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Physica A 236 (1997) 105–113

PHYSICA A

Brewster angle microscopy of fullerene monolayers

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Abstract

The aim of this paper is to present a direct observation by means of Brewster angle microscopy of Langmuir films made of C_{60} along the process of their compression. We found coexistence of a gas and a condensed phase at low area densities. Our results agree with the formation of multilayers even at low area densities. We made compressions of the films at several speeds, with rapid compressions we found that the condensed phase formed foam-like structures and circular domains of different sizes at very small area densities.

PACS: 68.10.-m; 82.65.-i

Keywords: Langmuir films; Fullerenes; Brewster angle microscopy

1. Introduction

The aim of this paper is to report on a direct observation of Langmuir films made of C_{60} along the process of compression using Brewster angle microscopy [1,2].

The discovery of the carbon fullerenes [3] has triggered a new field of research where a great variety of new carbon structures have been discovered. The development of a synthetic method to obtain macroscopic amounts of fullerenes [4] enhanced the interest about them. In particular, thin films of fullerenes and fullerene derivatives are of interest because they exhibit several interesting properties [5–9]. But, it is still controversial whether or not C_{60} forms a monolayer at the air–water interface. On the basis of the surface-pressure area isotherms, some authors [10–15] have reported monolayer formation while others [5, 16–25], probably the most, have noted multilayer formation. For those in the latter case, the limiting area per molecule calculated from the pressure-area isotherms yields a value well below that, by a factor of almost three,

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expected for the case of monolayer formation. This lead them to conclude C_{60} tends to aggregate at the air–water interface rather than forming a monomolecular layer. This conclusion is also supported by the lack of a hydrophilic moiety in C_{60} , as well as its readiness to form clusters in solution [23–25]. The controversy has continued, but no one has reported a direct observation of the films obtained in the experimental conditions reported by the different authors.

The absence of a liquid phase is another interesting property of C_{60} . Although, C_{60} is a nearly spherical molecule, its intermolecular potential is not of a Lennard–Jones type. A simple pair potential that should describe the intermolecular interactions of C_{60} has been proposed [26], where the ratio of the width of the attractive well to the diameter of the repulsive core of the potential is much less for C_{60} than for the case of the Lennard–Jones potential. The effect of this short range of the intermolecular interaction has been studied through Monte-Carlo simulation [27]. The results have shown that the sublimation line passes above the liquid–vapor critical point (~ 1798 K) suggesting that C_{60} has no stable liquid phase in three dimensions. This would be the first example of a pure substance that has no gas–liquid–solid triple point. If those simulations are representative of actual C_{60} , direct observation of Langmuir monolayers made of C_{60} should never show an expanded liquid phase, since the expanded liquid phase of a monolayer corresponds to the liquid in three dimensions, at least for the Lennard–Jones case [28]. As we will show below this seems to be the case here.

The formation of highly incompressible and stable Langmuir monolayers of C_{60} at the water–air interface was first reported by Obeng and Bard [10] at temperatures in the range of 5–35°C. They found that the limiting area per molecule calculated from pressure–area (Π – A) isotherms yielded a radius of 5.6 Å for the C_{60} in the monolayer. They concluded that this limiting area was in good agreement with the data obtained from other techniques. Bulhoes et al. [11] have given additional information about the proper experimental conditions to obtain Langmuir monolayers at the water–air interface such as C_{60} concentration, sample size and trough conditions, etc. Although, as mentioned above, there are many authors who have failed to obtain them [5, 16–22].

The C_{60} molecules also formed stable mixed films at the air–water interface with some organic compounds with some amphiphilic character. Some examples can be found in the recent literature as the case of arachidic acid/ C_{60} [10,20,13] and that of octadecanol/ C_{60} [29]. Also, several works have been devoted to obtain Langmuir films of fullerene derivatives. Some important examples can be mentioned, namely, films made of 1-ter-butyl-1,9-dihydrofullerene-60 [17], of $C_{60}O$ and $C_{61}H_2$ [14], of amphiphilic C_{60} carboxylic acid [30], of fullerene derivatives with a great variety of polar addends [31], of azacrown/fullerene complexes [32], and of calixarene/fullerene complexes [33].

Brewster angle microscopy (BAM) [1,2] is a relatively new technique that allows direct observation of the films onto the water/air surface. This technique is sensitive to the surface density and to the anisotropy of phase domains in monolayers. The reflectivity of a planar interface between two media depends on the polarization of the incident light and on the angle of incidence. For a Fresnel interface (an interface where

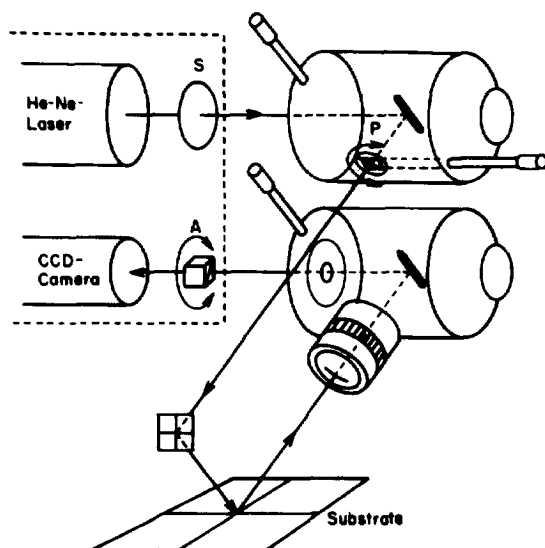


Fig. 1. Schematics of our Brewster angle microscope.

the refractive index changes steeply) and for a polarization where the electric field is in the plane of incidence, the reflectivity vanishes at the Brewster angle. For a real interface, the reflected light intensity has a minimum at the Brewster angle, but does not vanish. The low reflected intensity at the Brewster angle is strongly dependent on the interfacial properties. The reflectivity of a real interface at the Brewster angle for the mentioned polarization has three origins: (a) the thickness of the interface, (b) the roughness of real interfaces, and (c) the anisotropy of monolayers. Fig. 1 shows our Brewster angle microscope in a schematic way. The interface is illuminated at the Brewster incidence ($\sim 53^\circ$) with a polarized laser beam from an He-Ne laser. The reflected beam is received by a microscope. The beam is analyzed by a polarization analyzer and received by a CCD video camera to develop an image of the monolayer. Fig. 2 shows a BAM image of an arachidic acid monolayer close to the end of the coexisting region between gas phase and liquid condensed phase (smectic I, $\Pi \sim 0$, $A \sim 28 \text{ molec./\AA}^2$). Here, we can observe the coexistence of a gas phase (dark areas) and a condensed phase (the denser phase, the brighter to BAM). The condensed phase forms large domains and the gas phase is almost vanishing, since we are close to the end of the coexisting region. In this image, we can see a circular domain of condensed phase with areas of different contrast, due to monolayer domains with different tilting orientations with respect to the plane of incidence.

2. Experimental section

Reactants: C_{60} ($> 99.99\%$ purity) was supplied by Merck Corporation (Tucson, AZ, USA). Chloroform (HPLC grade, 99.9%) from Sigma-Aldrich (Sigma Chemical Co.



Fig. 2. BAM image of an arachidic acid monolayer close to the end of the coexistence region between gas phase and liquid condensed phase (smectic I, $H \sim 0$, $A \sim 28$ molec./ \AA^2). In all the figures the horizontal breadth corresponds to ca. $800 \mu\text{m}$ and the spatial resolution is ca. $4 \mu\text{m}$.

and Aldrich Chemical Co., Inc., USA) was used for cleaning the trough. As subphase for all the Langmuir films, we used Nanopure water (Nanopure-UV, model D7334, Barnsted/Thermolyne, IA, USA). Dry benzene (Chromatographic grade, > 99.7) was used as solvent for the spreading solutions. This was supplied by Merck (Merck-Mexico, Mexico).

Apparatus: All films were prepared on a computerized Nima LB trough (model TKB 2410A, Nima Technology Ltd, UK). All experiments were carried out in a dust-free environment. The Brewster angle microscope (BAM) observations were performed in a BAM1 plus (Nanofilm Technologie GmbH, Germany) using the previously described through. The subphase was at constant temperature within a precision of 0.1 K .

Procedure: Prior deposition onto the water–air surface, we observed the surface with the BAM to verify that there were no surface-active contaminants on it. Fresh solutions of C_{60} in benzene were deposited onto unbuffered water subphase at the working temperature. Small amounts ($5 \mu\text{l}$) of these solutions were applied at several sites on the water surface with a $50 \mu\text{l}$ Hamilton syringe. When $25 \mu\text{l}$ of the solution were deposited on the water surface and after some waiting time to allow for solvent evaporation ($\sim \frac{1}{2} \text{ h}$), observations with the BAM were made to verify that there were no multilayers. Afterwards, we added another $25 \mu\text{l}$ of dilute solution in the same way.

Then, after further waiting ($\sim \frac{1}{2}$ h) the compression started in the Nima LB trough continuously, at 298 K.

3. Results and discussion

C₆₀ was deposited onto the water–air interface and the films were observed with Brewster angle microscopy, during the process of their compression at 298 K. We present here only the case when the spreading solution is quite dilute ($\sim 1 \times 10^{-5}$ M) in the same way as Obeng and Bard [10].

As we noted that speed of compression could be an important parameter to take into account, we made several experiments at the lowest speed of compression allowed in our equipment, $95 \text{ \AA}^2 \text{ molec.}^{-1} \text{ min}^{-1}$. This lowest speed of compression value is actually not as low as commonly used, but it is determined by the very small concentration of fullerenes onto the surface and the lowest compression speed of our trough (minimum speed $5 \text{ cm}^2/\text{min}$). Also, we made experiments in a quasi-static way, i.e., compressing 20 cm^2 and waiting 2 min. In all the cases, at the beginning of compression, we observed, as expected, very wide areas of gas phase (dark areas) coexisting with small irregular grains. The images of the grains were very bright and we were unable to focus them. As the compression proceeds the grains increased in number and size. These events occurred at very early stages in the compression process ($13\,600\text{--}2000 \text{ \AA}^2/\text{molec.}$). This evidence makes clear to us that fullerenes deposited onto the air–water surface tend to form multilayers. Unexpectedly, as we increased the speed of compression, we observed the formation of a very different kind of condensed phase structures. Below, we will describe our BAM observations of several experiments for which the speed of compression was in the range of $560\text{--}180 \text{ \AA}^2 \text{ molec.}^{-1} \text{ min}^{-1}$ ($\sim 20 \text{ cm}^2/\text{min}$).

The compressions of the films started at a very large area per molecule ($\sim 29\,000 \text{ \AA}^2/\text{molec.}$) with a nondetectable surface pressure ($\Pi \sim 0$). Here, we found coexistence of a gas phase and a condensed phase. The condensed phase can be focussed easily and apparently it has a uniform thickness. At the beginning of compression, we observed very wide areas of gas phase (dark areas) and some condensed phase structures forming circular domains (disks) of different sizes and foam-like structures. Examples of those structures are shown in Figs. 3(a) and (b) (the denser phase, the brighter to BAM). In all the figures the horizontal breadth corresponds to ca. 800 \mu m and the spatial resolution is ca. 4 \mu m . The larger circular domains usually showed holes inside (gas phase bubbles), while small domains looked like perfect circular disks. The area where our BAM is in focus is not very large. Thus, some parts of the images shown are not completely in focus. This situation is quite different when one is wandering over the liquid surface with the microscope, since one can move freely and at will to observe in focus every section of a whole structure. The mentioned structures were surrounded by many little disks that are difficult to focus in the whole view because they are very small. Although, they can be observed clearly

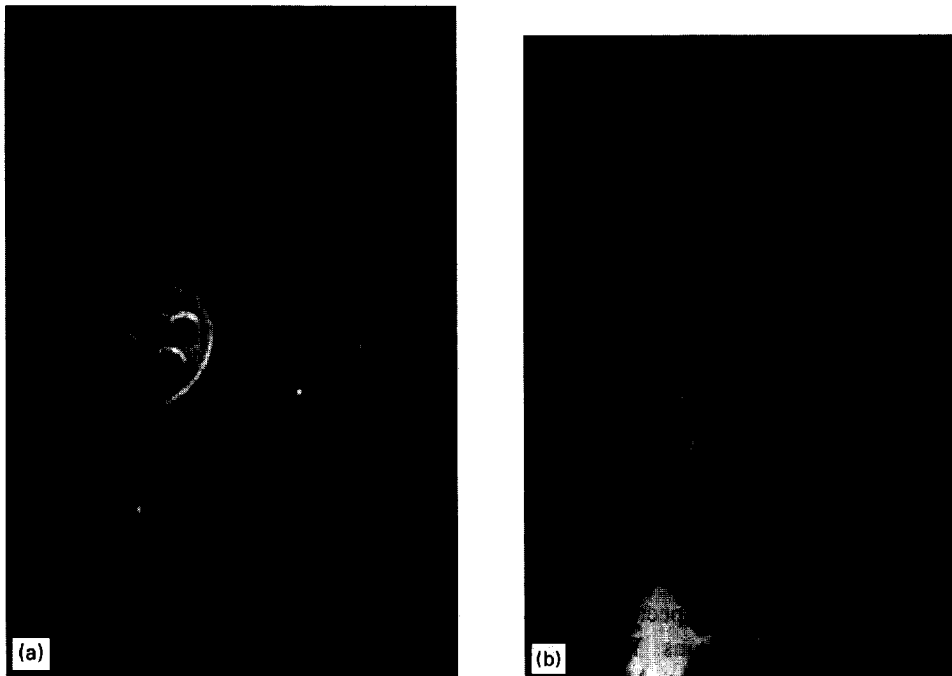


Fig. 3. Films of C_{60} . (a) Gas phase (dark areas) and circular domains of condensed phase (disks) with holes (gas phase bubbles). (b) Gas phase (dark areas) and foam-like structures of condensed phase.

when they are specifically focussed. When many of them are presented in an image, it appears to be spotted, like a superposition of many Newton rings. Those small circular disks can be easily seen in Figs. 4(a) and 4(b). In Figs. 4(a), we can see a beautiful disk with holes of gas phase that has a bright spot probably due to a multilayer seed in the center. In Fig. 4(b), we can see there a very large disk also with circular holes of gas phase inside, surrounded by small disks. Also close to this large disk, there is large spotted area of those very small disks. We believe that those very small disks probably have some holes, but due to the BAM resolution it is not possible to observe them. After some time of observation and continuous compression, larger disks of all sizes were observed, all of them having holes with gas phase. Foam-like structures were observed only occasionally and usually they were quite stable. They did not change much during the observation time. It is not clear what kind of mechanism triggers the formation of those structures. The formation of foam structures by condensed phases is quite unusual. As far as we know, there is only one report of a foam formation by a liquid condensed phase in coexistence with a liquid expanded phase [34]. As far as we know, this is the first report of foam formation by a condensed phase in coexistence with gas phase. There are other examples of structures found during the compression process ($29\,000\text{--}2000\text{ \AA}^2/\text{molec.}$). In one of them we observed stripes with many holes with gas phase. In the center of the stripes usually, there is a bright spot typical of multilayers. It looks like a

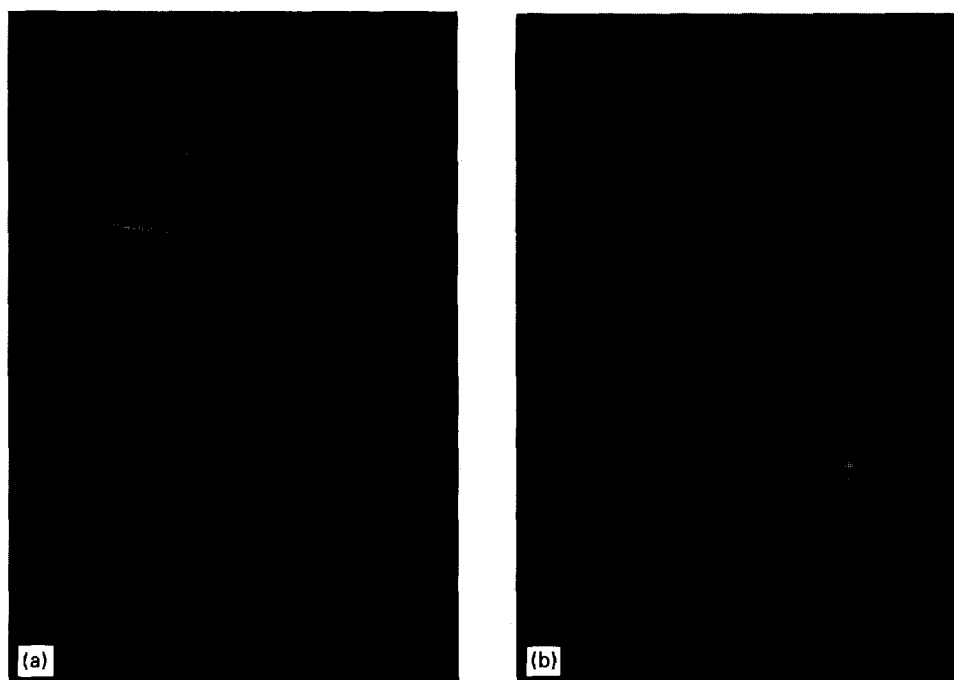


Fig. 4. Films of C_{60} . (a) Disk of condensed phase with holes of gas phase that has a bright spot probably due to a multilayer seed in the center. (b) Big disk of condensed phase, also with circular holes of gas phase inside, surrounded by small disks. Close to this big disk, there is large spotted area of very small disks.

multilayer seed. Most of the observed structures have the same kind of seed (they look as those grains mentioned in the quasi-static or very slow speed of compression). In all the observations we used the beam analyzer to find some evidence of regions of different molecular orientation in the condensed phase. As expected, that was not the case.

As far as the compression continues, the number of small disks increased and as a consequence, the size of spotted areas formed by the small disks also increases. Close to $80\text{--}120 \text{ \AA}^2/\text{molec.}$ we never observed a monolayer. We always observed spotted areas formed with very small disks, now impossible to focus probably because they have different heights. Although, there were some surviving structures of those mentioned above, most of the views were spotted areas. The increase in reflectivity and the difficulty to focus those very small disks convinced us that we were observing small disks with several layers. At a lower area per molecule ($<100 \text{ \AA}^2/\text{molec.}$) the surface appeared as a bright spotted area, clearly not a monolayer. All our observations are consistent with a picture of very small disks that are not prone to coalesce. Therefore, as they are forced by compression to coalesce, they prefer to form multilayers instead of healing and of coalescing. This probably only shows the tendency of C_{60} to avoid the water surface, because of its lack of an hydrophilic moiety.

In summary, with the use of Brewster angle microscopy we have found by direct observation that fullerenes do not form stable monolayers on the water/air surface along the process of compression at 298 K. In particular, we observed multilayer formation long before reaching the monolayer limiting area of $\sim 96 \text{ \AA}^2/\text{molec.}$ claimed by several authors [10–15]. In addition, we found that the condensed phases formed several structures when the film undergoes compression at relatively large speeds. However, it is necessary to understand the way and the mechanism they evolve during the compression. This work as well as the study of C_{70} films is underway.

Acknowledgements

We acknowledge the partial support of DGAPAUNAM Project IN100595 and of CONACYT Grants 0134PE9506 and 2027E9302.

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