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# Kinetics of phase transitions in monolayers: collapse

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## Abstract

Although monolayers at the air/water interface have been the subject of intense study over the past 15 years, they continue to be actively investigated as evidenced by the topics discussed in this workshop. Such films continue to be employed for investigations of subjects as diverse as chain packing, critical phenomena, two-dimensional flow and wetting, biological catalysis, membrane physics and the kinetics of phase transitions. We examine the kinetics of monolayer collapse, the transition between two and three dimensions, for 2-hydroxytetracosanoic acid. The studies include measurements of surface pressure–area isotherms and imaging *in situ* by light-scattering microscopy. Three mechanisms of collapse have been observed: (1) slow collapse by the nucleation and growth of multilayer islands; (2) the formation of giant folds into the subphase; and (3) long multiple folds of small amplitude. Both folding modes are reversible. The slow collapse occurs at low surface pressures and the folding at high pressures, with the giant folds appearing only at low compression rates.

## Introduction

Although insoluble monolayers at the air/water interface have been studied for over a century, during the past 15 years there has been a flurry of interest in the area. It has been stimulated by the advent of new techniques such as grazing incidence x-ray diffraction (GIXD) and Brewster-angle microscopy (BAM), which allow the microscopic and mesoscopic structures of monolayers to be determined. It is reasonable to ask, ‘After 15 years, is there still anything of interest left to do?’ A brief review of the contributions of many of the participants to this workshop and their recent publications demonstrates that the answer is, ‘Yes’.

Much has been learned about the structures of monolayers of simple amphiphiles and progress has been made in understanding the topology of the phase diagrams in terms of Landau–de Gennes theory [1], but a full understanding of how the stability of the monolayer

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phases is determined by the interactions between head groups and chains is yet to be achieved. The effects of chain length and the mismatch in size between head groups and tail have been addressed recently for simplified model systems [2], which can be compared with BAM and GIXD investigations of mixtures of acids and esters [3]. Critical phenomena in monolayers are also currently being examined. Electrochemical methods [4] are being used to study the gas–liquid transition and liquid–liquid critical points in phospholipid mixtures and their relationship to membrane physics is being investigated by fluorescence microscopy [5].

The use of Langmuir monolayers as models for biological membranes continues to be an important direction. Lösche and co-workers [6] have pioneered the combination of x-ray and neutron methods to determine the head-group organization in phospholipid monolayers and the way in which drugs bind to them. Enzymatic reactions at interfaces have been examined by Brezesinski and his collaborators [7] with GIXD. They have been able to employ biologically inactive isomers to separate the effects of physical interaction from chemical binding. Lee has focused as well on biological applications of monolayers, among them a study of the interaction of lipid monolayers with amyloid peptides associated with Alzheimers disease [8]. The structure and self-organization of apolipoproteins have recently been studied by GIXD and BAM by Castillo and Mas-Oliva [9].

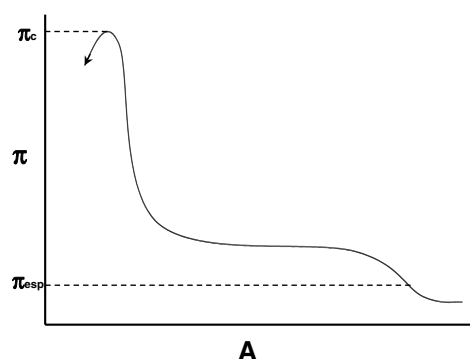
Langmuir monolayers provide a means for studying physics in two dimensions. Current research includes investigations of the flow properties of monolayers in different phases [10] and the coupling between monolayer flow and molecular tilt [11]. Fischer and co-workers [12] have employed optical tweezers to study the viscous drag of islands of a condensed phase. Although the structures of foams are complex in three dimensions, they are much simpler in two and this has driven studies of the stability [13] and dynamics [14] of monolayer foams.

There are two classes of phase transitions involving monolayers, transitions between two-dimensional phases and those in which there is a change of dimensionality from two to three dimensions. Transitions within the monolayer are particularly interesting because they can involve a number of order parameters, both conserved and non-conserved. We have begun studies of the kinetics of a transition from an untilted to a tilted monolayer phase, a case in which the order parameter (molecular tilt) is not conserved [15]. Unfortunately there is insufficient time to discuss this work. We will consider only the second class of transition, which is generally called monolayer collapse, a topic of relevance to the research of many of the workshop participants [16–19].

### Some background

A schematic surface pressure–molecular area isotherm is shown in figure 1. Isotherms typically show plateaus and changes in slope that are associated with phase transitions between various monolayer phases. The pressure  $\pi_{esp}$  indicated on the ordinate is the equilibrium spreading pressure (esp), the pressure at which the monolayer is in equilibrium with the bulk phase. Thus, for much of the monolayer phase diagram, the monolayer phases are metastable with respect to the equilibrium 3D phase. At high pressures the isotherm may go through a maximum or there may be a plateau that extends to molecular areas that are smaller than the cross section of the amphiphile. These are the hallmarks of collapse, the process by which the monolayer transforms to a bulk phase.

Gaines [20] proposed that there may be a ‘monolayer stability limit’ (msl), which he defined as a ‘pressure of equilibrium between the film and freshly collapsed material’. The three-dimensional phase in this case would have a stability intermediate between that of the monolayer and the equilibrium bulk phase. It could be, for example, a multilayer or a metastable crystalline form.



**Figure 1.** Schematic surface pressure–area isotherm. Collapse at  $\pi_c$  is signalled by either a drop in the pressure or a plateau that extends to molecular areas smaller than that of a single amphiphile. The esp,  $\pi_{esp}$  is lower than the collapse pressure. In some cases, collapse to a metastable three-dimensional phase at the msl, which lies above the esp.

Smith and Berg [21] considered quite generally the consequences of collapse by nucleation and growth. If the film is held at a constant pressure, its area will decrease with time as a result of the nucleation of the 3D phase and its subsequent growth, which they took to be diffusive. With this scenario, the relation between the area  $A$  and the time  $t$  is found to be

$$\ln \frac{A}{A_0} = -\alpha t - \beta t^2 \quad (1)$$

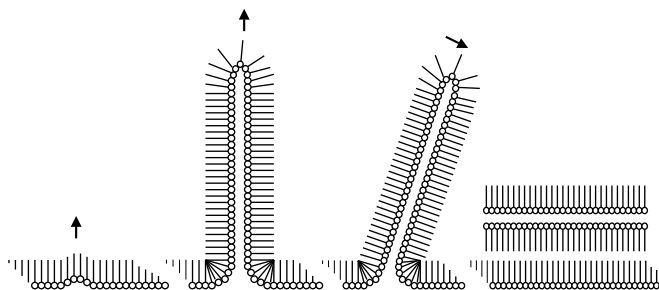
where the zero subscript indicates  $t = 0$  and the coefficients  $\alpha$  and  $\beta$  are characteristic of the nucleation and growth, respectively. Measurements on monolayers of fatty acids and alcohols [21] showed that equation (1) represented the collapse behaviour well. More recently, Vollhardt and his collaborators [22] have employed this approach and considered in detail the effects of the shapes of critical nuclei. We will use the term ‘slow collapse’ for collapse attributable to nucleation and growth.

It is clear, however, that slow collapse is not the entire story. Isotherms often show one or more plateaus at collapse. From the lengths of these plateaus one can deduce that the film is being converted to a layered structure [23]. Ries and collaborators [24] found layered structures when they imaged Langmuir–Blodgett films of collapsing monolayers by electron microscopy. They proposed that trilayers were formed when the film buckled under compression, folded over and broke into a bilayer on top of the monolayer, figure 2. Most remarkable are micrographs of 2-hydroxytetracosanoic acid (cerebronic acid, 2-OH TCA) [25] in which a periodic array of ridges perpendicular to the compression direction is evident. Shadowing with platinum showed that some ridges were 2000 Å high.

This so-called Ries mechanism of collapse is often taken as the explanation of collapse of monolayers at high pressures [26], which is sometimes called ‘catastrophic collapse’. There are several objections that can be raised to this mechanism. Nikomorov [27] showed on energetic grounds that the barrier to folding was very high compared to the thermal energy  $k_B T$  and therefore highly improbable. He argued that collapse by the formation of folds requires the presence of defects. Milner *et al* [28] carried out a linear stability analysis that leads to similar conclusions. They write the free energy of a monolayer as a function of its local height  $h(r)$ :

$$F = \frac{1}{2} \int d^2r \{ \gamma (\vec{\nabla} h)^2 + \kappa (\nabla^2 h)^2 + \rho g h^2 \} \quad (2)$$

The first term in the brackets is the cost of expanding the area of the film against the surface tension  $\gamma$  and the second is the energy associated with the bending, with  $\kappa$  the bending rigidity.



**Figure 2.** The Ries mechanism of collapse. A buckling instability is assumed to grow in amplitude, tilt over and then break apart into a trilayer.

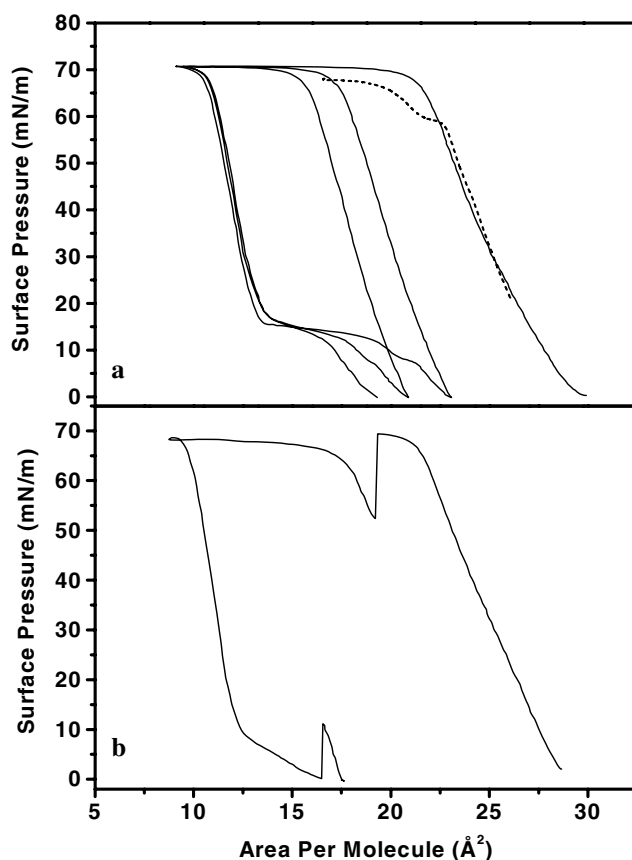
The gravitational work is represented by the third term in which  $\rho$  is the density and  $g$  the acceleration of gravity. When the capillary spectrum is calculated from (2) it is found that for  $\gamma > 0$  all modes are stable. The film first becomes unstable at a wavevector  $q^* = \left(\frac{\rho g}{\kappa}\right)^{\frac{1}{4}}$  at  $\gamma = 0$ . Thus, at room temperature collapse by buckling is predicted to occur only at  $\pi = \gamma^\circ - \gamma = \gamma^\circ \approx 72 \text{ mN m}^{-1}$  and initially with a wavelength  $1/q^* \approx 0.1 \mu\text{m}$ , conditions generally remote from those seen in experiments. Buckling at slightly lower pressures is predicted if the spontaneous curvature is included in the free energy [29], but they are still considerably higher than the collapse pressures typically found in experiments.

There is experimental evidence of buckling, however. It can be seen in the x-ray diffuse scattering of very rigid monolayers such as polymerized octadecyltrichlorosilane [30] and 10, 12 pentacosadiyonic acid [31]. Light scattering and BAM studies of monolayers of disteoyl phosphatidylcholine on a formamide subphase [32] also show buckling. In these cases the amplitude is small,  $\approx 2 \text{ nm}$  and the wavelength is of the order of  $1 \mu\text{m}$ . Large-scale folds have been observed in fluorescence microscopy studies of phospholipid mixtures employed as models for lung surfactant [17, 18, 33]. The folding arises in films in which there is coexistence between a condensed phase and an isotropic fluid phase. Folds start at a boundary between the phases and extend tens of microns into the subphase. They unfold reversibly when the film is expanded. In contrast, light-scattering microscopy (LSM) images [34] of the pure phospholipid dipalmitoyl phosphatidylcholine show no evidence of folding. Instead ‘buds’ appear at boundaries between condensed phase domains and proliferate across the surface at collapse. They are reincorporated into the film upon expansion. They project above the monolayer rather than into the subphase and have heights ranging from 5 to 20 nm.

The understanding of collapse might best be described as confused. There are many experimental studies, some of which appear to be contradictory, and a number of theoretical treatments, none of which is definitive. We therefore felt it useful to return to collapse in 2-OH TCA [35], the classic example of buckling, and to examine the phenomenon by techniques that were not available to Ries and his collaborators.

## Experimental

Samples of *dl*-2-OH TCA were obtained from Matreya and were claimed by the supplier to be 99+ % pure. Monolayers were spread from chloroform (Fischer, spectra-analysed) solution onto milli-Q water. Surface pressure–area isotherms were measured on a NIMA Type 611 trough equipped with a ribbon barrier. Pressure measurements were carried out with a filter-paper Wilhelmy plate.



**Figure 3.** Surface pressure–molecular area isotherms for 2-OH TCA at 22 °C. (a) The full curve represents a series of compressions and expansions at a rate  $>1 \text{ \AA}^2 \text{ molecule}^{-1} \text{ min}^{-1}$  and the dotted curve is a compression at  $<1 \text{ \AA}^2 \text{ molecule}^{-1} \text{ min}^{-1}$ . (b) Relaxation of the pressure on the compression and expansion plateaus. The drop in pressure occurred over a period of 149 min and the pressure rise over 174 min. The lower plateau is not well defined because of the prolonged halt at the upper plateau to follow the relaxation.

The method for obtaining dark-field or LSM images is closely similar to that described by Schief *et al* [34]. The monolayer, which was formed in a  $5 \times 20$  cm teflon trough, was placed on the stage of a POLYVAR-MET microscope. It was illuminated by a 50 mW solid-state laser ( $\lambda = 532$  nm, Enlight Technologies, Model MGL-S) which struck the film obliquely. The direct beam was outside the field of view of the  $20\times$  objective, so only the scattered light was imaged. A silicon wafer in the subphase reflected the transmitted beam out of the field of view and its polished surface minimized scattering. The images were captured by a CCD camera (Dage 772S) and recorded on video tape. Surface pressure was measured by a Wilhelmy plate with an R&K transducer and compression was carried out with a single teflon barrier.

## Results and discussion

*Isotherms.* A surface pressure–molecular area isotherm for 2-OH TCA at 22 °C is shown in figure 3(a). The portion before the onset of collapse agrees generally well with that reported by

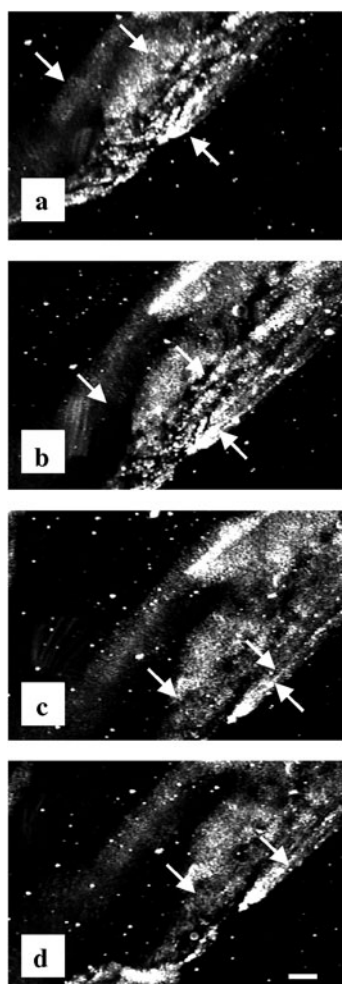
Ries and Swift [25] except at large areas, where their isotherm does not fall as rapidly. We have found similar behaviour in samples that were not freshly prepared. GIXD studies [36] show that there is a phase with nearest-neighbour tilt at low pressures that undergoes a transition to one with next-nearest-neighbour tilt at about  $35 \text{ mN m}^{-1}$ ; at  $60 \text{ mN m}^{-1}$  there is a transition to an untilted phase. There is a change in the slope of the isotherm that may be associated with the transition between the tilted phases but no indication the tilted/untilted transition at higher pressure.

Collapse of the monolayer is indicated by a plateau at  $69 \text{ mN m}^{-1}$ . If the film is expanded, the pressure drops immediately and there is a plateau at  $35 \text{ mN m}^{-1}$ . A loss of material is evidenced by the decrease in area at zero pressure. Subsequent isotherms follow the same pattern. Similar behaviour has been observed for compression–expansion cycles in stearic acid monolayers [26]. If the compression is stopped on the collapse plateau, the pressure drops slowly; it rises sharply back to the plateau if the compression is restarted, figure 2(b). On the other hand, if the compression is stopped on the expansion plateau, the pressure rises and it falls immediately when the expansion is begun again.

From the relaxation on the collapse plateau, it appears that the pressure is falling to a constant value that lies between the two plateau regions. (This cannot be the esp, which we find from a study of crystals of 2-OH TCA spread on the interface to be immeasurably low at this temperature.) Such behaviour has been observed in esters by Lundquist [23] and for fatty acids by Sims and Zografi [37], who took it as evidence of the existence of the msl. The rise in pressure along the expansion plateau is consistent with a metastable coexistence of the collapsed monolayer with the monolayer. Thus, the pressure relaxation downward from the collapse plateau and upward from the expansion plateau should therefore reach the same limiting value. This cannot be demonstrated in 2-OH TCA because the relaxation is very slow. Relaxation is much faster in the methyl ester, however, and the msl pressure is reached from both plateaus [38] and is independent of the compression/expansion speed.

In a typical case of nucleation and growth, the supersaturation falls once the more stable phase is nucleated. The subsequent growth then occurs at the equilibrium pressure at coexistence (or close to it if the domains of the new phase are so small that there are curvature corrections to the pressure). Why does the growth of the metastable collapsed phase of 2-OH TCA not occur at the msl? It is possible that the growth involves the sliding of one portion of the monolayer over another and the friction between them must be overcome. If this is the case, the plateau pressures should depend on compression rate. This has been observed by Gourier [31] who found that the collapse pressure of 10,12 pentacosadiyonic acid depended linearly on the logarithm of compression speed. A similar relation is found for the variation of the frictional force between LB monolayer films with speed [39]. Although identical behaviour has been observed for the methyl ester of 2-OH TCA [38], the plateau pressures for the acid change very little if the compression rate is greater than about  $1 \text{ \AA}^2 \text{ molecule}^{-1} \text{ min}^{-1}$ . A change is evident at lower speeds, however—a plateau at  $60 \text{ mN m}^{-1}$  becomes evident. Its significance will be discussed below.

*Light scattering microscopy.* All the images obtained with LSM show the presence of small islands even at low pressures that are the result of slow collapse. Atomic force microscopy studies on LB films show that they consist of multilayers. Very large folds, which we call ‘giant folds’ appear on the  $60 \text{ mN m}^{-1}$  plateau, which can be accessed at low compression rates. The folds do not start at the multilayer islands. They first appear as a shimmering spot that spreads laterally, figure 4. The LSM image is a projection of the fold and not all of it is in focus at the same time. It is clear as the different parts of the folds are brought into focus that they extend  $10\text{--}20 \mu\text{m}$  below the surface. By following the motions of the islands formed by slow collapse

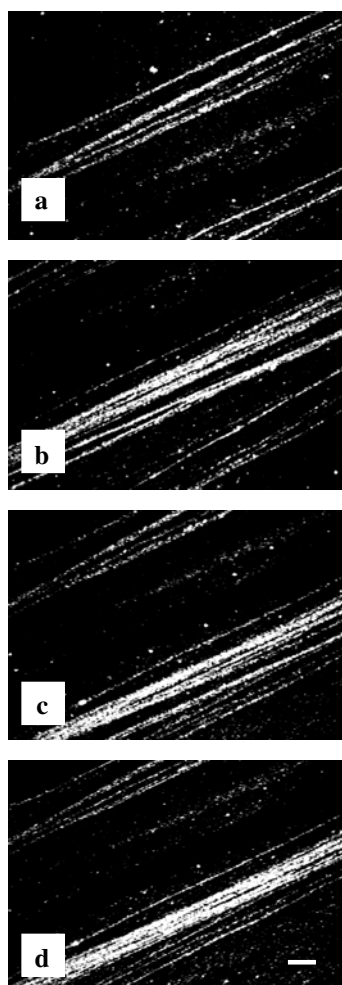


**Figure 4.** Light scattering microscope images of the formation of giant folds at a pressure of  $65 \text{ mN m}^{-1}$ . The interval between images is 5 s. The fold is connected to the monolayer only at the right-hand edge. Movement of the monolayer into the fold is evident from the trajectories of the slow-collapse islands. The three islands that lie just behind the tails of the arrows can be followed. Note that the islands to the left pass across the fold, which lies below the surface and are subducted at its right-hand edge. The line represents  $20 \mu\text{m}$ .

we can see that the subduction of the monolayer occurs along a single line. With changes in focus one can often see lines within the fold that are evidence of folding on a smaller scale.

The giant folds are crumpled and they fluctuate as they grow. They eventually become inactive and folds appear at other places within the film. When the monolayer is expanded, the folds open reversibly along the lower pressure plateau. The subducted material re-enters the monolayer along the fold edge and the body of the fold can be observed to move below the plane of the monolayer (as defined by the slow-collapse islands) as it is drawn upward toward the edge. When all the fold has been drawn to the surface, it fades away, leaving no obvious trace. Upon recompression, the folds reappear close to the spot in which they originally appeared, suggesting that folds are formed at defects within the monolayer. Many of the folds are roughly perpendicular to the compression direction but other orientations also occur.

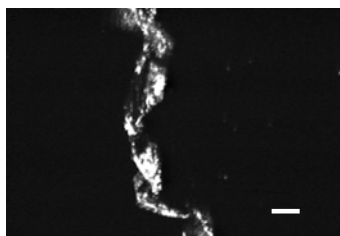




**Figure 5.** Light scattering images of the formation of multiple folds at a surface pressure of  $69 \text{ mN m}^{-1}$ . The interval between images is 4 s. Folds to the lower right move in abrupt steps to the fold at the left, which becomes broader as the lines pile up. The displacement downward between (b) and (c) arose because the stage was moved to keep the lines in view during the compression. The line represents  $20 \mu\text{m}$ .

Occasionally, some of the giant folds have a tubular shape, i.e. they are subducted along a closed curve rather than along a line. Similar structures have recently been observed by Gopal and Lee [33]. Folds that have disconnected from the monolayer to form fragments of crumpled bilayers are sometimes observed floating below the monolayer. Budding into the subphase followed by formation of micelles has also been recently observed in a phospholipid [33].

The morphology of the collapsing film is very different at higher compression speeds when the process occurs at  $69 \text{ mN m}^{-1}$ . Scattering is first observed throughout the monolayer and then a series of long narrow lines perpendicular to the compression direction appears, figure 5. Lines pile up in a series of discrete steps in which a portion of the film is rapidly displaced as a rigid object, much like successive accordion pleats. The entire pattern falls within the depth of field of the objective so its height cannot be determined from LSM. As the process



**Figure 6.** Light scattering microscope image of a twisted ribbon fold. The line represents 20  $\mu\text{m}$ .

continues wider lines are formed, each of which is made up of up to 30 narrower lines. Like the giant folds, these ‘multiple folds’ are reversible. The wide lines separate upon expansion into a series of narrow lines. They do not remain parallel, however, but undergo a buckling instability whose wavelength decreases as the film area increases. The lines eventually break up and disappear without a trace. If the expansion is reversed before this point, the lines become straight as they are compressed.

The giant folds are like the folds that have been observed in the phospholipid mixtures [17, 18] in that they are similar in scale, directed into the subphase and reversible. Unlike those folds, however, the giant folds in 2-OH TCA occur in a one-phase region. Thus, models that rely on the height discontinuities that arise because of differences in spontaneous curvature between phases [18] cannot be applicable. The giant folds are stabilized by the strong van der Waals interactions between the tails. They fold because they are not under tension, as the monolayer is. (The attractive picture of collapse as occurring because the monolayer is under compression is not correct; it is under tension as long as the surface tension is not negative.)

The scale of the multiple folds is similar to that of the folds shown in the Ries and Swift [25] electron micrographs, but it is evident that they are not hundreds of nanometres high. We believe that the high structures in the shadowed images are the multilayer islands caused by slow collapse and that the multiple folds are only several monolayers high. This view is supported by AFM images of LB films of the collapsed monolayer [35].

Finally, collapse structures in the form of twisted ribbons have been observed in electron micrographs of transferred films [25, 40] and in phase contrast microscopy images of floating monolayers [41]. We have also found this morphology in 2-OH TCA, figure 6. The ribbons may be associated with collapse at an intermediate compression speed. The key conclusion is that collapse morphologies may have many forms even with a single substance.

We have overlooked a recent paper on collapse of DPPC monolayers [42]. Both folding into the subphase and the formation of vesicles were observed in electron microscope studies of films transferred to grids by the Langmuir–Blodgett technique. While the phenomena appear similar to those that we have reported, the surface pressures and densities of the films were not determined.

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