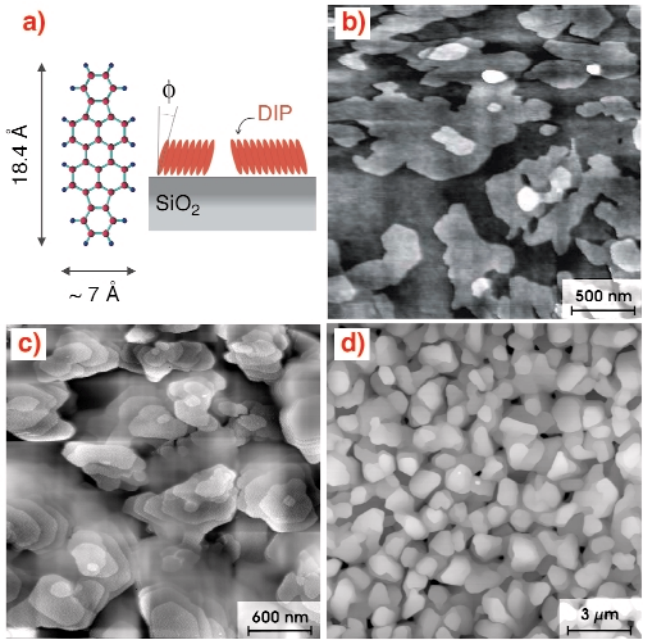

Fig. 1: (a) The molecule DIP ($C_{32}H_{16}$) and a sketch illustrating the formation of tilt-domains; NC-AFM images for films with various thickness: (b) D = 126 Å, (c) D = 1100 Å, (d) D = 9000 Å. An analysis of the AFM images reveals a = 0.628 ± 0.05.

Remarkably, an unusually large growth exponent β = 0.748 ± 0.05 of the DIP film (see **Figure 2**) is found, which is beyond the well-known kinetic limit for randomly deposited material $\sigma \propto D^{1/2}$ Also, $1/z$ = 0.92 ± 0.20 is unusually large. At present, the only model which consistently explains the *rapid roughening* related to the observed scaling exponents involves random spatial inhomogeneities in the local growth rate, which are fixed during the growth process.

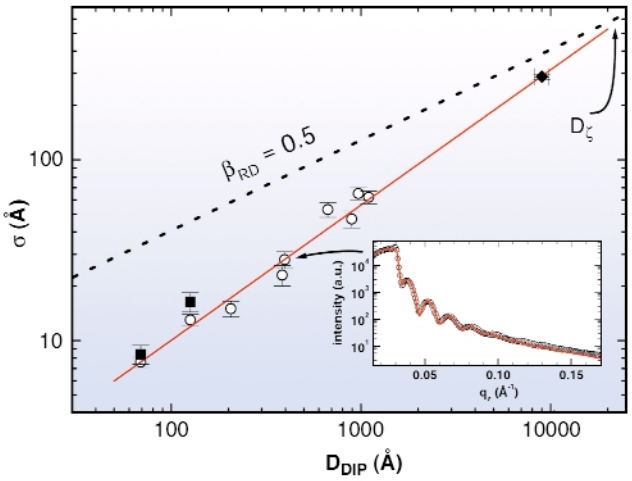

Fig. 2: Log-log plot of σ vs. D and a linear fit to the data which gives α = 0.748 ± 0.05. For D ≤ 1100 Å, X-ray-reflectivity was used to determine σ (O), see inset as a typical example for a sample with D = 396 Å. For some samples the saturation roughness σ has been determined (also) by AFM-measurements (ı = OMICRON AFM, ? = DI AFM). The black dotted line with slope σ_{RD} = 0.5 corresponds to the random deposition limit σ_{RD}, which would be reached at D = D_ζ .

We attribute these spatial inhomogeneities to the tilt-domains of the film (**Figure 1a**). The latter form as a consequence of the shape anisotropy of the individual molecules in combination with the crystalline structure of the thin film (upright standing molecules). We hope that our study will spark interest in detailed investigations into the microscopic origin of rapid roughening in organic thin films to arrive at a more thorough understanding - and control - of the growth mechanisms for this new class of materials.

References

[1] A.-L. Barabási and H.E. Stanley, *Fractal Concepts in Surface Growth* (Cambridge University Press, 1995).
[2] J. Krug, *Adv. Phys.* **46**, 139 (1997).
[3] A.C. Dürr, F. Schreiber, M. Münch, N. Karl, B. Krause, V. Kruppa, and H. Dosch, *Appl. Phys. Lett.* **81**, *2276 (2002)*.

Principal Publication and Authors

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Two-stage Freezing of a Single Top Layer in a Smectic Membrane

Melting in two dimensions (2D) remains one of the unresolved and challenging problems in condensed matter physics. In the defect-mediated theory, the first melting step of a 2D crystal is the dissociation of dislocation pairs. This produces an anisotropic (hexatic) liquid characterised by quasi-long-range bond-orientational order while the positional order is limited to a finite correlation length. Only after a subsequent step of disclination unbinding an isotropic phase is realised [1]. Among the systems with hexatic ordering, smectic liquid crystals are particular suitable for investigations as they can be suspended as membranes of controlled thickness over an opening in a solid frame.

Smectic-A (Sm-A) membranes consist of stacks of liquid layers. Upon cooling an hexatic Sm-B phase may occur, and subsequently a 3D crystalline-B phase (Cr-B) with a hexagonal in-plane lattice and a weak coupling between the crystalline layers. We studied smectic membranes of the compound abbreviated as 4O.8, in which the Sm-A phase proceeds into Cr-B in a layer-by-layer fashion

involving an intermediate hexatic Sm-B phase. With decreasing temperature the surface layers undergo transitions (in °C) Sm-A 61.1 Sm-B 54.5 Cr-B, well before the second set of layers start their own freezing transitions at 51.1°C. Hence, the top layer at each side of the membrane may serve as a perfect model system to study crystallisation of a liquid in 2D.

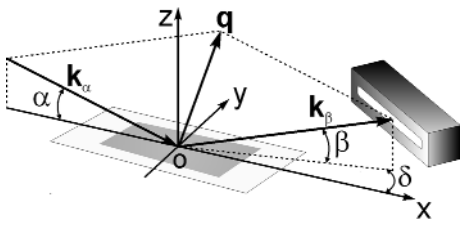

Fig. 1: Scattering geometry with smectic membrane and linear detector.

Grazing-incidence X-ray diffraction has been performed on 4O.8 membranes at beamline **ID10B**. The beam was focussed in the incident plane to about 24 µm and the incident and the exit angles were symmetrically set slightly above the critical angle. A linear detector was mounted parallel to the plane of the sample, catching in a single shot the lineshape associated with the in-plane positional ordering. **Figure 2a** shows for a seven-layer film the X-ray peak at q_0 = 14.3 nm^{-1}, corresponding to local in-plane hexagonal packing. It consists of a relatively narrow diffraction peak from the outermost hexatic Sm-B layers (fitted by a square-root Lorentzian) on top of a broad Lorentzian liquid peak from the five Sm-A interior layers. The integrated intensity of the former part is independent of the membrane thickness, which proves its origin in the two surface layers. The latter peak scales linearly with the number of liquid interior layers and its Lorentzian width $\xi \approx 1$ nm is independent of temperature (**Figure 2b**). With decreasing temperature the positional correlation length ξ of the hexatic top layers increases continuously from about 2.5 nm to more than 40 nm and then saturates. Clearly a pre-transitional growth of ξ is present above the hexatic-isotropic transition at 61.5°C. As we did not observe any thermal hysteresis in the hexatic linewidth, this surface transition is second order. Upon cooling the 4O.8 membrane further, at 55.5°C another transition occurs in the top layers: the hexatic peak condenses into a sharp, resolution-limited peak from the Cr-B phase. This hexatic-crystal transition is weakly first-order with an abrupt change of the in-plane positional correlations.

In conclusion the two-step surface freezing of a single top layer in smectic membranes as seen by grazing-incidence X-ray diffraction agrees qualitatively with defect-mediated theory. However, other measurements do not give singularities as predicted. Hence the 2D melting scenario is probably not universal and the results may depend on the specific interactions in the system.

References

[1] P.M. Chaikin and T.C. Lubensky, *Principles of condensed matter physics* (Cambridge University Press, Cambridge, 1995).

[2] W.H. de Jeu, B.I. Ostrovskii and A.N. Shalaginov, *Rev. Mod. Phys.* **75**, 181 (2003).

Principal Publication and Authors

W.H. de Jeu (a), A. Fera (a), O. Konovalov (b) and B.I. Ostrovskii (a, c), *Phys. Rev. E* **67**, 020701 (2003).

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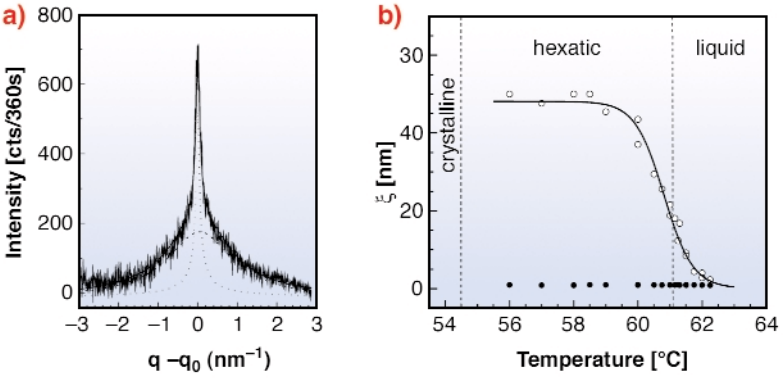

Fig. 2: (a) X-ray profile for a seven-layer membrane at 60°C with outer hexatic surface layers on a 'substrate' of five liquid inner layers. (b) Temperature dependence of the in-plane positional correlation length of the single hexatic surface layers (open circles) and the interior liquid layers (filled circles).