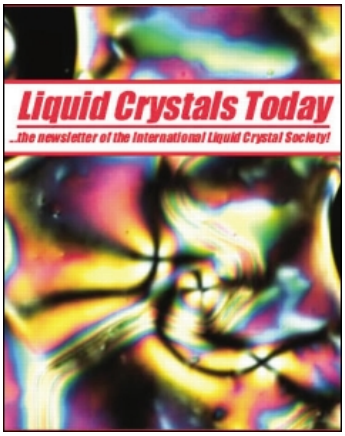

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New insights into the nematic to smectic-A transition: X-ray measurements in a strong magnetic field

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New insights into the nematic to smectic-A transition: X-ray measurements in a strong magnetic field

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The nematic to smectic-A (NA) phase transition would appear to be the simplest example of a freezing transition in nature. However, it has proven to be one of the most challenging problems of liquid crystal science and equilibrium statistical mechanics. One quantitative method to study this transition, that yields high quality data of almost transparent interpretation, has been X-ray measurements of the divergence of smectic order correlations as the SmA phase is approached from the nematic side. However, even data from these experiments have proved difficult to interpret because of the imperfect magnetic alignment or "mosaic spread" of the nematic phase. This mosaic spread limits the experimental transverse resolution and hence affects the data very close to the transition. Previous studies employed magnetic fields of $\sim$0.1–0.8 T. The use of a high (5 T) field, in the work we recently completed, improved the effective transverse resolution by almost two orders of magnitude allowing us to obtain results essentially *free of mosaic spread*. The generally used technique for removing this effect has now been tested. The high field results shed new light on this transition and reveal a new and proper way to apply the mosaicity correction.

The nematic to smectic-A (NA) phase transition is one of the most interesting and puzzling transitions in condensed matter physics. In the nematic (N) phase, elongated molecules are aligned, on average, parallel to the director $\hat{n}$ but have complete translational freedom. In the smectic-A (SmA) phase molecules are still aligned along $\hat{n}$ but their translational freedom is constrained to the equidistant smectic layers perpendicular to $\hat{n}$. Thus, it seems that the NA transition is a rather simple example of one-dimensional melting (freezing) and for that reason should be rather simple to understand. However, when it comes to the subject of the NA transition, this simplicity is deceiving!

Two order parameters are used to model the NA transition [1]: the well-known scalar nematic orientational order parameter, S and the complex smectic order parameter Ψ. The amplitude of Ψ is a measure of the translational order, while the phase factor defines the position of the smectic layers. Although Ψ vanishes in the N phase the spatial and temporary fluctuations of the smectic order still exist in the pretransitional region above the transition. The size of these fluctuations is determined by the short-range smectic correlations which persist over a distance characterized by the *correlation length*, ξ. Because of the anisotropy of the SmA phase there are two different correlation lengths, $\xi_{\parallel,\perp}$, in the directions parallel and perpendicular to the smectic layer normal. As the NA transition is approached by lowering the temperature from the nematic phase, the smectic fluctuations grow larger and larger resulting in corresponding increase of $\xi_{\parallel,\perp}$. In fact, in an infinitely large sample these correlation lengths are expected to diverge to ∞ precisely at the NA transition temperature. The very rapid variation of certain quantities for a continuous (or, second order) phase transition is described by the transition's critical behaviour. The critical behaviour of the smectic correlation lengths is characterized by the critical exponents $\nu_{\parallel,\perp}$ describing the power-law divergence of $\xi_{\parallel,\perp}$.

According to the *universality* concept, which follows from renormalization group calculations, the critical behaviour of any system depends only on the spatial dimension, the symmetry, and the number of components of the order parameter, and the range of interactions. Therefore, all systems which belong to the same *universality class* (i.e., same dimensionality and the number of components of the order parameter) should exhibit similar critical behaviour in spite of the differences in other regards, e.g., their chemical composition. This is a fundamental concept in the condensed matter physics which has been experimentally tested on many different systems. Reliance on this concept led scientists to expect the second order NA transition to have the same critical behaviour and

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exponents as those obtained in the normal fluid-superfluid transition in liquid helium and the normal metal to superconductor transition. All three systems are 3-dimensional and the transitions are described by a two component complex order parameter and, hence, should belong to the universality class known as 3d-xy. Thus, the NA transition provides a good system for testing the universality concept [2,3].

However, past studies have shown that the NA transition is very elusive, puzzling and complex. It does not exhibit simple 3d-xy behaviour. The complexity originates from several factors, whose relative importance is yet to be understood. Layering of molecules in the SmA phase restricts their rotational freedom and enhances the nematic order parameter S. This is called Ψ–S coupling and is expected to drive the NA transition first order with decreasing nematic range and cause a crossover from critical to tricritical behaviour [4,5]. The effects of the Ψ–S coupling are minimal in materials with a wide nematic range because the nematic order parameter saturates before the NA transition occurs. Another type of coupling is between Ψ and director fluctuations. Molecules in the SmA phase prefer to be normal to the smectic layers. Director fluctuations result in rotation of the molecules away from their preferred local orientation which, in turn, causes local distortions of the layers described by the phase fluctuations of Ψ. This is called $\delta\hat{n}$–Ψ coupling. This coupling could drive the transition weakly first order [6] and lead to anisotropic critical behaviour [7]. Significantly, the effects of $\delta\hat{n}$–Ψ coupling cannot be avoided in experiments since a complete quenching of director fluctuations requires a magnetic field of hundreds of tesla [8]. The situation is further complicated because the average thermal fluctuations of the phase of Ψ diverge logarithmically with the sample size in systems, such as the SmA, with translational order in one dimension. This effect is known as the Landau–Peierls instability [9] and, for large enough samples, layer distortions comparable with the layer spacing occur. These distortions destroy the true long-range order in the SmA phase. Thus, it is often stated that the SmA phase has a quasi long-range order.

The complex nature of the NA transition has attracted great attention and some of the best scientists in the field of critical phenomena have tried to understand its puzzling behaviour. In spite of the tremendous efforts, no clear picture of the NA transition has emerged. Experimentally [2], the values of the critical exponents $\nu_{\|,\perp}$ vary from material to material, which raises the issue of non-universal critical behaviour. Furthermore, these exponents have unequal values indicating an anisotropic divergence ($\nu_{\|}/\nu_{\perp} \sim$ 1.1–1.4) of the correlation lengths. This should be contrasted with different theoretical approaches that predict either a) isotropic ($\nu_{\|} = \nu_{\perp} = \nu_{xy}$) [10] or b) strongly anisotropic ($\nu_{\|} = 2\nu_{\perp}$) [3,11] divergence or c) a crossover from isotropic to strongly anisotropic behaviour [3,7]. Although some aspects of the experimental results agree with predictions of one model or another, none of the existing theories can explain all features of the results obtained by X-ray diffraction, light scattering, and heat capacity measurements.

The major experimental challenge is to obtain reliable quantitative structural information at temperatures very close to the transition where a crossover to strongly anisotropic behaviour is expected [3,7]. One of the most reliable techniques for obtaining such data is high-resolution X-ray diffraction, which directly probes the mass density fluctuations. However, X-ray scattering measurements very close to the transition are hindered by poor *effective* transverse resolution which is limited by the sample mosaicity, i.e., imperfect alignment of smectic layers. All previous X-ray measurements [2] have been done using low magnetic fields ($\sim$0.1–0.8 T), with the mosaicity substantially larger than the instrumental transverse resolution. Therefore, the effects of the mosaicity could mask the true divergence and yield misleading results. Though mosaicity corrections have been attempted [12–15], the assumptions underlying the method used have never been verified. The importance of mosaicity was also pointed out by Dasgupta [16] who suggested that it could be the factor responsible for the puzzling non-Lorentzian behaviour of transverse X-ray lineshape above the NA transition.

For a number of years, we worked on constructing an experiment to completely eliminate the mosaicity issue. A strong and uniform magnetic field was used to achieve near perfect alignment and minimize the sample mosaicity. Such a field was produced by a custom-designed split-coil, superconducting, 5 T magnet with two orthogonal horizontal bores, accessible at room temperature. The X-ray beam passed through one of the bores, while the field was parallel to the axis of the second bore which contained the sample and oven. The only negative feature of such a geometry was that the exit angle for diffracted X-rays was limited to $\sim 6.5^{\circ}$. A molybdenum target was used for some measurements to access a larger range of q-space. An additional complication was that extra care had to be taken to shield the X-ray detector and stepping motors of the spectrometer from magnetic field leakage.

A second crucial factor in obtaining high quality data was good temperature control. We used a two-stage copper oven specially designed to fit inside the magnet. The inner stage had beryllium windows and the outer stage openings were covered with thin Mylar films. The

outside of the oven was cooled via two cooling coils made of thin copper tubing through which cold liquid circulated. This lowered the ambient temperature to a nearly constant value $\sim 15^{\circ}$C. The long term (~ 24 hours) temperature stability of the oven was found to be ± 1 mK and its short term (~ 1 hour) stability was ± 0.5 mK. The temperature gradients inside the sample did not exceed the temperature stability of the oven. This was confirmed by the absence of coexistence of the N and SmA phases very near T_{NA}. Since the widths of the peaks in transverse scans from the N and SmA phases are very different, the shape of the measured peak, in case of their coexistence, should display a sharp smectic spike on top of a relatively broader nematic peak [17]. Such "spiky" peaks were indeed observed in the preliminary studies with a one-stage oven without Be windows, which was more prone to temperature gradients. However, no such effects were seen with the two-stage oven used in our final measurements, as confirmed by the fact that the same function fitted the lineshape over the whole temperature range.

A detailed report of our investigation has recently been published [17]. Here, we are going to discuss some of the unique results of this work. The material under study will be referred to as D6.15AOB [17]. It is a mixture of two homologues of two-benzene-ring non-polar compounds with simple isotropic-N-SmA-crystal phase sequences. It is important because the presence of other underlying LC phases, such as a smectic-C, or one of the frustrated (polar) smectic phases, might influence the behaviour of the NA transition in unknown ways. D6.15AOB has a wide nematic range of $\sim 36^{\circ}$ thus allowing the nematic order parameter to saturate and its distance from the tricritical point is described by the McMillan ratio $T_{NA}/T_{NI} = 0.89$. Although this is far from the record value of $T_{NA}/T_{NI} = 0.66$ reported for certain polar materials [2], the NA transition in D6.15AOB is well removed from the tricritical point [18]. Therefore, it was a good system for critical behaviour studies with minimal Ψ–S coupling. One more advantage of D6.15AOB is that it has the near room temperature $T_{NA} \simeq 20.5^{\circ}$C. This makes temperature control somewhat easier and has the added advantage of being less prone to chemical degradation, so a resulting shift in T_{NA} is less than in materials with higher transition temperatures.

The experiments were done using a 12 kW Rigaku RU-200 rotating anode generator, a two-circle Huber goniometer with a pair of Si(111) single crystals as monochromator and analyser, and the superconducting magnet (SCM) mentioned above. A schematic diagram in Figure 1 depicts the experimental arrangement. K_{α} lines emitted by the target (Cu or Mo) are Bragg diffracted from the monochromator. Several xy-slits were used to collimate the beam and define its cross section. The slit S_3 before the magnet was also used to block the Cu $K_{\alpha 2}$ line. This resulted in a loss of intensity but simplified the data analysis. Unfortunately, we could not do the same with the Mo $K_{\alpha 2}$ line as it was spatially too close to $K_{\alpha 1}$ line and the loss of intensity was unacceptable. The monochromatic X-ray beam impinged on the sample inside the oven inserted in the magnet. The magnet was mounted on the θ-circle of the goniometer, which permitted changes in θ and 2θ with a precision of 0.00025°. The X-rays scattered by the sample were Bragg reflected from the analyser and collected in an Na(T1)I scintillation detector. To avoid effects of any power fluctuations in the X-ray source, the diffracted intensity beam was measured against the incident flux of X-ray. The three experimental resolutions were: $\Delta q_{\parallel} \simeq 2 \times 10^{-4}$ Å^{-1}, $\Delta q_{\perp} \simeq 10^{-5}$ Å^{-1}, and (out-of-plane) $\Delta q_z \simeq 4 \times 10^{-2}$ Å^{-1}.

Recalling from our earlier discussion different smectic domains (or, correlated volumes) just above the NA transition are not perfectly parallel to each other but have a finite distribution known as the mosaic spread or mosaicity. The effect of mosaicity is

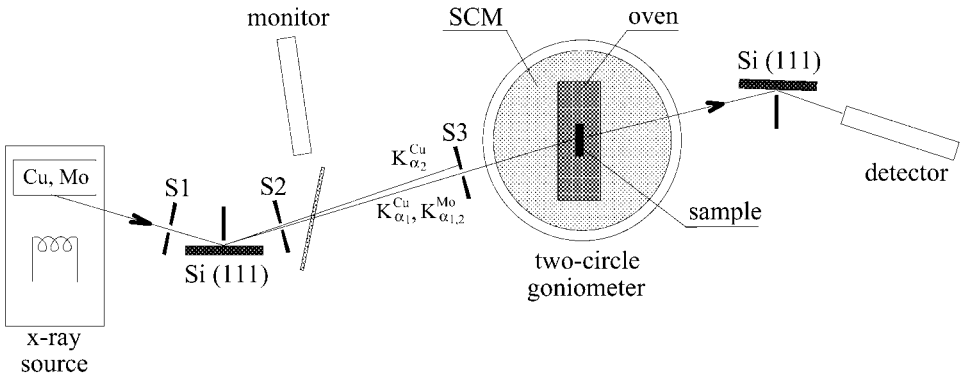

Figure 1. The X-ray scattering set-up.

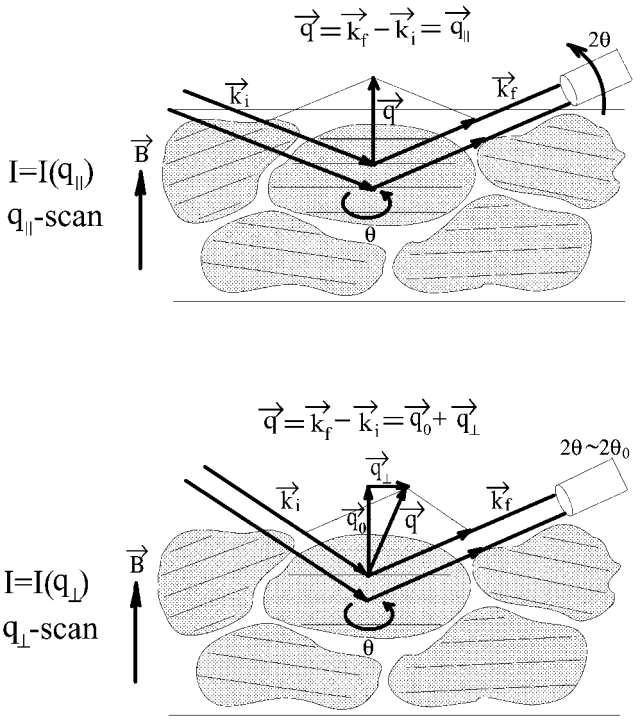

Figure 2. Schematic diagrams of the longitudinal ($q_\parallel$) and transverse ($q_\perp$) X-ray scans performed in the critical region above the NA transition.

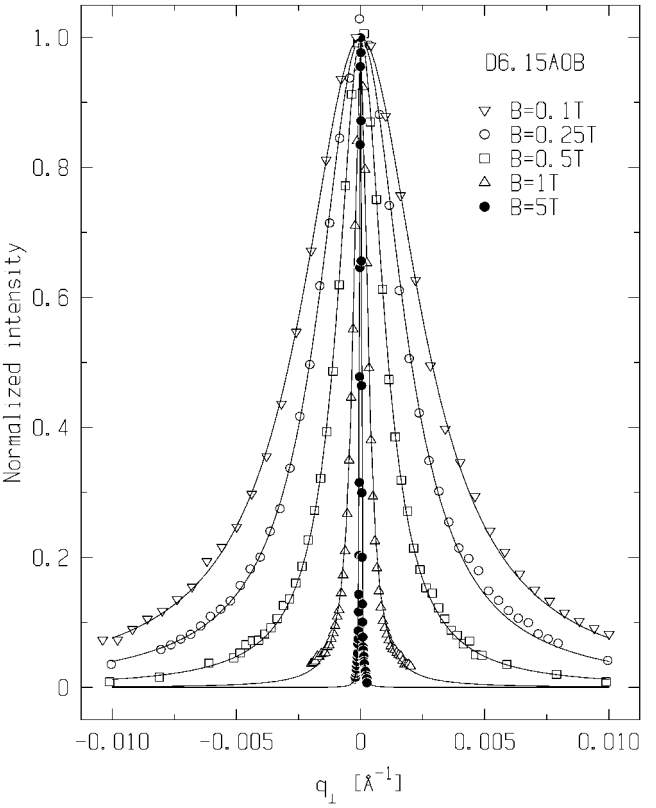

Figure 3. The sharpest $q_\perp$-scans for D6.15AOB obtained at the temperature point closest to T_{NA} and normalized for comparison. These scans represent the effective transverse resolution at different fields. The solid lines are the fits to a triple Lorentzian (5 T) and a single Lorentzian (other fields).

illustrated in figure 2, which shows the geometries of the longitudinal ($q_\parallel$) and transverse ($q_\perp$) X-ray scans performed in the critical region above the NA transition. The width of a $q_\parallel$-scan is inversely proportional to $\xi_\parallel$ and decreases as T approaches T_{NA} until it reaches the value of the longitudinal instrumental resolution, $\Delta q_\parallel$. On the other hand, during a $q_\perp$-scan far from T_{NA}, where the mosaicity effect is small, the width of the $q_\perp$-scans is roughly inversely proportional to $\xi_\perp$. However, close to T_{NA} the mosaicity becomes significant and the width of $q_\perp$-scans saturates at the mosaicity limit, i.e., Δq_M, rather than at the instrumental transverse resolution $\Delta q_\perp$. Since typical high-resolution X-ray spectrometers have $\Delta q_\perp \leq 10^{-5}$ Å^{-1}, the effective transverse resolution in the scattering plane is always determined by the sample mosaicity.

Figure 3 shows the normalized sharpest $q_\perp$-scans at fields ranging from 0.1 to 5 T, taken at the closest experimental temperature to T_{NA}. These scans represent the effective transverse resolution at different field strengths and their width $\Delta q_M(B)$ is closely related to the mosaicity width at the transition. It is important to note that the 5 T scan is several times sharper than the longitudinal resolution $\Delta q_\parallel$ and is essentially limited by the instrument, ($\Delta q_M(5\,T) \sim \Delta q_\perp$). The use of a 5 T field improved the effective transverse resolution by 80 times compared to a 0.1 T field [12] and by 60 times compared to a 0.25 T field [13]. Clearly in the temperature range of these experiments the effects of sample mosaicity are largely eliminated with the use of a 5 T field.

Critical behaviour of D6.15AOB was studied in magnetic fields, $B = 5$, 0.5, and 0.25 T over $\sim$3.5 decades of reduced temperature, $t = (T - T_{NA})/T_{NA}$. The data were first analysed without mosaicity correction by simultaneously fitting both $q_\parallel$ and $q_\perp$ scans to the convolution of the structure factor with the instrumental resolution function. We used the well-established structure factor given by the modified Lorentzian with the empirical fourth order term in $q_\perp$ direction [19]. The fitting yielded the values of $\xi_{\parallel,\perp}$ and the smectic susceptibility σ_o for every temperature point. Figure 4 shows log–log plots of dimensionless quantities $q_o\xi_{\parallel,\perp}(t)$ and $\sigma_o(t)$ where q_o is the nearly temperature-independent smectic wave vector $\approx 2\pi/d$, where d is the layer spacing. The 5 T data lie on straight lines indicating single power-law divergences $\sigma_o \propto t^{-\gamma}$,

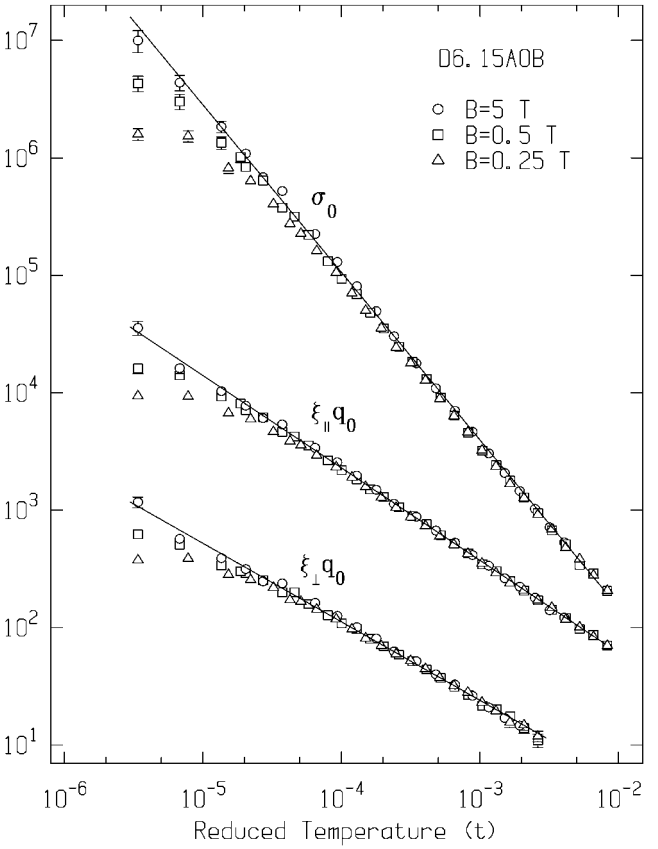

Figure 4. Log–log plots of $q_o\xi_{\parallel,\perp}$ and σ_o vs. reduced temperature t for D6.15AOB without a mosaicity correction at different fields ($q_o = 0.237\,\text{Å}^{-1}$). The solid lines are the single power-law fits for the 5 T data only. The bending of the low field data at $t \lesssim 10^{-5}$ is an artifact of mosaicity.

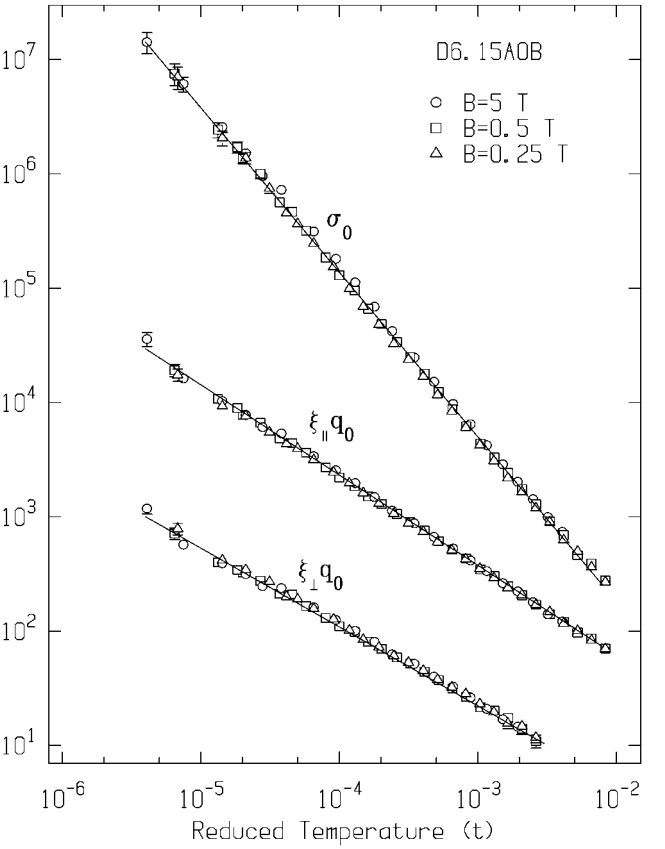

Figure 5. Log–log plots of $q_o\xi_{\parallel,\perp}$ and σ_o vs. reduced temperature t for D6.15AOB at different fields. The low field (0.5 and 0.25 T) data were corrected for mosaicity using the 5 T results as a reference. The solid lines are the single power-law fits with the exponents given in the text.

$\xi_\parallel \propto t^{-\nu_\parallel}$, and $\xi_\perp \propto t^{-\nu_\perp}$ with the corresponding critical exponents $\gamma = 1.46 \pm 0.04$, $\nu_\parallel = 0.79 \pm 0.02$, and $\nu_\perp = 0.69 \pm 0.02$. As expected, no mosaicity effects can be seen in the 5 T results. In contrast, the low field data at 0.5 and 0.25 T clearly show the signature of mosaicity. Far from the transition, where the mosaicity effects are insignificant, the values of $\xi_{\parallel,\perp}$ and σ_o for high and low fields are the same. However, as one approaches the transition, around $t \leq 10^{-5}$, the effects of mosaicity become important and cause the bending of $\xi_{\parallel,\perp}(t)$ and $\sigma_o(t)$ away from the 5 T data. *This bending is a pure artifact of mosaicity* and has nothing to do with crossover behaviour or a weakly first-order transition [5].

To correct the D6.15AOB data for the effects of the sample mosaicity, the smectic structure factor was convoluted with the instrumental resolution function and the sample mosaicity modeled by a Gaussian distribution. The Gaussian mosaicity width σ_M was first set to the width of the sharpest $q_\perp$-scans (i.e., $\sigma_M = \Delta q_M$) as has been done before [12–14]. The corrections for the 5 T data were found to be negligible, in full agreement with our expectations. On the other hand, the mosaicity correction with $\sigma_M = \Delta q_M$ applied to the low-field data resulted in unrealistically large changes in the values of the correlation lengths and the susceptibility. These calculations indicate that fixing the mosaicity width σ_M from the sharpest scan is *not a proper correction for the mosaicity*.

Since the traditional $\sigma_M = \Delta q_M$ correction failed, we tried a different approach. We chose one data point in proximity of the transition and varied σ_M until the corrected values of $\xi_{\parallel,\perp}$ and σ_o became close to the corresponding values obtained with 5 T field. Once such a value of σ_M had been found, it was used to correct the rest of the data. Using this procedure, we obtained an *excellent agreement* (see figure 5) between the corrected low field data and the mosaicity-free 5 T data. However, the value of σ_M necessary to obtain such a good agreement was roughly 3.5 times smaller than

measured Δq_M for both sets of the low field (0.5 and 0.25 T) data. Thus, our results support one of the previously used assumptions that the mosaicity width does not vary with temperature in the N phase, but reveal that the actual mosaicity width is significantly smaller than the width of the sharpest $q_\perp$-scan (Δq_M). This is consistent with the Bouwman and de Jeu [15] assumption that the sharpest $q_\perp$-scan overestimates the mosaicity.

Now, as we have mentioned, Dasgupta [16] suggested that the non-Lorentzian behaviour of the $q_\perp$-scans in the nematic phase was related to the sample mosaicity. Our experiments provided a good test of this assumption. If Dasgupta's argument were to hold, there should be no need for the fourth-order term in the structure factor to fit the 5 T data. However, our studies under 5 T field indicated that the fourth-order term was necessary to obtain acceptable fits [17]. Moreover, the high- and low-field values of the fourth-order term coefficient were essentially the same ruling out any significant effects of mosaicity on the X-ray scattering profile.

To summarize, we have carefully investigated the effects of mosaicity by studying critical behaviour under different magnetic fields ranging from 0.25 to 5 T. The use of a high (5 T) field improved the effective transverse resolution by almost two orders of magnitude over previous studies and allowed us to obtain results, which were essentially *free of mosaicity effects*. The low field data, analysed without mosaicity correction, clearly demonstrated the artifact of mosaicity, which could be mistakenly attributed to crossover behaviour. Using high-field, mosaicity-free results as a reference revealed a new and proper way to correct the low-field data for the effects of mosaicity. No significant effects of mosaicity on the non-Lorentzian behaviour of transverse X-ray scans were observed.

We managed to dissipate only one of the clouds blocking the clear view of the NA transition. Much more work (and not only with X-rays) focusing on measurements very near T_{NA} needs to be done before we can see the entire picture.

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