Surface Science 289 (1993) 370–380
North-Holland

surface science

Thermally induced disorder and conformational defects of alkane monolayers on graphite

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Received 23 November 1992; accepted for publication 27 January 1993

The two-dimensional molecular lamellar arrangement of long chain alkanes adsorbed on the basal plane of graphite and its thermally induced disordering has been studied by variable temperature scanning tunneling microscopy. Atomic scale resolution of the disordered phase is achieved by studying the quenched high temperature phase. Overall as well as conformational disorder, in particular molecular kink defects, have been observed. High temperature snapshots show that the thermal evolution towards molecular disorder proceeds via small longitudinal fluctuations of molecules or blocks of molecules around their average positions. For increasing temperatures, molecular excursions along the long axis of the molecules become larger until eventually the lamellae lose their individuality, accompanied by substantial loss of lateral order.

1. Introduction

Two-dimensional overlayers on solid surfaces constitute a suitable class of systems for studying basic aspects of phase transitions in two dimensions [1]. In this context, a whole set of studies are concerned with the role played by imperfections and vacancies in the ordering–disordering kinetics [2]. These problems have been studied both theoretically and experimentally and should provide fundamental insight on the way originally ordered structures approach disorder. At the solid–gas interface the investigation of physisorbed rare gas adlayers on single crystal surfaces, in particular on graphite (0001) [3] and on Pt(111) [4], has contributed substantially to the understanding of two-dimensional phases and their mutual transitions. In particular the energetics and dynamics of domain wall defects, driving the transition between commensurate and incommensurate solid 2D phases has largely been explored, and a detailed microscopic understanding has been achieved [1,4]. Matter of controversial discussions remains, however, the importance of defects in the 2D-melting transition. In particular the existence of an intrinsic hexatic-like orientationally ordered fluid phase generated by unbinding of dislocation pairs has still not been settled [5].

With the help of novel and improved experimental techniques, namely scanning probe microscopy (e.g. STM, AFM) [6–11] and grazing incidence synchrotron X-ray diffraction [12], it has recently become possible to probe in situ the structure and dynamics of solid–fluid interfaces. Detailed studies at the interface between the basal plane of graphite and organic solutions of long chain alkanes and alkyl derivatives have revealed the spontaneous formation of highly ordered two-dimensional molecular monolayers with lamellar structure. While the presence of ordered monolayers at the solid–fluid interface of alkanes and graphite has been postulated already some times ago on the basis of calorimetric measurements [13,14], only recently have STM images provided detailed real space information on self ordering, in-plane molecular arrangements, as well as on the registry between the adsorbed molecules and the substrate surface [6–11]. Structural defects are easily visualized and even the spontaneous 2D motion of domain boundaries has been observed at the interface of octadecanol [9], didodecilbenzene [10], alkanes [11] and the graphite substrate. These motions are inferred from consecutive STM images recorded at an interval of several seconds. On the time scale of an image, typically 1 s, temperature induced fluctuations mainly appear as blurred domain boundaries [15]. In particular, it is not possible to resolve defects with lifetimes inferior to a few 10 ms. As an example, for long chain alkanes at 325 K in the bulk phase, translational jumps occur about once every 10 ps [16]. Although this value may change slightly for alkanes on graphite, an STM image taken under such conditions would certainly show an information averaged over many configurational jumps.

In this paper, we report on a novel approach to study the thermal disordering of alkane monolayers on the basal plane of graphite by STM. Alkanes, also called paraffins, are hydrocarbons of the C_nH_{2n+2} type, with fully saturated bonds. These rod-like molecules form simple model systems for chain-like molecular compounds and can be used for understanding ordering and chain packing of more complex compounds like liquid crystals, lipid layers and even polymers. Contrary to a recently published approach [15], where the interface is probed at high temperatures (above room temperature), we only perform STM at room temperature or below, after the sample has been submitted to well defined thermal treatments [17]. In order to generate real low temperature equilibrium structures of self-organized alkane monolayers, the graphite–alkane interface system has been carefully annealed. This operation consists in heating the sample to a temperature where thermal motion is sufficient to allow molecular rearrangements. The sample is then cooled at equilibrium (with a very flat temperature ramp) to room temperature or below in order to perform the STM analysis.

In order to study thermal disordering upon approaching the two-dimensional melting of the alkane monolayer, the graphite–alkane interface is thoroughly tempered close to the melting temperature of the corresponding bulk alkane (340–350 K) followed by a rapid temperature quench of the sample. The frozen-in molecular arrangement is subsequently imaged with STM below room temperature. This technique allows us to study in great detail (with atomic scale resolution) the frozen-in conformational disorder of the high temperature phase at a temperature where tip induced effects are negligible.

2. Experimental technique

The variable temperature STM is a homebuilt instrument of the Besocke type [18,19]. The temperature variability from 250 to 400 K is obtained by coupling the sample to a Peltier element. The highly oriented pyrolytic graphite (HOPG) sample is fixed to the sample holder by means of a silver epoxy. The temperature is measured at the interface by a chromel-constantant thermocouple to better than 0.3 K. Electrochemically etched Pt–Ir tips were employed and the images were obtained in the constant current mode with currents of about 1 nA and a tip bias of 1 V. Details of the experimental arrangement will be described elsewhere [20]. Only the highest quality HOPG from Union Carbide is used as a substrate. The interface of the basal plane of graphite and the following even numbered alkanes was studied: $C_{12}H_{26}$ (dodecan), $C_{18}H_{38}$ (octadecan), $C_{28}H_{58}$ (octacosan) from Fluka and $C_{32}H_{66}$ (dotriacontane) from Aldrich, with the following purity grades: > 99%, > 98%, > 97%, > 97%, respectively. Dodecan is used as a solvant for the longer chain alkanes while $C_{18}H_{38}$ is used in a mixture with $C_{28}H_{58}$.

Two solutions have been used in this work:

(1) A mixture of 7.5 mg of $C_{18}H_{38}$ and 11.5 mg of $C_{28}H_{58}$ in 10 ml of dodecan.

(2) 8.5 mg of $C_{32}H_{66}$ in 10 ml of dodecan.

Immediately after cleavage of the graphite sample, two drops of a solution of 2,2,4-trimethylpentane were applied to the sample in the way described by McGonical et al. [7] followed by four drops of one of the solutions described above. To start with well defined initial conditions, the sample with the solution on top of it was annealed to a temperature of about 313 K prior to STM analysis.

In the following discussion of STM images, we should keep in mind that STM provides us with an information that is related to a local density of electronic states at the Fermi energy of the substrate–adsorbate system. The fact that the STM image contrasts of the graphite substrate is enhanced locally by the alkane molecules indicates that the electronic structure of the underlying graphite is modified.

3. Results and discussion

Fig. 1a shows a high resolution STM image of $C_{28}H_{58}$ on HOPG obtained with solution (1). Prior to STM, the sample has been cycled to 313 K and cooled down to 281 K at a rate of −1.0 K/min. STM data aquisition was performed at 281 K, it takes about 6 s to scan a zone 150 × 150 Å^2 corresponding to 512 × 512 pixels. As observed in previous studies [7,9], the molecular layer is found to exhibit a lamellar structure with alkane molecules oriented parallel to each other and perpendicular to the lamellae boundaries. The STM image in fig. 1, however, shows for the first time atomic resolution of the lamellae boundaries as well as of the space in between the lamellae. The pattern is similar although more compact than the ones observed previously [7]. The higher density of this structure appears mainly in the reduced longitudinal spacing between molecules, equal to 1.0 lattice spacings of the graphite substrate rather than ~ 2.0 as in previously observed structures (also observed by us). Subsequent analysis of the underlying graphite shows that the long range molecular

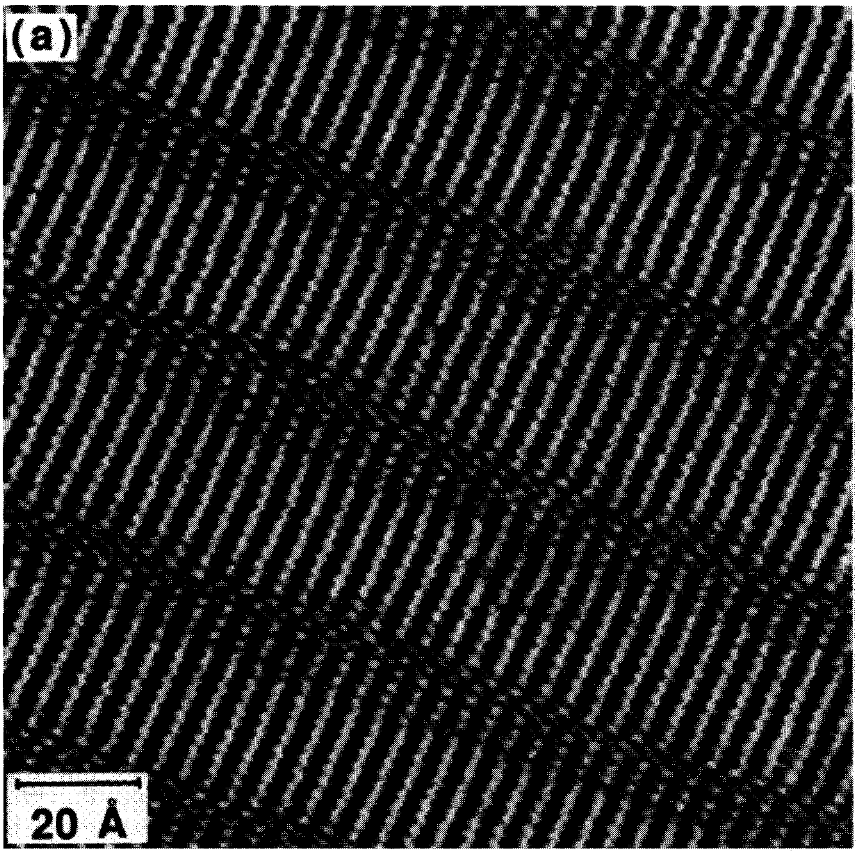

Fig. 1. (a) STM image of $C_{28}H_{58}$ molecules at the interface of the solution and graphite. The sample has been cycled up to 313 K. The image has been recorded at 281 K with a tip bias of 0.77 V at 1.3 nA. (b) Detail showing individual molecules and the lamellae boundaries.

arrangement is commensurate with the substrate although there may be some longitudinal intramolecular mismatch. In the low temperature phase, self-ordered lamellar structures of this type are observed over a very large area, typically 1500 × 1500 Å^2, with very few packing defects. An important and related conclusion of our study is that $C_{28}H_{58}$ is preferentially adsorbed from a mixture of $C_{18}H_{38}$ and $C_{28}H_{58}$ (solution (1)). This point will be developed in further detail in a forthcoming publication [20].

Fig. 1b shows that the alkane molecules arrange themselves in such a way that the methyl groups of adjacent lamellae point towards each other (see also fig 2). The resulting geometrical pattern is characteristic of even alkanes (with an even number of carbon atoms) that have their carbon skeleton parallel to the substrate. The symmetry of alkane molecules (even or odd) is known to play an important role in the packing mechanism [21,22]. The lateral separation between molecular rows in fig. 1 is commensurate with the graphite lattice and has a value of 4.26 Å, smaller than the separation of alkane molecules with in-plane zigzags in the crystalline phase, which is 4.85 Å [22]. This rather constrained packing (see also ref. [7]) is not the only possible configuration, and a packing where the zigzags are perpendicular to the substrate is possible as well [9].

Fig. 1b reveals variable STM contrasts along the molecular chain. While there is a strong enhancement of the STM signal of the substrate atoms in the middle of the chains, the ends appear less contrasted. End-effects have been identified in molecular dynamics simulations [23]

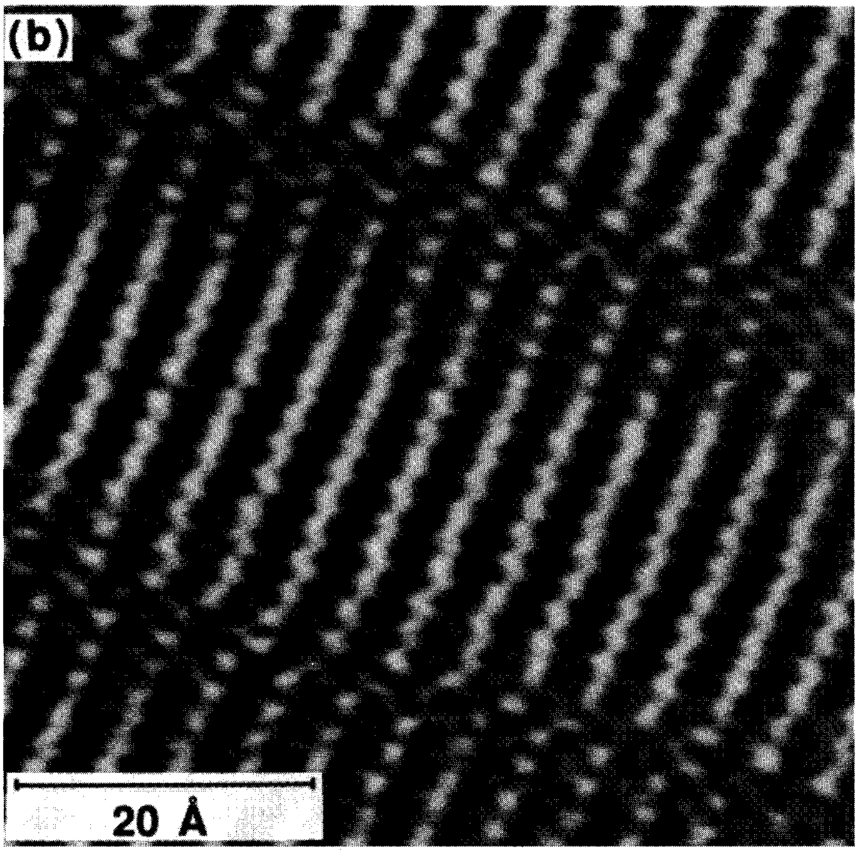

Fig. 1. Continued.

and seem to be due to chain ends that are not well anchored on the substrate. According to the authors of ref. [23], the blurred zones separating adjacent lamellae seen in all previously published room temperature STM studies are due to a higher mobility of the chain ends. This interpretation is consistent with our data although a slight mismatch between the alkane chains and the graphite lattice could also be invoked to explain the variable contrast [9].

The arrangements in fig. 2 have been deduced from our images on the basis of simple geometrical considerations and by counting atoms directly on the images, knowing that only one methylene group out of two produces an enhanced contrast on a graphite substrate. The usual lamellar structures of figs. 2a and 2b are not the only ordered structures observed. Fig. 3 shows an STM image of an interface of $C_{32}H_{66}$ molecules on graphite. After deposition of solution (2), the sample has

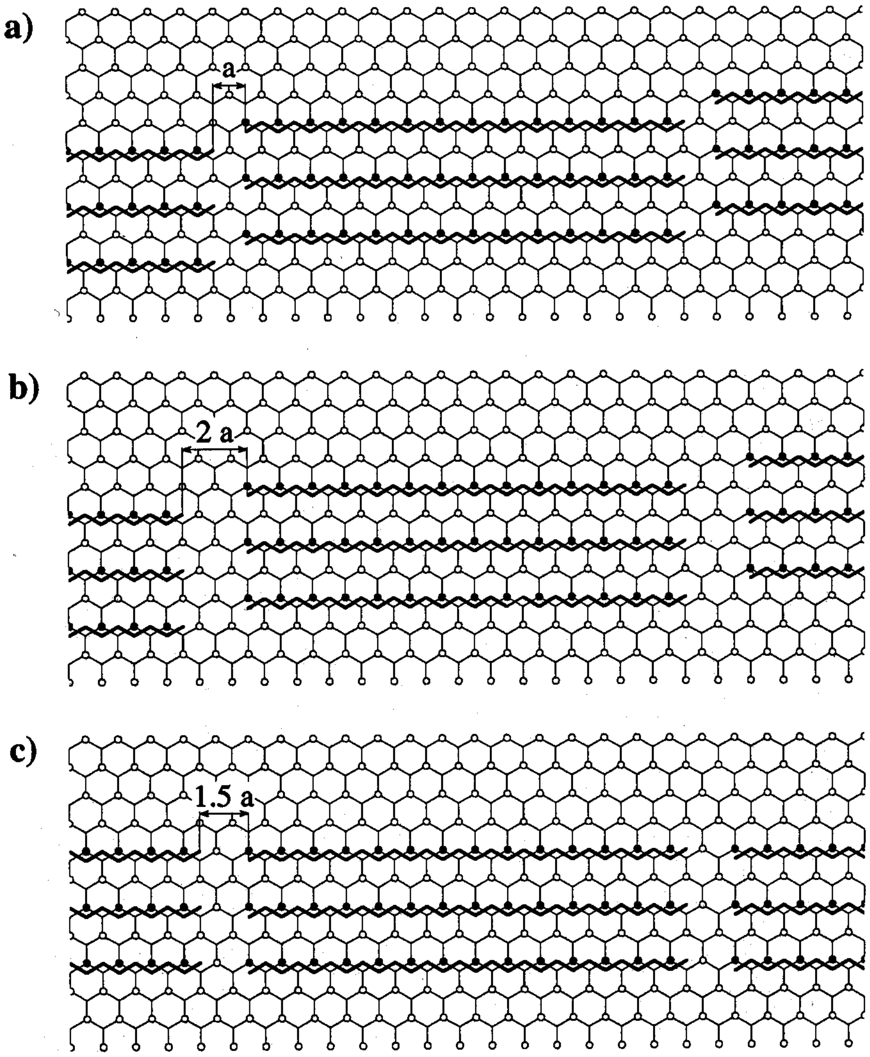

Fig. 2. Schematic representation of the $C_{28}H_{58}$ molecules adsorbed on the basal plane of graphite. The large dots represent sites of the graphite substrate that are enhanced by the presence of the molecules. (a) Representation corresponding to fig. 1. (b) Representation of another often found pattern [7]. (c) Possible configuration for fig. 3. These figures are only schematic and do not imply that the packings with C–C zigzags parallel to the substrate are always preferred.

been submitted to a temperature cycle at 310 K. Subsequent STM analysis has been performed at room temperature. The lateral packing is still commensurate with the periodicity of the underlying graphite lattice (4.26 Å), but longitudinally adjacent lamellae are no longer shifted by half this distance, and only one carbon row out of two of the graphite lattice is occupied, leading to seemingly uninterrupted molecular chains. The distance of the periodic modulation along the molecular chain corresponds to the length of the $C_{32}H_{66}$ molecules on graphite plus 1.5 ± 0.3 lattice units of the graphite substrate. This configuration was seen several times under identical conditions and thus seems fairly reproducible. Within our experimental errors, the distance between alternate carbon atoms along the molecule was found to be identical to the spacing between two hollow sites of the graphite basal plane (2.46 Å).

The variety of ordered structures observed experimentally reflects the rather complex interplay between experimental parameters. In particular, the molecular concentration of single and binary mixtures, and unavoidable temperature gradients within the solution may strongly affect the adsorption process. Since the chemical potential is imposed at the interface, the solution acts as a buffer reservoir for providing or removing molecules from the interface. Therefore, despite the close to equilibrium cooling, metastable states may well appear. In a recent molecular dynamics simulation of alkane molecules on graphite, Hentschke et al. [23] found that small density changes could strongly affect the order pattern of the adsorbate. In particular a small extension

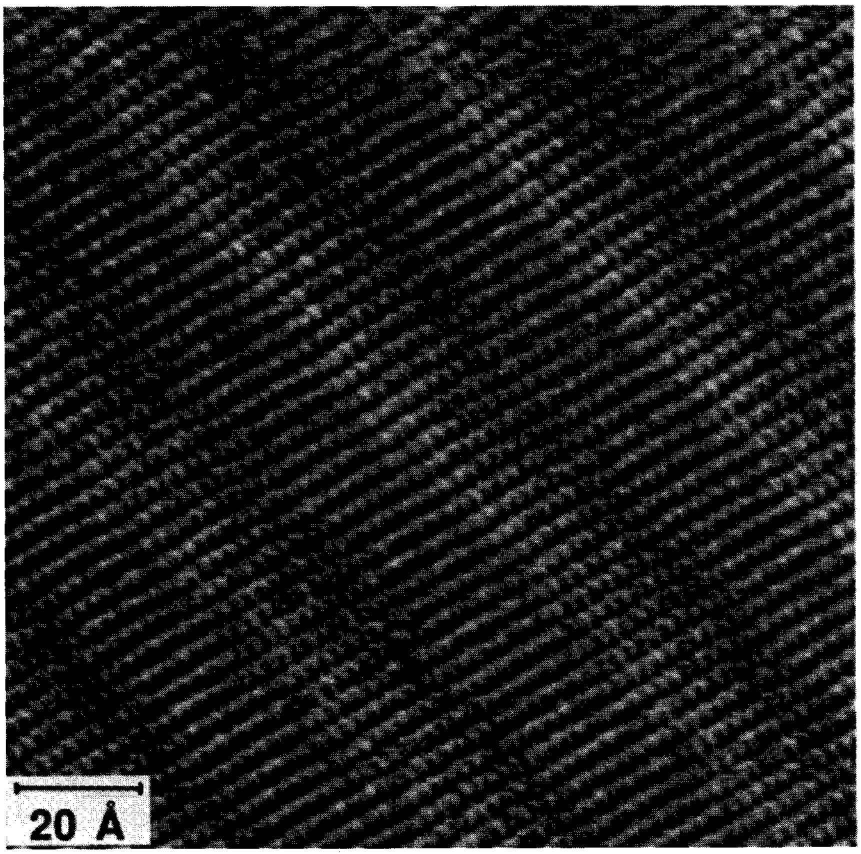

Fig. 3. STM image of $C_{32}H_{66}$ molecules on graphite after temperature cycle to 310 K. The image has been recorded at 300 K. The tip bias was 0.74 V and the current 0.8 nA.

(~ 4%) of the unit cell along the longitudinal direction can produce a transition from the conventional lamellar structure to the fully linear arrangement, in good agreement with our experimental results of figs. 1 and 3.

The appearance of thermally induced disorder in both $C_{28}H_{58}$ and $C_{32}H_{66}$ molecular layers on HOPG has been investigated by the quench technique. It consists in heating up the sample to a temperature close to the bulk melting temperature of the alkane under consideration. The sample is then quenched down to a temperature of 283 K at a rate of about ~ 200 K/min. This is achieved by rapid inversion of the current flowing through the Peltier. During this operation, the STM tip is withdrawn from the solution in order to avoid tip–surface interactions during the heating and the cooling process. These interactions would occur even in the absence of a mechanical contact since the solution would mediate the thermal contact between the sample and the tip. Subsequent STM examination at low temperature allows to study the frozen-in structure of the high temperature phase. The low temperature study of the quenched high temperature phase, presents the additional advantage to minimize field enhanced diffusion due to the tip which starts to become important even for C_{30}-alkanes above room temperature [24].

Figs. 4a and 4b show the interface of $C_{32}H_{66}$ molecules on graphite. The sample has been annealed at 342 K shortly below the bulk melting point and subsequently quenched. STM analysis has been performed at 287 K. Despite increasing

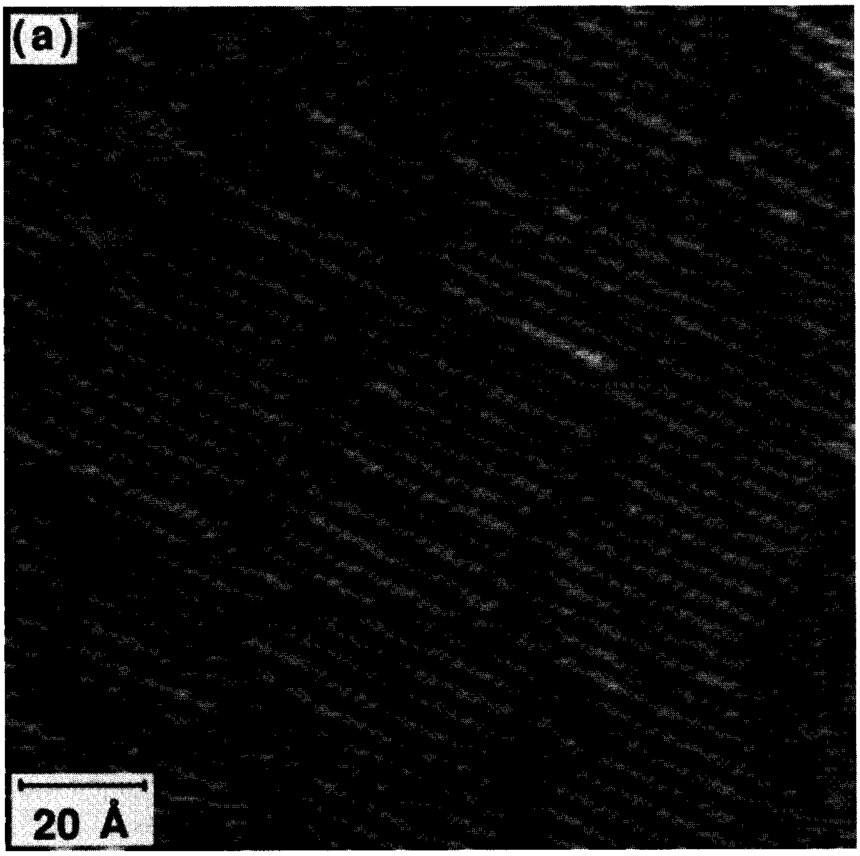

Fig. 4. (a) STM image of the disordered phase of $C_{32}H_{66}$ on graphite obtained after quenching the sample from 342 to 283 K within 40 s. The STM image has been recorded at 287 K with a tip bias of 0.82 V and a current of 0.8 nA. (b) Grain boundary, under the same conditions as before. The inset shows the detail of a kink defect.

disorder, the alkane chains show some registry with the substrate and the contrasts reveal quite well the overall as well as the conformational disorder. The identity of individual lamellae is lost since blocks of molecules are displaced with respect to each other by several C–C distances. These displacements are similar in magnitude to those observed by Askadskaya and Rabe for $C_{24}H_{50}$ on graphite at 313 K (see fig. 2c of ref. [15]). However, while their picture mainly represents a superposition of different thermal configurations, our STM images represent a specific pattern at a given time (snapshot), determined by the random fluctuations in the initial state before the quench. As a result, our fig. 4 reveals many conformational defects (not seen in a thermal average picture), in particular kinks appearing within individual molecules (see inset of fig. 4b). These defects create lateral empty spaces in the plane of the layer, but do not seem to propagate farther than the nearest molecule. Subsequent examination of the graphite basal plane at lower tip voltage shows that the grain boundary apparent in fig. 4b (lower right) is not due to defects in the graphite substrate.

One point we would like to discuss in more detail concerns the original temperature of the frozen-in structure. A priori, the frozen-in structure could correspond to a snapshot at any temperature between the initial temperature and the final temperature, although, the substantial disorder observed in fig. 4 could certainly not be ascribed to a low tempererature structure, at least not below 310 K. To test this point, we changed the starting temperature of the quench process. Starting the quench at 323 K with the

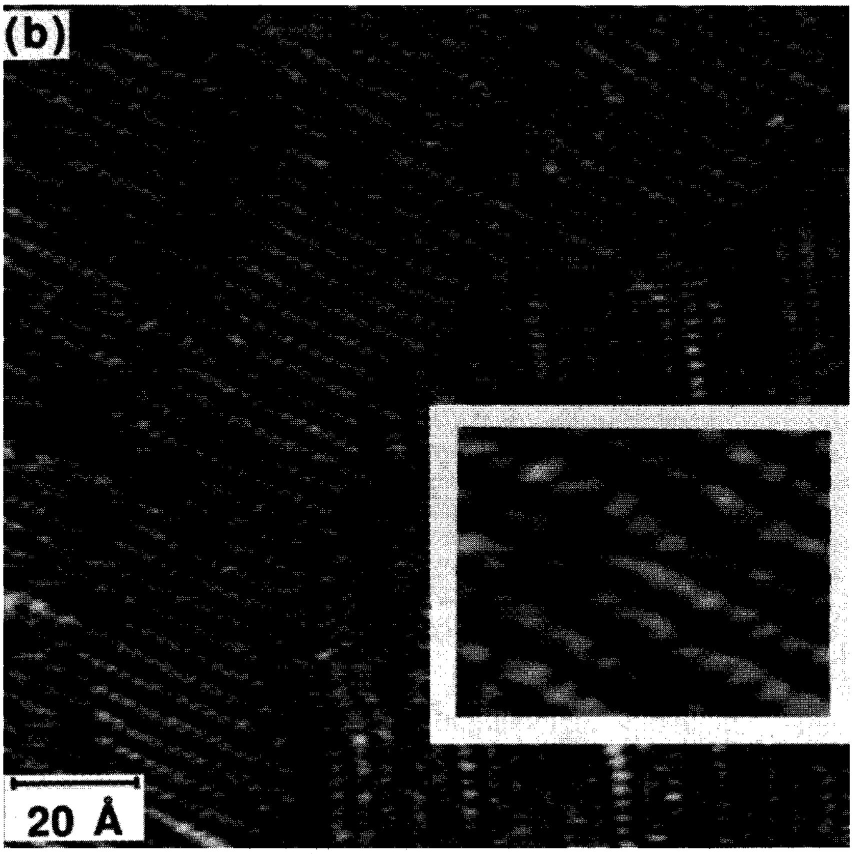

Fig. 4. Continued.

same cooling rate as before, only revealed minimal disorder (few defects within the lamellae). Our opinion is that the frozen in longitudinal disorder observed in fig. 4 is necessarilly a snapshot of a high temperature configuration, say between 342 K (the starting point), and 323 K. The frozen-in structure is quite stable. Both, figs. 4a and 4b are part of a set of images taken at time intervals of several seconds. The frozen-in longitudinal disorder is stable over the whole data set (several minutes). Kink defects on the other hand are only stable over seconds and sometimes disappear after several STM scans indicating that tip induced effects on these highly metastable structures cannot be excluded. The relative stability of these structures is consistent with the fact that longitudinal jumps are highly unprobable at these temperatures, rotational jumps are even less probable and are usually only observed in the so-called high temperature rotator bulk phase just before melting (see ref. [16], and references therein).

Fig. 5 shows the interface of $C_{28}H_{58}$ molecules on graphite quenched under slightly different conditions. The choosen annealing temperature of 346 K is slightly above the bulk melting point of the alkane. The observed loss of intramolecular order is substantial. Although the alkane chains seem to be oriented along well defined atomic rows of the graphite substrate, the lack of defined periodic contrast indicates dramatic longitudinal disorder. This phase shows some resemblance with the hexatic-liquid predicted in 2D melting theories. Because the interaction between the alkane and the graphite surface is strong, it can, however, not be excluded, that the

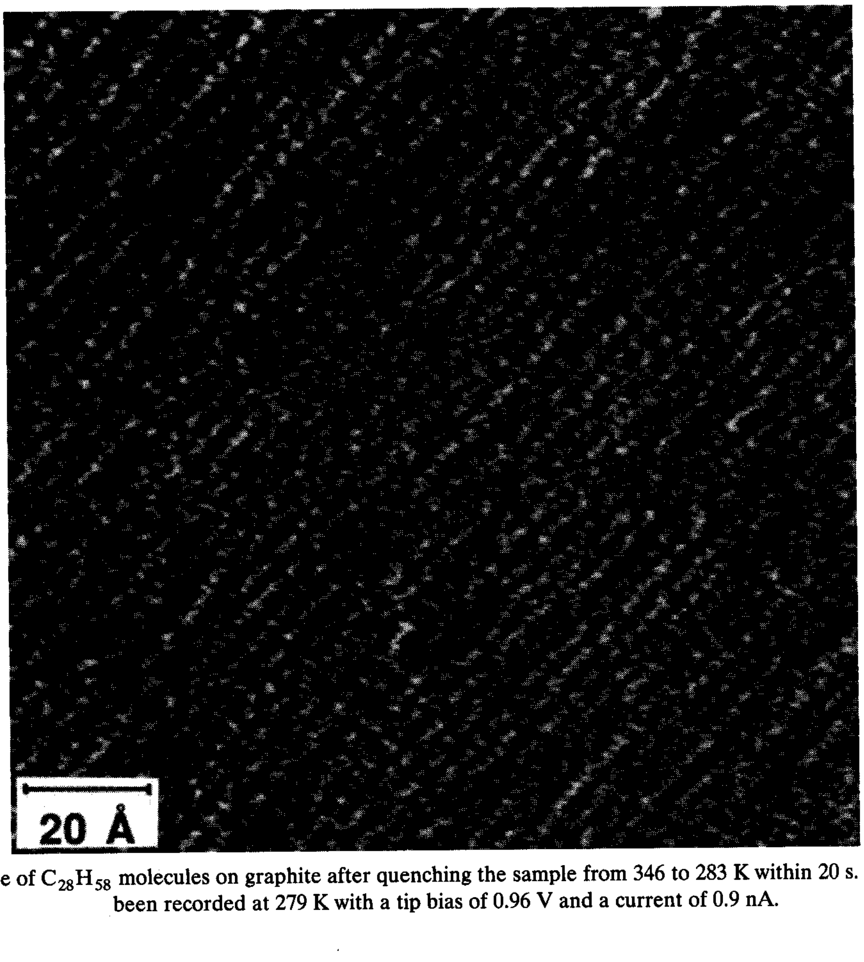

Fig. 5. STM image of $C_{28}H_{58}$ molecules on graphite after quenching the sample from 346 to 283 K within 20 s. The STM image has been recorded at 279 K with a tip bias of 0.96 V and a current of 0.9 nA.

residual orientational order is induced by the substrate.

The formation of kinks in the high temperature rotator phase [25], has been inferred already some years ago from infrared spectroscopic measurements on bulk alkanes [26,27]. To our knowledge, our work presents the first "real space" image of such defects. Maroncelli et al. [27] found that in the rotator phase the highest concentration of conformational defects (mainly gtg′ kinks) is found at the chain ends and decreases exponentially when going towards the middle of the molecule. Our results show that lateral disorder is closely connected with longitudinal disorder, in good agreement with previous observations that defect formation is coupled to solid–solid phase transitions. In the rotator phase of bulk alkanes, longitudinal disorder as well as the intramolecular defects were observed to increase linearly with chain length [28]. This may explain why shorter chain alkanes on graphite still exhibit well defined domains close to the melting temperature of the bulk [7,15].

In conclusion, we have demonstrated the potential of variable temperature STM in identifying packing and conformational defects of alkane molecular layers on graphite as a function of temperature. We have evidenced different molecular arrangements not seen before. Among others we found that the separation between lamellae is subject to changes, depending on the thermal history. At low temperatures, the surface density of adsorbed molecules was found to determine to a large extent the way the molecules occupy the available graphite lattice. In addition to the usual arrangement we found that under certain conditions molecules also form linear chains, one alkane after the other along preferential directions of the graphite substrate. By using the quench technique we were able to study the thermal evolution towards molecular disorder. The scenario is the following: as the temperature increases, first small longitudinal fluctuations of the molecules around their average positions take place. At higher temperatures, the molecules are subject to large amplitude motions along their long axis until finally the lamellae lose their indentity. This last phase is accompanied by an important lateral disorder. While the low temperature phase shows some resemblance with the smectic phase of 3D liquid crystals, the high temperature phase is quite close to a nematic one, since longitudinal order is destroyed and only some degree of orientational order is retained. A better understanding of the graphite–alkane system will, no doubt, contribute to the controversial discussion about the nature of 2D melting.

Acknowledgement

We gratefully acknowledge financial support from the Swiss National Science Foundation.

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image ($\sim$ 6 s in our experimental setup). For the alkane $C_{28}H_{58}$, $C_{32}H_{66}$/graphite systems, studied here, this condition restricted the measurements of STM images in the isothermal quasi-equilibrium mode to temperatures below about 310 K.

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