direction refers to the xy plane of the smectic film. The bulk elastic constants K and B are associated with bending and compression of the smectic layers, respectively; γ represents the surface tension. Investigation of the dynamic properties of this Hamiltonian [2,3] involves a demanding calculation of the time dependent correlation function $G(\mathbf{q}_\perp, z, z', t) = \langle u(\mathbf{q}_\perp, z, 0) \times u^*(\mathbf{q}_\perp, z', t)\rangle$. The starting point is the equation of motion which involves both the viscous and the restoring elastic force:

$$\rho_0 \frac{\partial^2 u(\mathbf{r})}{\partial t^2} = \eta_3 \frac{\partial}{\partial t}\nabla_\perp^2 u(\mathbf{r}) + (B\nabla_z^2 - K\Delta_\perp^2)u(\mathbf{r}) \qquad (3)$$

with appropriate boundary conditions at $z = \pm L/2$. Here ρ_0 is the density and η_3 the viscosity for shear of the smectic layers. The inertial term [left-hand side of Eq. (3)] leads to a fast response, which in general can be separated from the slow branch. The latter is calculated by equating the viscous and elastic forces while neglecting inertia. Assuming in addition incompressible films and conformal fluctuations, for the slow branch a spectrum of relaxation modes is found which for $q_\perp = 0$ reduces to a single fundamental relaxation time $\tau_1 = \eta_3 L/(2\gamma)$. This relation has been confirmed for thick films by Price *et al.* [7].

Disregarding the inertial term is valid provided $\rho_0 K/\eta_3^2 \ll 1$. For bulk systems this parameter is small (about 10^{-4} to 10^{-6}) due to the absence of a term proportional to $q_\perp^2$ in the free energy [1]. However, for thin freely suspended films the situation changes because of an additional surface contribution $\gamma q_\perp^2$ [9]. For conformal fluctuations in the long wavelength limit ($q_\perp \to 0$) the latter term prevails over the bending term $Kq_\perp^4$ and the inertial term becomes important [2,3]. Taking values typical for 4O.8: $\gamma = 0.021$ N/m, $K = 5 \times 10^{-12}$ N, $\eta_3 = 0.05$ kg/ms, $\rho_0 = 10^3$ kg/m^3 we arrive at a marginal value $q_{\perp c} \approx 2.10^{-3}$ nm^{-1}. Theoretical results for finite size Sm-A films calculated taking inertia into account are displayed in Fig. 3a. The inverse relaxation time corresponding to the first response mode can be written in the long wavelength limit as [3]

$$\frac{1}{\tau_1} = \pm i\sqrt{\frac{2\gamma}{\rho_0 L}}\,q_\perp + \frac{\eta_3}{2\rho_0}\,q_\perp^2. \qquad (4)$$

The relaxation time appears to be complex for $q_\perp < q_{\perp c}$: the real part leads to relaxation while the imaginary part produces oscillations in the correlation function. As our instrumental resolution is of the same order of magnitude as $q_{\perp c}$, oscillations in $G^{(2)}(t)$ should be observable for sufficiently thin films, in agreement with Fig. 2.

In order to make the complex behavior of the smectic layer relaxation clearer we calculated the time-dependent part of the intensity-intensity correlation function $G^{(2)}(t)$ by convoluting the theoretical correlation function with the

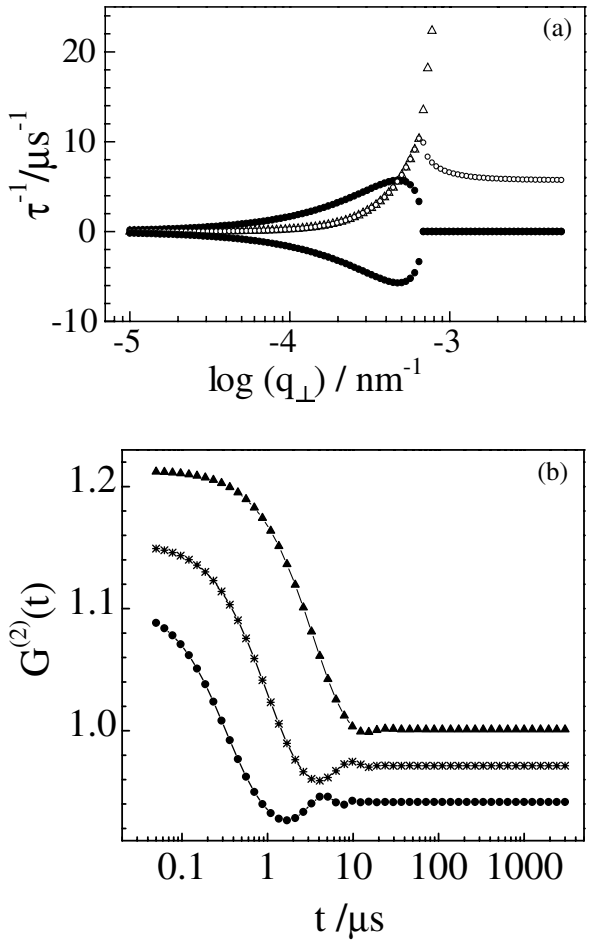

FIG. 3. (a) Calculation of the complex behavior of the first fundamental relaxation mode for a 50 layer Sm-A film (parameters as given in text). The triangles and circles show the real part of the relaxation of the fast and the slow branch, respectively; the dots show the imaginary part of the first relaxation time of both branches. (b) Calculation of the experimental correlation function $G^{(2)}(t)$ according to Ref. [3] for various film thickness $N = 1000$ (triangles), $N = 200$ (asterisks), and $N = 50$ (dots). The last two curves have been moved down by 0.03 for clarity; same parameters as under (a).

experimental resolution [10]. Figure 3b shows the results for Sm-*A* films of different thickness. The oscillatory behavior of nonoverdamped layer fluctuations for $q_\perp < q_{\perp c}$ is well reproduced for thin films. The oscillations become less pronounced with increasing film thickness and finally completely disappear for a 1000 layer film (thickness about 3 μm). The resulting values of τ and $2\pi/\omega$ are of the right order of magnitude; they differ by a factor 2 to 3 from the experimental ones. A more extensive comparison with theory waits for more experimental results at various film thicknesses. The theoretical results depend strongly on the long wavelength cutoff used. A value of 100 μm has been chosen, which is about the effective (projected) speckle size at the Bragg position. The prediction of disappearing oscillations for thick films is in agreement with the simple exponential decay reported for films between 5 and 50 μm in Ref. [7].

In conclusion, we have used dynamic x-ray scattering to characterize thermal fluctuations in free standing smectic-*A* films. We have demonstrated the feasibility of DXS experiments with standard 8 keV x rays on thin films leading to relaxation times in the microsecond range. For such thin Sm-*A* films we resolved both an oscillatory and a damping behavior of the intensity-intensity correlation function. In agreement with recent theory this indicates that the inertial term in the dynamic equations cannot be disregarded anymore in thin films for which the surface contribution becomes important.

The authors wish to thank G. H. Wegdam for valuable discussions. A. N. S. and B. I. O. acknowledge the hospitality during their stay at the FOM-Institute for Atomic and Molecular Physics in Amsterdam. This work is part of the research program of the "Stichting voor Fundamenteel Onderzoek der Materie," (FOM), which is financially supported by the "Nederlandse Organisatie voor Wetenschappelijk Onderzoek" (NWO).

*Corresponding author.
Email address: dejeu@amolf.nl

[1] See, for example, P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, Cambridge, England, 1995).

[2] A. Ponierewski, R. Holyst, A. C. Price, L. B. Sorensen, S. D. Kevan, and J. Toner, Phys. Rev. E **58**, 2027 (1998); A. Ponierewski, R. Holyst, A. C. Price, L. B. Sorensen, *ibid.* **59**, 3048 (1999); H. Y. Chen and D. Jasnow, *ibid.* **61**, 493 (2000).

[3] A. N. Shalaginov and D. E. Sullivan, Phys. Rev. E **62**, 699 (2000).

[4] S. Dierker, NSLS Newsletter, 1 July 1995, 1; G. Grübel and D. L. Abernathy, Proc. SPIE Int. Soc. Opt. Eng. **3154**, 103 (1997); D. L. Abernathy, G. Grübel, S. Brauer, I. Mc Nulty, G. B. Stephenson, S. G. J. Mochrie, A. R. Sandy, N. Mulders, and M. Sutton, J. Synchrotron. Radiat. **5**, 37 (1998).

[5] S. Brauer, G. B. Stephenson, M. Sutton, R. Brüning, E. Dufresne, S. G. J. Mochrie, G. Grübel, J. Als-Nielsen, and D. L. Abernathy, Phys. Rev. Lett. **74**, 2010 (1995); S. B. Dierker, R. Pindak, R. M. Fleming, I. K. Robinson, and L. Berman, *ibid.* **75**, 449 (1995); T. Thurn-Albrecht, W. Steffen, A. Patkowski, G. Meier, E. W. Fischer, G. Grübel, and D. L. Abernathy, *ibid.* **77**, 5437 (1996); S. G. J. Mochrie, A. M. Mayes, A. R. Sandy, M. Sutton, S. Brauer, G. B. Stephenson, D. L. Abernathy, and G. Grübel, *ibid.* **78**, 1275 (1997); T. Thurn-Albrecht, G. Meier, P. Müller-Buschbaum, A. Patkowski, W. Steffen, G. Grübel, D. L. Abernathy, O. Diat, M. Winter, M. G. Koch, and M. T. Reetz, Phys. Rev. E **59**, 642 (1999); D. O. Riese, W. L. Vos, G. H. Wegdam, F. J. Poelwijk, D. L. Abernathy, and G. Grübel, *ibid.* **61**, 1676 (2000).

[6] Some reviews on free standing films are P. Pieranski *et al.,* Physica (Amsterdam) **195A**, 364 (1993); C. Bahr, Int. J. Mod. Phys. B **8**, 3051 (1994); T. Stoebe and C. C. Huang, Int. J. Mod. Phys. **9**, 2285 (1995).

[7] A. C. Price, L. B. Sorensen, S. D. Kevan, J. Toner, A. Ponierewski, and R. Holyst, Phys. Rev. Lett. **82**, 755 (1999).

[8] E. A. L. Mol, J. D. Schindler, A. N. Shalaginov, and W. H. de Jeu, Phys. Rev. E **54**, 536 (1996); E. A. L. Mol, G. C. L. Wong, J.-M. Petit, F. Rieutord, and W. H. de Jeu, Phys. Rev. Lett. **79**, 3439 (1997); A. Fera, D. Sentenac, B. I. Ostrovskii, I. Samoilenko, and W. H. de Jeu, Phys. Rev. E **60**, R5033 (1999).

[9] R. Holyst, Phys. Rev. A **42**, 7511 (1990); **44**, 3692 (1991); A. N. Shalaginov and V. P. Romanov, Phys. Rev. E **48**, 1073 (1993).

[10] D. Sentenac, A. Shalaginov, A. Fera, and W. H. de Jeu, J. Appl. Crystallogr. **33**, 130 (2000).