Langmuir monolayers of C\textsubscript{17}, C\textsubscript{19}, and C\textsubscript{21} fatty acids: Textures, phase transitions, and localized oscillations

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The phase diagrams of Langmuir monolayers of heptadecanoic (C\textsubscript{17}), nonadecanoic (C\textsubscript{19}), and heneicosanoic (C\textsubscript{21}) acids have been determined from pressure-area isotherms, and from direct observations of the monolayers using Brewster angle microscopy. In this paper, we describe the observed domains, textures and phase boundaries for all mesophases presented by these fatty acids between 2\textdegree{} and 45\textdegree{} C. The phase diagrams of the three fatty acids can be superposed moving the temperature scale according to the number of carbons in the tail of the fatty acids. The L\textsubscript{2}/O\textsubscript{1} phase transition, which is not detected through isotherms, was observed in all the fatty acids under study.

At low temperatures, CS, L\textsubscript{2},\textsuperscript{r} and L\textsubscript{2}\textsuperscript{s} phases of C\textsubscript{21} were observed, as well as, the transitions among them. Also, we observed in C\textsubscript{21} a new phase located among the phases L\textsubscript{2}, L\textsubscript{2},\textsuperscript{r} and L\textsubscript{2}\textsuperscript{s}. This phase was found recently, in the relative same place, in the fatty acid C\textsubscript{20} with a tilting azimuth between the nearest-neighbor and the next nearest-neighbor directions. In the crystalline phases of the monolayer of C\textsubscript{21}, L\textsubscript{2},\textsuperscript{r} and CS, we observed localized oscillations. These localized oscillations can be observed by long periods of time. The number of localized oscillations in the monolayer can be modified by long periods of relaxation or by heat treatment. Our results seem to indicate that these localized oscillations are areas with high density of defects, expelling material out of the monolayer. Therefore, they could be important in the events previous to the collapse.

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I. INTRODUCTION

Phase diagrams of Langmuir monolayers of fatty acids on the surface of water have been studied intensively for decades. Nevertheless, significative advances have been obtained only in the last years due to new experimental techniques. X-ray diffraction (XRD), using intense and highly collimated x-rays available from synchrotron, gives the most explicit information about the monolayer organization.\textsuperscript{1} Nevertheless, this kind of experiment is time consuming and expensive to obtain an entire phase diagram. Other powerful techniques have been developed to study monolayer organization, such as, polarized fluorescence microscopy (PFM)\textsuperscript{2} and Brewster angle microscopy.\textsuperscript{3,4} These techniques complement the information given by XRD experiments, since they survey larger scales (>1 \mu m) providing information about homogeneity, textures, structure, and dynamics of monolayers. These optical techniques are quite sensible for observing very fine details in phase transformations such as molecular tilting.

All these new experimental techniques have revealed that singularities in the surface pressure-area isotherms, observed since the time of Stenhagen\textsuperscript{5} and Lundquist,\textsuperscript{6,7} are due to phase changes. Each phase has a different molecular organization. Bibo, Knobler, and Peterson\textsuperscript{8} have shown that molecular organization of condensed phases in fatty acid monolayers can be seen as a direct analog of some specific smectic phases. Thus, each phase can be described in term of four order parameters. These parameters are:\textsuperscript{11,12} (a) positional order; (b) bond or lattice orientational order; (c) tilt order, which is the order of the molecular tilt azimuth with respect to the local orientational order; (d) herringbone order or broken axial symmetry, which is the staggered ordering of the planes of all-trans hydrocarbon chains. For these order parameters a distinction has been made between quasi-long-range order, in which the order decays accordingly to a power law, and short-range order where the order falls off exponentially with distance.

Among the experimental techniques mentioned above, Brewster angle microscopy\textsuperscript{3,4} probably is the best suited to be used in direct observations during compression of monolayers, in a Langmuir trough. This is a technique based on the study of the reflected light coming from an interface illuminated at the Brewster angle, by a laser beam polarized in the plane of incidence (p). When the angle of incidence of the laser beam is the Brewster angle, there is no light reflected, from a clean and perfect interface, i.e., the refractive index changes abruptly form one medium to another. For a real interface which has a transition region where the refractive index changes smoothly form one value to another, the reflected intensity at the Brewster angle is a minimum, but it does not vanish completely. The reflected intensity depends strongly on the interfacial characteristics, such as, molecular density and molecular anisotropy. These properties are particularly modified when a monolayer is located at the interface. Thus, a monolayer on an interface is able to produce reflection of light. In tilted phases, the anisotropy is sufficiently strong to have enough light reflection to make quite visible the mosaic of textures due to tilted domains. In un-
tilted phases with rectangular lattice symmetry, textures are also visible, but with much less contrast. This is probably due to the anisotropy of the unit cell (herringbone alignment). Phase transitions are visible either as a dramatic change in the degree of contrast or as a sudden alteration of the mosaic of textures and domain borders. Many of the textures and domain morphologies found in monolayers using the Brewster angle microscope (BAM), have been explained using model calculations of monolayers with tilted molecules.\(^9,10,26\)

The work of many different groups has contributed to obtain a general picture of the phase diagram of fatty acid monolayers, as well as, the structure of their phases using XRD, PFM, and Brewster angle microscopy. This picture can be reviewed as follows: At very low surface densities, when the average area per molecule, \(a\), is much larger than the cross section area of an isolated molecule, an amphiphilic monolayer behaves as a two dimensional gas. Here, a molecule in a monolayer is still free to show all the conformational entropic contribution without any interference from neighbors. A first-order phase transition from the gas phase to a liquid-expanded (LE) phase is observed upon compression of the monolayer. LE phase is isotropic and molecules are tilted. The gas-phase side of the transition is of the order of \(a = 300–1500 \text{ Å}^2/\text{molec}\), whereas on the LE side \(a\) is of the order of the cross section area of an isolated chain (\(30–40 \text{ Å}^2/\text{molec}\)). A second phase transition to a liquid condensed (LC) state is observed upon further compression of the monolayer; \(a\) is of the order of \(22–25 \text{ Å}^2/\text{molec}\). Here, \(a\) is just barely larger than the cross sectional area of a fully stretched (all-trans) chain. Actually, condensed phase is made up of a variety of mesophases, i.e., phases where the translational order of the molecules is short ranged and the orientational order of the bonds between the molecules is long range. At low surface pressures, there are several phases showing molecular tilt with distinct symmetry. \(L_2\) phase has a collective tilt towards a nearest neighbor (NN), \(14,16,20,22,24,30\) \(L'_2\) and \(O\)v phases tilt to a next-nearest neighbor (NNN) molecule.\(^14,16,20,22,24,30\) The \(L_2/O\)v transition is quite peculiar, since it was found through BAM observations only,\(^17\) since it cannot be detected with surface pressure-area isotherms, due to the lack of an area/molecule change during the transition.\(^16\) At high pressure, there are two untitled phases, the super liquid phase, \(L_S^{19,21,25}\) and the solid phase, \(S^{19,21,23}\) Structure of mesophases can be locally hexagonal (LS) or distorted hexagonal, i.e., centered rectangular (\(L_2\), \(L'_2\), \(O\)v, \(S\)). In addition to mesophases, crystalline phases have been found with a positional quasi-long-range order. They show positional correlations larger than 500 Å. They are \(CS\) and \(L_2\) phases, both are centered rectangular with herringbone order. \(L'_2\) is at two-dimensional crystal with a NN-tilt\(^14\) and \(CS\) is untitled.\(^14,22–25\) At very high pressures, all phases collapse in multilayers. The details of the multilayering process are quite unknown. Textures of condensed phases and the precise coexistence lines between phases have been obtained mainly using PFM and Brewster angle microscopy. This is the case for \(L_2/L'_2\) and \(L'_2/CS\) transitions,\(^15\) for \(L_2/L'_2/L''_2\) transitions,\(^27\) and many more presented with detail by Riviere \textit{et al.}.\(^18\)

Tilt to an intermediate direction breaks the chiral symmetry of a monolayer. The breaking of inversion symmetry allows nonchiral molecules to arrange in chiral structures. Phases in which molecular tilt is intermediate between NN and NNN directions have been observed. Durbin \textit{et al.},\(^13\) have found a intermediate phase (\(I\)) for a monolayer of eicosanoic acid (\(C_{20}\)) using surface pressure-area isotherms and x-ray diffraction. These authors also found that the transition from \(I\) phase to an NN-tilted structure is first order, with a \(\sim 60^\circ\) change in the tilt direction, whereas, the transition to an NNN-tilted structure is apparently continuous.

In this paper, we will present a detailed study to obtain all the boundaries in the phase diagrams of three fatty acids: Heneicosanoic (\(C_{21}\)), nonadecanoic (\(C_{19}\)), heptadecanoic (\(C_{17}\)), in the temperature range of \(2–45^\circ\)C. A partial phase diagram of \(C_{21}\) has been presented by Fischer \textit{et al.}\(^29\) Also for \(C_{19}\), Teer \textit{et al.}\(^28\) have presented a whole phase diagram, which has been obtained by shifting the temperature axis (6 °C per methylene group) from other phase diagrams previously reported.\(^18\) Our phase diagrams were determined using surface pressure-area isotherms and BAM observations. Therefore, in this paper, we will show the mosaic of texture of the phases as observed with the BAM, as well as, the phase transitions between those phases. Fatty acids with an odd carbon tail have been less studied than the case of even carbon tail acids. For the case of \(C_{17}\), we present the change of textures during the phase transformations: \(L_2–O\)v, \(O\)v–\(LS\), and \(L_2–LS\). As far as we know, they are not previously reported. The same phase changes are presented for \(C_{19}\), although we included the \(L_2–L'_2\), \(L'_2–LS\), and \(L'_2–S\) transitions. \(C_{21}\) is the richest phase diagram, since in addition to the mentioned phase transitions, we observed the \(L_2–L'_2\) and the \(L_2–CS\) transformations at low temperatures. Also, we will report here a new intermediate phase for \(C_{21}\), which has been reported quite recently for the case of \(C_{20}\).\(^11\) In addition, we will present an outstanding observation made with the BAM in \(C_{21}\), which has not been reported before, as far as we know. We observed localized oscillations in the monolayer, in the crystalline phases \(L'_2\) and CS. Localized oscillations are related to energy and stress concentration in some relative large areas with high concentration of defects in the monolayer. They could be important in the events previous to the collapse.

II. EXPERIMENT

\(C_{17}\) (97%), \(C_{19}\) (99%), and \(C_{21}\) (99%) were purchased from Aldrich (U.S.A.), and they were used without any further purification. With the aid of an spreading solution, fatty acids were spread onto a subphase of ultrapure water (Nanopure-UV) at pH=2. The spreading solution was made with chloroform (Aldrich U.S.A., HPLC). HCl (Merck, Mexico) was used to modify pH.

All monolayers were prepared on a computerized Nima Langmuir–Blodgett trough (TKB 2410A, Nima Technology Ltd., England) using a Wilhelmy plate to measure the surface pressure \(\Pi = \gamma_{0} - \gamma\), i.e., the surface tension difference of the
clean subphase and that of the amphiphile covered subphase. The trough is isolated from vibrations using a pneumatic tube incorporated into a steel base. The barriers are made of polytetrafluoroethylene (PTFE) fitted with stiffening bars defining a working circular area starting at 1000 cm$^2$. All experiments were carried out in a dust-free environment. The speed of compression was in the range of 1–5 Å$^2$/molec.min.

The BAM observations were performed using a BAM1 Nanofilm Technologie GmbH, Germany with a spatial resolution of $\sim 4$ μm. The BAM analyzer gave the best contrast while kept at $\sim 0^\circ$ or $\sim 180^\circ$.

The Nima LB trough and the BAM were placed on a concrete table cemented to the ground floor of our building. Temperature in the trough was kept constant with the aid of a water circulator bath (Cole-Parmer 1268-24, U.S.A.).

III. RESULTS AND DISCUSSION

A. General features

Figures 1–3 show the different phases found for C$_{17}$, C$_{19}$, and C$_{21}$, in the range of temperatures worked in this study (2–45 °C). The coexistence lines were obtained from the temperatures and the pressures, where phase changes do occur. The phase changes were determined from our $\Pi-a$ isotherms and from BAM observations. The three phase diagrams are displaced in some regular fashion. They follow the known rule that the addition of one CH$_2$ group to the tail of a fatty acid, displaces the phase boundaries to higher temperatures by a value in the range of 5–8 °C.

We identified the phases for the three fatty acids studied here, with the aid of the information given for the even carbon tail acids mentioned in the Introduction. The C$_{17}$ monolayer (Fig. 1) presents three phases in the worked temperature range: L$_2$, LS, and the relative new Ov phase. For surface pressures above 35–45 mN/m the monolayer is collapsed. The C$_{19}$ monolayer (Fig. 2) presents five phases in the worked temperature range: L$_2$, L$_2^\prime$, Ov, S, and LS. The monolayer collapses for surface pressures above 45 mN/m, at low temperatures. The collapse occurs at pressures of the order of 70 mN/m for temperatures in the range of 10–25 °C. At higher temperature, the collapse pressure falls down as temperature is increased. As expected, the C$_{21}$ monolayer (Fig. 3) presents the richest phase diagram, because high-density phases can be observed. The phases presented in Fig. 3 are: L$_2$, L$_2^\prime$, L$_2^\prime$, Ov, CS, S, and LS. Here, we also included the $\Pi-a$ isotherm data of Lin et al. In this phase diagram, we also show a phase I, where the boundary with L$_2$ was obtained with isotherms and the boundary with the L$_2^\prime$ was determined with BAM observations. In the same relative place of the phase diagram, recently, Durbin et al. have reported a similar phase for C$_{20}$ fatty acid using XRD. The molecular tilt of this new phase is intermediate between NN and NNN directions. They named this phase as I phase, so we did the same for C$_{21}$. The C$_{21}$ monolayer presents the collapse when $\Pi$ reaches values of the order of 60 mN/m.

In BAM images, all tilted phases L$_2$, Ov, L$_2^\prime$, and L$_2^\prime$ show the same general pattern: A mosaic of irregularly shaped domains. The contrast between domains comes from the different tilting of the all-trans hydrocarbon tails. This contrast is relatively strong in tilted phases. Each shade of
gray corresponds to a different azimuthal tilt direction. At low pressure, in $L_2$, the contrast is quite large and the mosaic pattern is outstanding. As temperature is lowered the contrast decreases. Also, at low temperatures, the number of mountain-shaped structures and Newton rings increase. These structures are multilayers defects, since it is not possible to focus them, and they do not change rotating the polarizer. The number and occurrence of these mountain-shaped structures or Newton rings depend on how the monolayer is compressed. We will come back to this issue in more detail below. The untitled phases $S$ and $CS$ also present a mosaic of textures, but with a very low contrast between their domains. Here, each shade of gray corresponds to a different lattice orientation of the all-trans alkane chains (herringbone order). $LS$ is a phase where the contrast is completely lost in BAM images. This is consistent with the untitled hexagonal lattice symmetry of this phase. Here, the molecules could be rotating freely (rotator structure)."},"B. Phase transitions

We have followed here, the method for grouping monolayer phase transitions used by Rivière et al.\textsuperscript{18} Therefore, our phase transition observations were grouped into four categories described below. Some phase transitions will be illustrated with BAM images. In all the images, we have a few multilayer defects in the field of view (like Newton rings or mountain-shaped structures), which do not disappear during the phase transition under discussion. These defects help us to assure that we are making observations in the same area of the monolayer, before and after the phase transition.


$L_2$–LS and Ov–LS transitions are visible as a lost of contrast when they are observed with the BAM, due to the lack of tilting in the hexatic LS phase. This lost of contrast corresponds to a big kink in the isotherm. These transitions are reversible and the mosaic pattern of the tilted phases are recovered on decompressing the monolayer, despite the domain boundaries in the LS phase have disappeared. The lost of contrast is gradual, but rapid in both transitions. This is consistent with a continuous decrease in the anisotropy of the monolayer. Figure 4 shows a compression–expansion cycle along the transition Ov–LS, for C$_{17}$. The defects shown in Fig. 4 for this monolayer do not change during the transition. Thus, in the field of view confined by those defects, we can easily see domains of the Ov phase with different shades of gray, at a pressure slightly below the transition pressure. These domains disappear when the transition Ov–LS is reached and they reappear when the pressure drops again.

In C$_{17}$ or C$_{21}$, it is not so easy to see domains growing in the $L_2$–LS phase transition, as in the case of C$_{19}$. In C$_{19}$, it is easy to see how the domains of the new phases ($L_2$ or Ov) grow when the monolayer is relaxing from above the coexistence line, i.e., when pressure drops and the monolayer reaches the coexistence line slowly. Figure 5 shows the lost of domains form $L_2$ phase when the pressure is increased and the $L_2$–LS transition is reached.

We classify $L_2$–LS and Ov–LS transitions as first order. Because, when the monolayer is relaxing from slightly above the transition line, it is possible to see domains of the new tilted phases growing steadily. Also, there is hysteresis in the pressure of the phase change.

In C$_{21}$ and C$_{19}$, the $L_2$–LS phase transition is seen in the BAM as a sudden loss of contrast. This transition also corresponds to a big kink in the isotherm. The images are quite similar to the case of $L_2$–LS or Ov–LS, therefore, a specific observation of this transition is not presented. It is usual to observe in the $L_2$–LS phase transition, the shortening of the $L_2$ domains during the compression. Nevertheless, the growing of domains is more clearly seen when the monolayer is relaxing from the LS phase. We classify this transition as first-order transition.

2. Transitions between a highly anisotropic tilted phase and a weakly anisotropic untitled phase ($L_2$–CS, $L_2$–CS, and $L_2$–S)

In these phase transitions, the decrease in the level of contrast among domains is a common feature. However, the weak anisotropy in $S$ and CS phases is visible to the BAM yet. In C$_{21}$, the $L_2$–CS transition can be seen in the BAM as a rapid growing of irregular domains many of them elongated and some with a needle shape [see Figs. 6(a) and 6(b)]. Isotherms show this transition with a big kink. Relaxing the monolayer from the CS phase allows us to see how the needle-shaped structures start to grow up to irregular domains, when the border of the $L_2$ is reached. These needle-
shaped structures also appear in the transition $L_2^\alpha - CS$ [see Fig. 6(c)]. We classified both transitions as first order.

The $L_2^\alpha - S$ transition can be seen as a big kink in the isotherm and as a change in level of contrast in the BAM. This change is not as rapid as in the $L_2 - LS$ transition. Nevertheless, contrast is not lost completely as in the $LS$ case. It is possible to see a mosaic pattern with a very low difference in contrast among domains, as well as, how the contrast is advancing in the field of view along the transition. We classify this transition as first order. BAM observations made possible to estimate where the boundary between $S$ and $LS$ phases is, due to the difference in contrast between $LS$ and $S$ phases. This boundary is shown in Fig. 2 for $C_{19}$ ($\sim 8.6 \, ^\circ C$) and in Fig. 3 for $C_{21}$ ($\sim 19.50 \, ^\circ C$).

3. Transitions between two anisotropic phases with approximately the same degree of anisotropy ($L_2 - L_2^\alpha$, $L_2^\alpha - L_2^\beta$, $L_2 - L_2^\alpha$, $L_2 - O_v$, and $S - CS$)

Transition from $L_2$ to $O_v$ is very clear using the BAM, whereas, it cannot be noticed with isotherms. In spite of the change from NNN to NN tilting, as mentioned in the introduction, during the transition the surface area/molecule does not change. Figure 7 presents an example of this transition for a monolayer of $C_{17}$, which is compressed and decompressed on several occasions, around the transition line. The change of domain shapes is evident in these pictures. Most of the times, in this kind of compression–decompression cycles, domains reform almost to the same shapes, suggesting some kind of memory. Figures 7(a) and 7(c) show this feature. Also there, we can observe how the monolayer evolves from domains with boundaries with many sharp kinks ($L_2$) to domains with boundaries with an irregular shape ($O_v$). In $C_{19}$, the contrast change is not so clear as in the case of $C_{17}$, but we can see the same features. In $C_{21}$, the $L_2$ phase is more fluid than in the other fatty acids. Thus, it is more difficult to observe the $L_2 - O_v$ transition. In this case, it is easy to mistake a phase transition with a rotation of the whole monolayer in the field of view of the BAM. Domains
can be seen disappearing steadily from one phase ($L_2$) to the other ($OV$), decompressing the monolayer. All our observations are consistent with a first-order transition, in agreement with the observations of Rivière et al. In C$_{21}$, one part of the $L_2 - OV$ boundary must be almost vertical since, it was impossible for us to catch more experimental points for this phase transition close to 37 °C. See Fig. 3.

The transition from $L_2 - L_2'$ was observed with the BAM in C$_{19}$ and C$_{21}$. This transition is characterized by a change of domain shapes. The contrast between domains is low but clearly visible, as well as the phase transition. These features can be seen in Fig. 8. The low level of contrast is due to the same degree of anisotropy in both phases. We can see how rapid domains grow, decompressing the monolayer. We classify the transition as first order, however, the lack of contrast between domains does not allow to see the growing of domains as clearly as in other cases previously mentioned.

Compressing the $L_2$ phase of C$_{21}$ fatty acid, at low temperature, allowed us to reach the outstanding phase transition
Isotherms show this transition as a small kink. Here, suddenly, an irregular change of phase front passes along the field of view of the BAM. This front modifies the mosaic of domains. An observation of these events is presented in Fig. 9. The front travels quite rapid, but at a finite speed in the range of 150–550 μm/s. In some cases, previous to the pass of the front, a deformation of the domain pattern is observed. In other cases, it is possible to catch how the change of phase grows up from some regions, like a growing tree, propagating the change of phase front to rest of the field of view. Decompressing the monolayer, the domain pattern of \( L_2 \) changes in a way which recalls a melting process. We classified this transition as a first-order transition.

\( \text{FIG. 8. Phases observed with the BAM close to the } L_2 - L_2'' \text{ phase transition.} \)

\( \text{FIG. 9. Front passing along the field of view of the BAM in the } L_2 - L_2'' \text{ phase transition at } T = 2.2 \text{ °C and } \Pi = 5.3 \text{ mN/m.} \)

\( \text{C}_{19} \) at \( T = 6.4 \text{ °C and } \Pi = 23.1 \text{ mN/m:} \) (a) \( L_2 \) phase and (b) \( L_2'' \). \( C_{21} \) at \( T = 21.0 \text{ °C and } \Pi = 26.5 \text{ mN/m:} \) (c) \( L_2 \) phase and (d) \( L_2'' \). In both cases, we can see the same place in the monolayer, if we use the defects as a guide to the eye. Defects do not changed during the phase transition.

\( L_2 - L_2'' \).
to another mosaic of domains, also with a very low level of contrast among domains. However, this transition is quite clear, and BAM images allow to see the needle-shaped domain characteristics of the CS phase. Isotherms show this transition with a small kink. In the $L_2^{*}$–$L_2^{1}$, we also observed a similar change from a mosaic of irregular domains to another mosaic of irregular domains. However, in this case the change occurs more rapid, and the level of contrast in $L_2^{*}$ is lower than in $L_2^{1}$.

4. Transitions between tilted phases (NN or NNN) to some intermediate position

As mentioned above, all our observations suggest that there is a phase $I$ in C$_{21}$, with an intermediate tilt between NN and NNN directions. One phase of this kind was observed in the same relative place in C$_{20}$, by Durbin et al.$^{13}$ In the present work, the phase transitions $L_2 - I$ and $I - L_2^{1}$ were detected in several isotherms as small kinks. Nevertheless, they are not so clear to be a conclusive evidence. $I - a$ isotherms showing these kinks are presented in Fig. 10. The transition between $I - L_2^{1}$ can be observed easily with the BAM. An example is shown in Fig. 11. There is no big change in contrast along the field of view during this transition, although, there is a clear change in the mosaic of domains. In some cases, it is possible to observe how domains grow.

Our borderline for the $L_2 - I$ transition agrees with experimental points of Lin et al.$^{14}$ In the isotherms of those authors, there are some small rounded kinks slightly above their $C - D$ transition, in the temperature range of 7.0–8.5 °C. That could correspond to the $I - L_2$ phase transition. Nevertheless, this is not clear from their isotherms. They did not make any comment about this feature. Our observations with the BAM did not allowed us to give a clear-cut transformation line. This is rather a continuous transition, where some light gray domains darken slowly becoming dark gray domains. This goes into the direction of a second-order phase transition. Our observations about the order of the phase transitions do not agree with the work of Durbin et al.$^{13}$ They classify them in the reverse way, i.e., $L_2 - I$ as a first-order and $I - L_2^{1}$ as a second-order phase transition.

C. Localized oscillations

In crystalline phases of the C$_{21}$ monolayer, i.e., $L_2''$ and CS, it is possible to observe localized oscillations. These are localized holes surrounded by Newton rings, which are blinking, i.e., they appear and completely disappear suddenly in the same place of the monolayer. They can be observed along the monolayer at several parts of the field of view of BAM. In Fig. 12, we present an example of these localized oscillations in four different images, coming from the same area of observation in the monolayer.
a second. Here, some localized oscillations are seen in one of
the images, but not in the others. We were unable to measure
a characteristic time of oscillation, because the period can go
form a half of a second to many oscillation per second, de-
pending on the chosen localized oscillation. The central part
of the blinking Newton rings (the holes in the images) has a
diameter size of the order of 23–31 μm. Localized oscilla-
tions can start at low temperatures (≈2–6 °C), and at low
pressures compared with the collapse pressure (≈12 mN/m).
However, as the pressure is increased, the number of oscil-
lations sites increases quite notoriously. The oscillations re-
main for a long time until pressure relaxes. In some cases,
these oscillations can be found at the boundary of domains.
We made several experiments to find the origin of those
oscillations. In some of the experiments, we used subphases
previously deaerated to exclude the possibility that bubbles
of air formed during the compression, and localized below
the monolayer, were the origin of the localized oscillations.
Deaeration apparently did not modify the number of local-
ized oscillations when compared with the same experiments,
but using nondeaerated subphases. We also prepared the
monolayer in different conditions to produce a qualitative
modification in the localized oscillation activity. Here, we
make a summary of our experiments: (a) A fully expanded
monolayer was deposited in a cold subphase (2–6 °C), after
a waiting time of the order of 5 h, the compression process
started on. In this experiment, the number of localized oscil-
lations decreased notoriously; (b) A fully expanded mono-
layer was deposited on deaerated warm subphase (45.0 °C),
temperature of the subphase was lowered slowly for 2 h.
When 2.3 °C was reached, the compression process started
on. Here, there was also a notorious reduction of the local-
ized oscillation; (c) A fully expanded monolayer was depos-
ited on a previously deaerated cold subphase (2 to 3 °C), and
compressed after the volatile solvent of the spreading solu-
tion was evaporated. In this experiment, there were many
fixed defects (fixed newton rings), as well as, too many lo-
calized oscillations along all the field of view of the BAM;
(d) A monolayer was deposited on a cold subphase at (2 to 3
°C), subsequently, the monolayer was compressed up to P
= 25 mN/m (~24 Å²/molec.). The next step in this exper-
timent was to increase temperature slowly up 15.5 °C (2 h),
but maintaining fixed the P. In this experiment, initially,
there were too many oscillations, but as temperature was
increased the number of localized oscillations decreased, as
well as, the area of the monolayer, i.e., there was a loss of
molecules in the monolayer. In the same way, as temperature
increased, multilayer defects as bright grains and mountain
shaped structures increased in number. It is important to
mention, that in all experiments if the speed of compression
is increased, the same does the number of localized oscilla-
tions. These results about the behavior of localized oscilla-
tions in C_{21} monolayer suggest that localized oscillations are
big areas with a high density of defects (dislocations, discli-
nations, etc.). Consequently, stress and energy are concen-
trated in those areas. The monolayer apparently relaxes ex-
pelling matter out of the monolayer. Localized oscillations
are quite interesting in themselves and they could explain
some events previous to the collapse. We are making
Langmuir–Blodgett films with monolayers where localized
oscillations are found, to study them with atomic force mi-
croscopy. This study is underway and will be published
shortly.

FIG. 12. Four images of a monolayer C_{21} in a period of time less than a
second, each one showing different localized oscillations. They can be seen
as small holes with newton rings surrounding them. In real time in the
BAM, they look like localized blinking Newton rings. Notice that we are
looking at the same area of the field of view, as it can be assured by the
persistent fixed defects.
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