

Isotropic to hexatic fluid transition in untilted phases of fatty acid Langmuir monolayers: a thermo-rheological study

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Two-dimensional (2D) melting is a problem that has attracted the interest of scientists for more than five decades by now. The most accepted theoretical framework is provided by the Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) scenario [1, 2, 3] in which a second order phase transition from the crystalline solid to a hexatic phase occurs, driven by dislocation unbinding, followed by a second transition from the hexatic fluid phase to an isotropic fluid phase, driven by disclination unbinding. Interestingly, the hexatic to isotropic fluid transition can be of either first or second order [4].

Experimental confirmations of such scenario have been found in several quite different physical systems. Regarding liquid systems, probably the most detailed confirmations of such scenario have been found in few-layer freely standing films of smectic liquid crystals [5] and colloidal particle laden interfaces [6]. However, most of the experimental and numerical checks of the predictions of KTHNY framework are based on the characterization of structural properties (positional and orientational order being either short or long range). Interestingly, the KTHNY framework contains also predictions regarding the mechanical properties of the 2D system (elasticity and viscosity) and their variations across both transitions, but much less quantitative experimental and numerical investigations are available on this aspect of the problem. Pindak et al. [5] studied the mechanical properties of thin films of smectic liquid crystals and described their changes across a scenario composed of a second order solid to hexatic transition followed by a first order hexatic to isotropic fluid transition with a coexistence region that shrinks upon decreasing the number of layers in the film.

Fatty acid Langmuir monolayers at the air/water interface in condensed states can be considered as the limiting case of single layer smectic films. Langmuir monolayers are one-molecule thick films of an insoluble surfactant spread onto a fluid subphase. Fatty acids at air/water interfaces are among the simplest systems that can form Langmuir monolayers. Despite their apparent chemical simplicity, fatty acid Langmuir monolayers may show a very rich phase behaviour [7, 8].

Phase diagrams of fatty acid Langmuir monolayers obtained structural (GIXD, [7]) and mechanical (interfacial rheometry, [8]) techniques coincide nicely and draw an scenario that we will describe roughly as follows. In high pressure phases (CS, S, and LS phases) the molecules show no tilt regarding the normal to the interface, while lower pressure phases (L2, L2, and L2 phases) the molecules show a well defined tilt with respect to the normal to the interface. Structural [7] and rheological [8] measurements show that the S and LS phases behave as solid and liquid, respectively. Hence, the S-LS transition appear to be a good candidate for a study of 2D melting in fatty acid Langmuir monolayers.

We will report on an experimental study of the S-LS transition in Langmuir monolayers of eicosanoic fatty acid ($C_{20}H_{40}O_2$) at the air/water interface through the measurement of their mechanical (dynamic moduli) and thermodynamic (thermal expansion coefficient) properties under isobaric cooling. The monolayers are, first, isothermally compressed, across the L2-LS transition line, till the desired interfacial pressure is achieved. Then, the pressure is kept constant while the temperature is decreased at a slow rate (typically about 0.1 K/min). Recording the area between the Langmuir trough barriers as a function of T allows to obtain the coefficient of thermal expansion, while the dynamic moduli are measured by means of a magnetic tweezers interfacial shear rheometer [9].

The main findings can be summarized as follows: i) the LS phase response is predominantly viscous and both dynamic moduli decrease upon decreasing the temperatures, ii) in the transition to the S phase there is an abrupt increase of both dynamic moduli although the temperature range in which the viscous modulus is larger than the elastic one is not small, iii) a bump appears in the expansion coefficient for a slightly lower temperature than the transition temperature seen in the dynamic moduli measurements, iv) experiments at different cooling rates show that for a low enough cooling rate there is no hysteresis in the transition temperature. Hence, the transition from the isotropic to the hexatic fluid appears to be second order.

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