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Novel pattern formation in the collapse process of floating monolayer at the air-water interface

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Abstract. We have observed a remarkable two-armed spiral in the collapse process of a floating monolayer at the air-water interface by phase contrast microscopy. This demonstrates that the floating monolayer as a form of soft condensed matter reorganizes itself due to a certain kind of macroscopic or collective behavior of molecules as it collapses. This pattern formation is caused by the breakdown of a critical dynamical balance between the deformation of solid domain and the applied surface pressure. The fragility as well as the flexibility of the floating monolayer can be associated with the observed pattern growth. There are also observed interesting, periodically arranged collections of molecules in numerous collapsed regions.

PACS. 68.18.+p Langmuir-Blodgett films – 68.35.Rh Phase transitions and critical phenomena – 82.40.Ck Pattern formation in vortices-diffusion systems

1 Introduction

In recent years, soft condensed matter physics has become of great interest as a field of condensed matter physics [1]. The remarkable property of soft materials is the ease with which they correspond to external forces, *i.e.*, they can easily be distorted. Soft condensed matter includes liquid crystals, colloids, biomolecules [2]. Floating monolayers at the air-water interface are also perfect examples, they are formed from amphiphilic molecules, possessing a polar head group and nonpolar hydrocarbon chains. When these molecules are spread on the water and compressed by a barrier, they spontaneously form structures that protect the hydrocarbon chains from contact with water. These monolayers constitute two-dimensional flexible surfaces, and deform their shape easily by varying their surface pressure. They are thus typical examples of soft materials.

In nature, on the other hand, spontaneous pattern formation can be found over a wide range of size [3]. Pattern growth in monolayers at the air-water interface [4,5], and in deposited monolayers [6] has been observed. However, no observation has yet been made of the pattern formation in the process of monolayer collapse upon compression. The observation of the collapse process attracts special attention, since this phenomenon is usually driven by a certain kind of critical dynamics, and therefore it is expected that the inherent characteristics in a monolayer, as one of the soft materials, will emerge remarkably.

In this paper we report for the first time pattern growth in a floating monolayer at the air-water interface in the collapse process, and demonstrate that a remarkable two-armed spiral occurs. Moreover, interestingly, periodically arranged collections of molecules are observed as the monolayer collapses.

2 Experimental

Monolayers of stearic acid (C18, 99% pure, Sigma Chemicals) in spreading solvent (benzene, 99% pure, Kanto Chemicals) were spread on a subphase (Millipore Mill-Q system filtered water, 18.0 MΩ-cm) at 20.0 °C. The subphase was adjusted to pH 6.8 with $NaHCO_3$ (99.5% pure, Kishida Chemicals). These materials were used without further purification.

A phase contrast microscopy makes it possible to visualize the morphology of the floating monolayer with no fluorescence, and without adding probing materials at the micron scale as it is compressed [7]. We observed monolayers using a phase contrast microscope (NIKON, OPTIPHOTO-2) equipped with a CCD camera followed by an image processor. The incident light was transmitted from the bottom of a glass trough equipped with the phase contrast microscope. Monolayers were compressed at a speed of 1 cm/min by a barrier. The process of collapse was recorded every 1/30 s by a video-recorder and the recorded pictures were examined one by one. We found that the collapse process (*i.e.*, motion of cracks) generally

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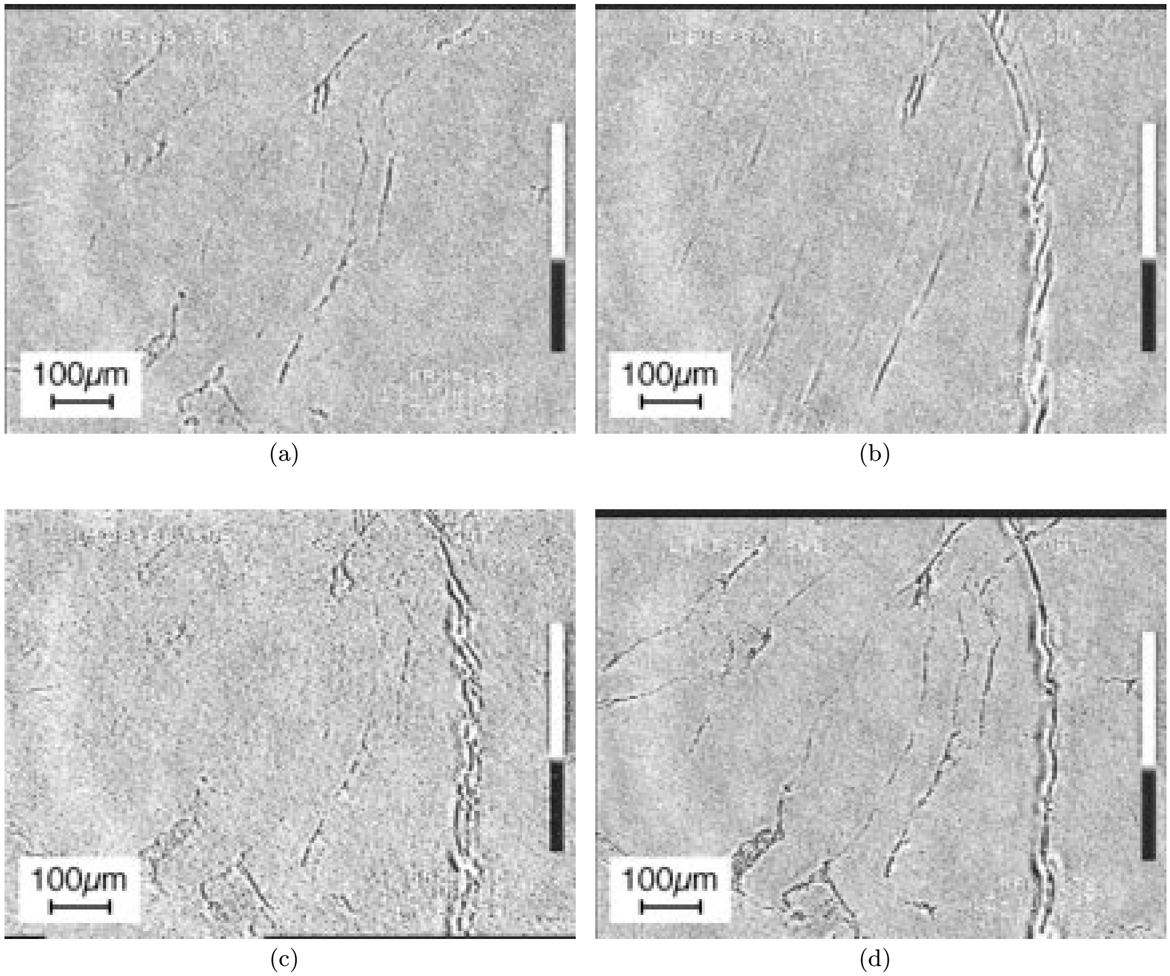

Fig. 1. Phase contrast micrographs of floating monolayer at the air-water interface in the collapse process. (b), (c), (d) are taken 0.03, 0.53 and 1.53 s after (a), indicating a two-armed spiral evolves into a single crack.

moved too rapidly to observe with our apparatus. It should therefore be noted that a rather slow collapse process is described below.

3 Results and discussion

When a monolayer at the air-water interface is compressed by a barrier, numerous solid domains nucleate and grow [7]. With further compression, cracks occur randomly in numerous parts of the solid phase immediately after the pressure (about 65 mN/m in this study) at which the monolayer begins to collapse. A typical motion of crack upon compression is shown in Figure 1. The barrier moves from left to right in this figure. This result demonstrates a remarkable feature: a two-armed spiral occurs around one curved common core. With further compression the two constituent spirals gradually merge and evolve finally into a single crack.

Since at the surface a new bulk phase (*i.e.*, two-armed spiral) is formed, it is evident that a new nucleation process operates in the collapse process. In other words, a collapse phenomenon of monolayer at the air-water interface can be considered as a precursor of nucleation with subsequent growth of the new three-dimensional bulk phase. Perhaps the reorganization of molecules as a form of self-organization results from a macroscopic or collective behavior of them, driven by the collapse process.

Examples of spiral waves have been observed in a variety of physical and chemical systems [8]. Such spiral wave patterns are known to occur in excitable media. The properties of *single* spiral waves as well as the conditions responsible for their motion have been studied in detail [9]. However, the problem of spiral interactions, especially the formation of *multi-armed* spirals, has scarcely been investigated [10]. Vasiev et al. performed numerical studies of the properties of multi-armed spirals [11]. They showed that multi-armed spirals can form spontaneously and rotate stably around one common core in low excitability media. They also proposed that these spirals are formed due to attraction of single spirals if they rotate in the same direction at distances less than the single-spiral wavelength. In our case, unfortunately, the formation process of two-armed spiral can not be observed because of the limited

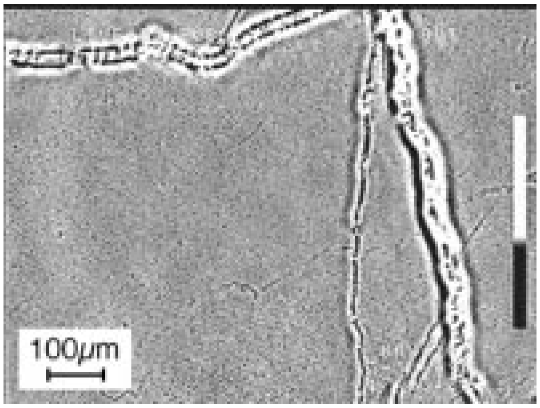

Fig. 2. A phase contrast micrograph of crack propagation in floating monolayer at the air-water interface. We can see a domain boundary in the lower half of the region. Note that crack propagation can be observed across two solid domains and that no crack branching can be seen in this scale.

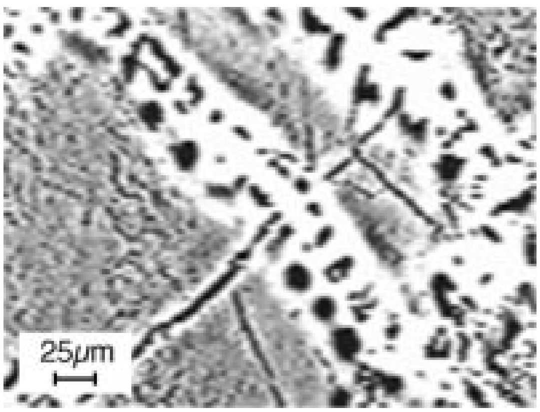

Fig. 3. A phase contrast micrograph of a periodically arranged collection of molecules observed in the collapse process of the floating monolayer.

resolving power of the video recorder. We therefore can not compare our result with the above model directly. However, we find that even in the collapse process individual solid domains are quite easy to deform upon barrier compression. The existence of high flexibility in the monolayer thus leads to the idea that a monolayer can be considered to be a low excitable medium. It is thus likely that the low excitability of the floating monolayer is a contributory factor in the two-armed spiral formation.

To obtain further information on the nature of the collapsed monolayer, we show another typical crack propagation in the floating solid domains in Figure 2. We can see a domain boundary in the lower half of the region. Some cracks occur from right top to right bottom in Figure 2. It should be noted that these cracks, interestingly, occur across the two solid domains and not along the domain boundary. This shows that the monolayer exhibits a certain kind of fragility. This fragility can drive the monolayer into a new bulk phase effectively. The coexistence of fragility with flexibility in the monolayer seems to support the idea that a monolayer at the air-water interface is very likely to reorganize itself due to the break down of a critical dynamical balance between the deformation of solid domain and the applied surface pressure. In fact, we have also observed quite interesting, spatially arranged, spherical collections of molecules as shown in Figure 3 in numerous collapsed regions.

4 Conclusions

We have observed pattern growth in a floating monolayer at the air-water interface in the collapse process. A remarkable two-armed spiral has been observed. With further compression the two constituent spirals merge and evolve into a single crack. Probably, this novel pattern formation results from the reorganization of molecules in a bulk form due to their collective behavior, driven by the monolayer collapse. As it collapses, a periodically arranged collection of molecules has also been found. However, a detailed mechanism for the pattern formation observed in this study remains open. Further investigation must be carried out to fully understand the present findings.

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