

Anisotropic Molecular Dynamics in the Vicinity of Order-Disorder Transitions in Organic Monolayers

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Variable-temperature scanning tunneling microscopy has been used to observe molecular dynamics in the vicinity of order-disorder transitions in alkane monolayers at the interface between graphite and organic fluids. In crystalline lamellae adsorbed from solution a reversible increase in longitudinal molecular motion with increasing temperature is observed, until the amplitude becomes comparable to the lamella width and the order disappears. A two-dimensional smectic and a columnar phase are observed at the interface with a neat melt and a solution of a particularly long-chain alkane, respectively.

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Order-disorder transitions at interfaces, like melting, roughening, and shape fluctuations, occur in various different condensed-matter systems, including metals, semiconductors, polymers, colloids, or biological membranes. Statistical mechanical models and scaling theories have been employed to investigate the underlying theoretical physics (see, e.g., [1,2]). Scattering techniques like ion scattering [3] and low-energy electron diffraction [4] allowed observation of surface premelting, holographic interferograms have been used to follow roughening transitions at the ^4He solid-superfluid interface [5], and optical microscopy was employed to study shape fluctuations in lipid vesicles as a function of temperature [6]. Scanning tunneling microscopy (STM) has been used before to investigate crystalline monomolecular layers adsorbed from liquid-crystalline ambients [7] or the frozen-in roughness of steps on a vicinal silicon surface [8]. However, for a molecular system a microscopical observation of order-disorder transitions directly on the molecular level has not yet been reported.

Monomolecular layers of long-chain *n*-alkanes, adsorbed at the interface between organic solutions or melts and the basal plane of graphite, are a simple model system for physisorbed organic monolayers. Their adsorption isotherms have been measured [9], and the molecular structure [10–12] and dynamics [13] of crystalline monolayers adsorbed from solution have been investigated recently by STM, indicating that long-chain alkanes may adsorb as epitaxial monolayers at room temperature. In the following we describe order-disorder transitions with increasing temperature and molecular weight and attribute them to anisotropic molecular dynamics within the monolayer.

The STM was homebuilt [14]. It allows scan rates up to 1 ms per line, corresponding to an image recording rate of up to 10 frames (100×100 points each) per second. Real-time video recordings can be used to directly observe sufficiently slow molecular dynamics, like molecular reorientations associated with annealing processes [11, 15]. They also offer a convenient way to identify thermal drifts. For variable-temperature STM studies between room temperature and 120°C the sample was mounted

on a Peltier element, which was heated by a constant current. The sample temperature was measured with a thermoresistor attached with silver paint to the side of the substrate (Fig. 1). High-resolution imaging was performed after a waiting period at a given temperature of a few minutes to an hour, depending on the temperature jump. $\text{C}_{24}\text{H}_{50}$, $\text{C}_{32}\text{H}_{66}$ (Aldrich), and $\text{C}_{192}\text{H}_{386}$ (donation of C. Kröhnke and G. Wenz) were used as received. Melts, or concentrated but not saturated solutions (2 mg/ml for the shorter-chain alkanes and 0.5 mg/ml for the very long alkane) in phenyloctane (Aldrich), were applied to the basal plane of highly oriented pyrolytic graphite (HOPG, Union Carbide, quality ZYB). All images presented here were obtained at quasiconstant height in the variable-current mode, using Pt/Ir tips. The average current was set to 2 nA and the tip bias was chosen, based on prior experience [11], between +1.2 and +1.5 V for alkanes and around 0.1 V for graphite imaging.

First, HOPG was imaged in air without any fluid applied, in order to assure that our simple experimental setup indeed allows atomic-resolution imaging in the specified temperature range. A snapshot image is shown in the inset of Fig. 1. From the video recording the thermal drift between tip and sample was determined to be lower than 1 nm/min at elevated temperatures.

Figure 2 displays STM images of a monolayer of

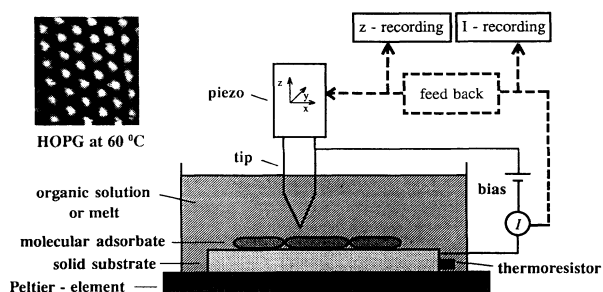


FIG. 1. Schematic of the experimental setup. Inset: Atomically resolved STM image of HOPG in air, recorded at 60°C. Image width, 1.4 nm.

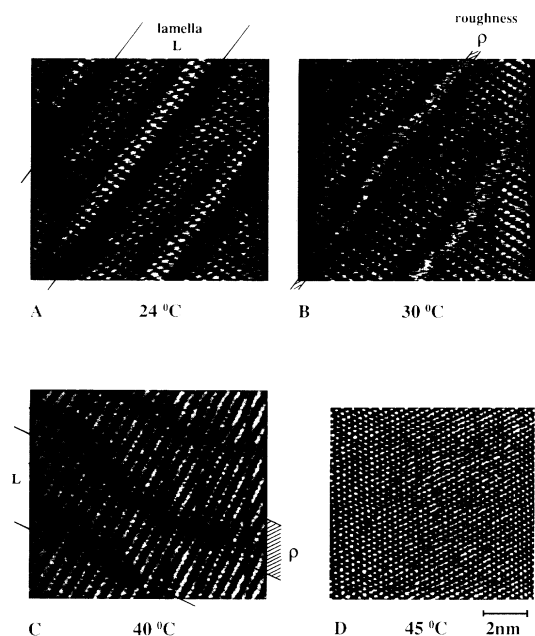


FIG. 2. STM images of a $C_{24}H_{50}$ monolayer at the interface between an organic solution and graphite, imaged at various temperatures.

$C_{24}H_{50}$, adsorbed to graphite from solution. At room temperature [24 °C, Fig. 2(a)] highly ordered lamellae of extended flat-lying molecules are observed. As described before [11–13] they are oriented perpendicular to the lamella boundaries and displaced from lamella to lamella by half a molecular spacing. The separation between the chains within the lamellae is about 425 pm. The repeat distance along an individual molecule is about 250 pm, corresponding to two methylenes. Since the image contrast is determined by both the substrate and the adsorbate, the contrast modulation along the molecules can be attributed to the incommensurability between the linear carbon chains in alkanes and graphite and, in addition, to a possible small tilt between them [11,13].

Upon heating to 30 °C a small but unequivocal dynamic roughening of the lamellae on the order of one methylene unit is observed within the monolayer plane [Fig. 2(b)]. Further heating to 40 °C causes a continuous increase in roughness [Fig. 2(c)], while the spacing between the molecules within a lamella remains constant. At 45 °C no molecular structure on top of the graphite lattice can be observed any more [Fig. 2(d)], as would be expected if the amplitude of the longitudinal molecular motion exceeds the average lamella width. Upon cooling the lamellae reappear and the same images as those shown in Figs. 2(a)–2(c) are observed at the respective temperatures. Qualitatively the same features have been observed for $C_{32}H_{66}$. It must be pointed out that the correlation times for the molecular motions are shorter than our scan time per image, and, therefore, an individu-

al image is not a true snapshot; i.e., the bottom of the image has been recorded about 1 s later than the top. For this reason the lamella width seems to vary substantially within a particular image and remains only constant on average [Fig. 2(c)]. From subsequent images a motion along the main molecular axis of at least 1 nm/s can be deduced. Nevertheless, it is still possible to identify individual lamellae due to the displacement of half a molecular width at the lamella boundaries, indicating a remarkably strong correlation between adjacent lamellae. One way to quantify the disorder is to measure the apparent roughness ρ within an individual image [see Figs. 2(b) and 2(c)], and average over a series of subsequent images.

The results reported above indicate a continuous increase in amplitude of the longitudinal motion of the molecules along their main axis, without a substantial loss of order within the lamellae, or a loss of registry between adjacent lamellae. The consequences of such motion are dynamically roughened lamellae of basically all-trans alkane chains, with only very few conformational defects. Also, the number of solvent molecules possibly incorporated in the monolayer must be rather small. This does not preclude, however, that they play a role by inducing some short-lived free volume in the crystalline layer. At a temperature above about 40 °C, i.e., well below the bulk melting point of 56 °C, the amplitude of the longitudinal motion becomes comparable to the lamella width and no order can be observed.

The proposed longitudinal molecular motion has been suggested before to drive phase transitions in other polymethylene systems, e.g., a solid-solid phase transition in a bulk alkane [16]. Moreover, considerable molecular dynamics and, at the same time, a low amount of intrachain disorder (i.e., gauche conformations) have been attributed to bulk alkanes [17], as well as to Langmuir-Blodgett films of fatty acid salts [18], below their melting point. Finally, a substantial mass transport in mixed alkane crystals [19,20], as well as in polyethylene [21], has been attributed to a considerable longitudinal mobility along the extended polymethylene chains.

A different partially ordered monolayer phase has been observed at the interface between graphite and the melt of neat $C_{24}H_{50}$ at 56 °C, i.e., about 6 °C above its bulk melting point. The STM image (Fig. 3) shows the graphite lattice and superimposed straight lines at a separation which is about equal to the width of the crystalline alkane lamellae. The orientation of the lines relative to the graphite lattice is the same as in the crystalline alkane monolayer phase. Therefore, the image is attributed to lamellae with basically extended molecules in all-trans conformation, with a mobility within the lamellae which is too high to allow direct imaging of individual molecules at STM scan speeds. A similar phase was found for the shorter alkanes $C_{17}H_{36}$ and $C_{16}H_{34}$ at room temperature [10,22], which for these materials corresponds also to

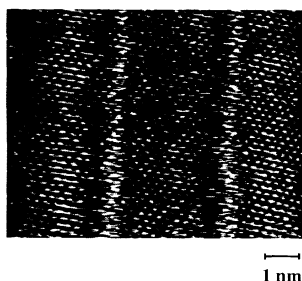


FIG. 3. STM image of a $C_{24}H_{50}$ monolayer at the interface between its melt and graphite, imaged at $56^\circ C$. The regular hexagonal pattern is due to the graphite lattice, while the vertical lines represent boundaries between alkane lamellae.

several degrees above their respective melting points. A possible type of molecular motion is a small cooperative tilt flip of basically extended molecules. This process has been observed in molecular-dynamics simulations, as well as experimentally in a crystalline phase of a longer-chain alkane ($C_{50}H_{102}$), where the correlation times were sufficiently slow for a direct observation by STM [13]. It would explain that the orientation as well as the width of the lamellae are equal to the crystalline phase, and it also means that in this phase the amount of gauche conformations is low. As a result of the molecular mobility along the lamellae the phase may be denoted as smectic in two dimensions. It is noteworthy that the lamellae do not roughen. The reason may be the lack of solvent molecules, which at the interface with the solution could provide some short-lived free volume.

A third type of partially ordered phase is observed in monolayers of very long alkanes. We report here on adsorbed monolayers of the longest monodisperse alkane, $C_{192}H_{386}$, which has been investigated so far. At room temperature no ordered phase could be obtained from solution. However, at $65^\circ C$ a partially ordered monolayer was observed, exhibiting areas with a very high degree of orientational order (Fig. 4). We denote this phase as columnar, since it exhibits a well-defined spacing between the molecules, while we cannot identify chain ends along them. The latter can be attributed to a considerable molecular mobility along the main molecular axis. The transition from a crystalline to a columnar phase upon increasing chain length can also be reproduced with an excluded-volume theory for a dense system of hard spherocylinders [23]. Experimentally, in $C_{50}H_{102}$, which is the longest alkane imaged so far by STM, both crystalline as well as only orientationally ordered phases were observed [12], indicating that this chain length marks the transition region. The orientational order even in very long polymethylene chains is reflected in the fact that the solution crystallization of bulk polyethylene on graphite also starts out with the molecules oriented preferentially parallel to a graphite lattice axis [24].

The work described above demonstrates that variable-

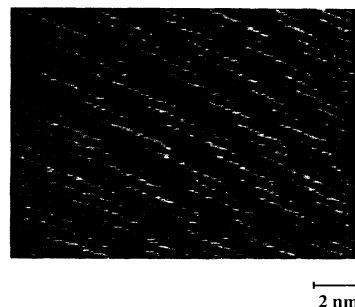


FIG. 4. STM image of a $C_{192}H_{386}$ monolayer at the interface between an organic solution and graphite, imaged at $65^\circ C$. The slight modulation in contrast, perpendicular to the main molecular axes, may be attributed to a finite angle with the carbon chain axis in the underlying graphite lattice (see also [11,13]).

temperature STM can be used to observe anisotropic molecular dynamics in the vicinity of order-disorder transitions at interfaces. In particular, the results revealed the existence of three different phases with partial order and constrained mobility in organic monolayers at solid-fluid interfaces, which may be described as crystalline with interfacial fluctuations within the layer, as smectic, and as columnar, respectively. Moreover, the molecular mechanism for a temperature-induced order-disorder transition in a crystalline alkane monolayer has been ascribed to an increase in amplitude of a longitudinal molecular motion without a loss of correlation between adjacent lamellae, leading to a progressive dynamic lamella roughening. This process may also be described within the framework of a scaling theory, and our initial data indicate that it should be possible to determine the scaling behavior for a number of related systems.

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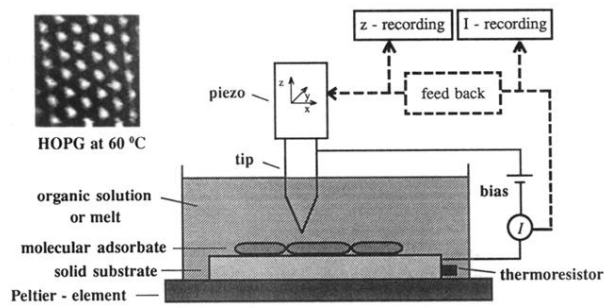


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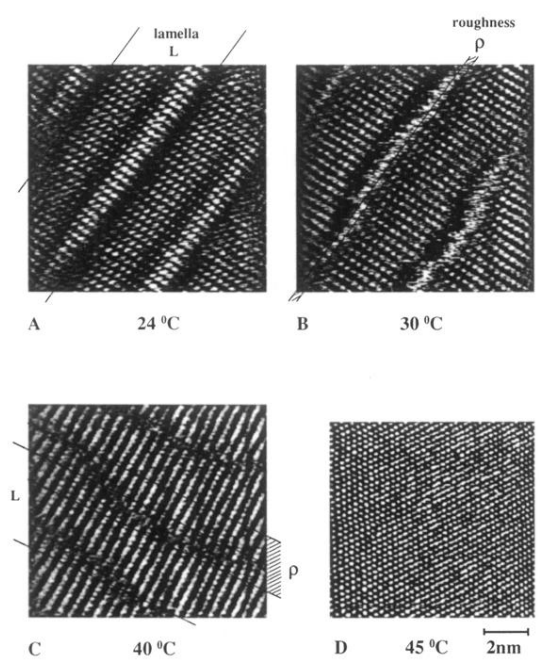


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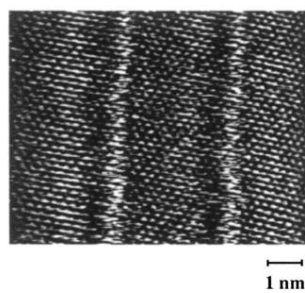


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