Instantaneous and Time-Lag Breaking of a Two-Dimensional Solid Rod under a Bending Stress

L. Pauchard and J. Meunier

Laboratoire de Physique Statistique de l'Ecole Normale Supérieure, 24 rue Lhomond, 75231 Paris CEDEX, France

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In a Langmuir monolayer of NBD-stearic acid, long rods (~1 mm long, ~20 μm wide) of a two-dimensional solid phase are obtained at the liquid-solid phase transition. A rod bent in the plane of the water under the effect of a bending stress breaks after a clearly defined delay. This delay is a function of the strain applied to the rod and of the temperature. For large deformations, a second mode of breaking appears and coexists with the previous one: A fraction of the rods break instantaneously while others break after a delay.

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Two-dimensional solids have been the subject of many experimental studies. Comparison of their mechanical properties with the predictions of the Kosterlitz-Thouless-Halperin-Nelson theory is one of the important problems. Among the studied systems are suspended films of liquid crystals [1,2] and Langmuir monolayers [3,4].

A first order liquid-solid phase transition displaying a large change in the area per molecule has been observed in Langmuir monolayers of NBD-stearic acid [5]. This molecule is bolaform: It has two polar heads, the acid group (-COOH) and the NBD fluorescent group which has a large dipolar moment. In the liquid phase a molecule lies flat on the water surface with the two polar heads in the water. The fluorescence of the NBD group is quenched. In the solid phase, the molecules straighten up, lifting the NBD group out of the water. When illuminated with blue light, the two-dimensional solid phase fluoresces in yellow and is easy to observe by fluorescence microscopy. The phase transition is observed in the range 33–84 $Å^2$ per molecule. It was recently demonstrated by electron scattering microscopy that the solid phase is a two-dimensional (2D) crystal [6]. The domains of solid phase obtained in the first experiments were needle shaped. In the absence of impurities due to oxidation of the molecule at room temperature and for low rates of compression, the solid domains are rodlike with two parallel sides [4,7]. The rods obtained by direct deposition (without solvent) of the pure product at the water surface are large. Their length can easily be more than 1 mm while their width e is in the range 5 to 40 μm. This shape is well adapted to micromechanical measurements. Studying the flexion of a rod in the plane of the water when a force is applied in its middle, we recently measured the two-dimensional Young's modulus of the solid phase [4]. Its value was found to be in agreement with the Kosterlitz-Thouless-Halperin-Nelson theory. During these experiments, it was noted that a deformed rod (flexion) breaks after a delay time t_B. In this paper we report on measurements of this time t_B.

The bending of a rod is accomplished with three parallel glass fibers, 10 μm in diameter and 2 mm in length. These fibers are perpendicular to the water surface. They are fixed on one end to two stainless steel pieces just below the water surface; the support of these pieces can be moved vertically with a screw. Two fibers (a and b) are supported by the same piece of metal. Their separation is $2L = 1$ mm. The remaining fiber (c) is fixed on the second piece of metal and can be moved with a micrometer screw in the horizontal plane along the perpendicular bisector of the line joining the two other fibers. The glass fibers are silanized to give a wetting angle close to $\pi/2$ under the experimental conditions (water covered with a dense monolayer). As the first step in each bending experiment, the three fibers are fully immersed in the water of a small Langmuir trough under a fluorescence microscope. A monolayer of NBD-stearic acid is deposited in the liquid state on the water surface and then slowly compressed to obtain long rods of 2D solid in the liquid phase. As the second step, the three fibers are moved up so that their free ends emerge from the water, two of them (a and b) on one side of a rod, the other (c) on the other side. The fiber c is moved with the micrometer screw to immobilize the rod between the three fibers, without bending. Since the rods are very sensitive to the light which produces oxidation and melting, these manipulations are made very quickly under a very low light intensity. The choice of the rod and its immobilization take about 40 s. The width of the rod is then measured. This requires a higher level of light for a few seconds. Finally, the fiber c is moved again with the micrometer to bend the rod. Because the three glass fibers are short, in contrast to those of Ref. [4], they are rigid. The displacement S_r applied to the middle of the rod is deduced from the micrometer screw. The strain is well defined but the stress is not measured because in this experiment it is very difficult to break a large number of rods using the previous experimental technique [4]. To avoid excessive illumination, the rod is not observed continuously. It is observed and illuminated at a very low light level during only 1 or 2 s after each interval of time Δt (Δt depends upon the experiment); the interval of time in which the rod has broken is determined. This procedure introduces an inaccuracy Δt on the measured breakage time t_B.

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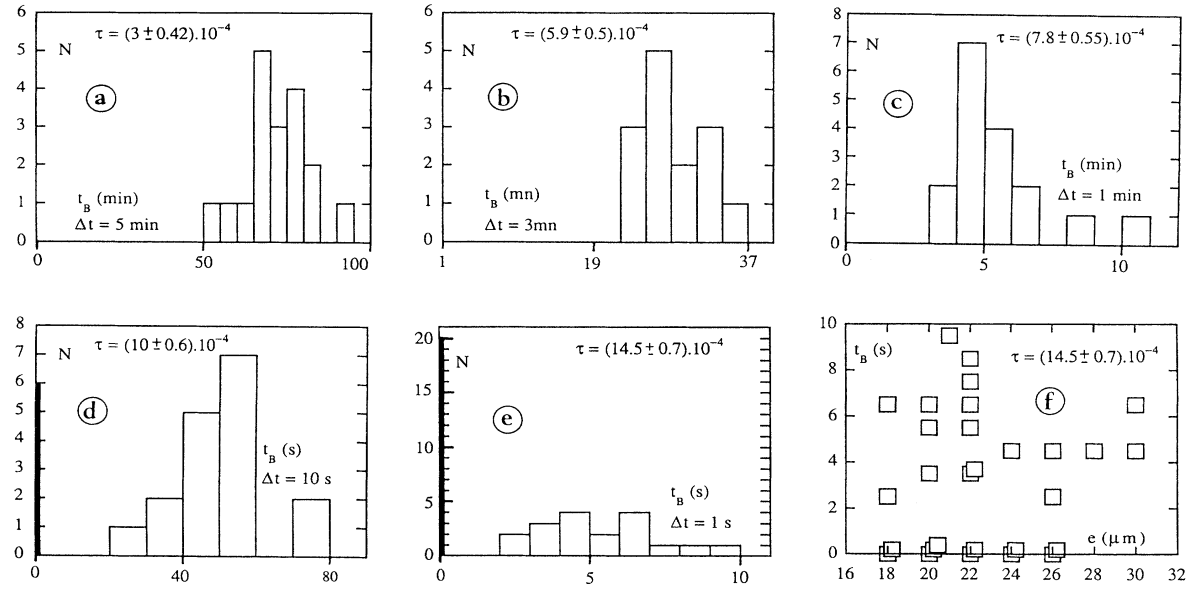

FIG. 1. Number N of rods which break vs the time t for different strains τ. (a)–(c) Low strains. (d),(e) Higher strains showing the apparition of an instantaneous breaking. (f) The time of breaking t_B vs the width e of the rod. t_B is independent of e.

One quantity of interest (see below) is the strain or rate of extension of the external side of the rod under bending. This is given by $\tau = eS_r/L^2$ if $S_r \ll L$ where S_r/L^2 is the curvature of the rod. (In practice a small correction to this formula is applied to take into account imperfections in the experimental setup. The fiber c does not move exactly on the bisector of the line joining a and b but on a line parallel and close to it.) The accuracy on L and e is 1 μm (they are measured using a graduated ocular) and that on the displacement S_r is 2.5 μm, the accuracy of the micrometer screw. The accuracy on τ is $\delta\tau/\tau \approx \delta e/e + \delta S_r/S_r$.

It takes about 60 min to achieve a monolayer with large rods stabilized in length and width. The chemical evolution of the monolayer (probably oxidation) imposes changing the monolayer every 2.5 or 3 h. The available time to study the breakage is thus only 1.5 or 2 h per monolayer. The water of the trough (pH = 2) was changed before each deposition of a new monolayer and its surface was carefully cleaned. If the solid domains obtained were not rodlike, the trough was cleaned a few times with alcohol and occasionally with a sulfochromic mixture.

The time of breakage t_B was measured for five different values of the strain τ in the range 3×10^{-4} to 14.5×10^{-4} at 19 ± 0.2 °C. After a rod is immobilized and its width e measured, the displacement S_r to obtain the chosen strain is calculated and applied. For each value of strain studied, about twenty rods were broken. Experimental difficulties make a much larger number of breakage events impractical and twenty is sufficient for reasonable statistics on the breaking time.

The results are given in Fig. 1. Sometimes during a measurement one of the glass fibers penetrates a few μm into the rod. These measurements were eliminated and do not appear in Fig. 1 because in these cases the displacement and consequently the strain is lower than calculated. At low strain ($\tau \lesssim 8\times10^{-4}$), breaking occurs after a certain period of time t_B; this will be called time-lag breaking. The different breakage times measured for a given value of τ are grouped, allowing the definition of a mean value $\bar{t}_B$ (Table I). At large τ ($\tau \gtrsim 10^{-3}$), the time-lag breaking remains but a second type of breakage coexists: instantaneous breaking [Figs. 1(d) and 1(e)]. The percentage of rods which break instantaneously increases with τ. It is about 30% for $\tau = 10^{-3}$ and 50% for $\tau = 14.5\times10^{-4}$. It must be remarked that for a given τ and a given temperature the breaking time is independent of the width of the rod [Fig. 1(f)].

After the breaking of a rod, the two pieces become straight again: No plastic deformation was observed. This was tested in another way. The stress was released a short time before breakage for one rod at each value of τ in the range 3×10^{-4}–10^{-3}; the time t_1 at which it was released was close to but smaller than $\bar{t}_B$ (Table I). In each case, the rod straightened instantaneously. No plastic deformation was observed within the 1 μm resolution of the microscope. The stress was applied again and the breaking time t_2 was measured. In each case, the sum of t_1 and t_2 is in the range $\bar{t}_B \pm \Delta\bar{t}_B$. The rods under stress keep the memory of the stress.

Nevertheless, in two singular cases at low stress ($\tau = 3\times10^{-4}$) a plastic deformation was observed. These two rods remained unbroken after 6000 s. The stress was released but these two rods remained slightly bent. For the two highest stresses, three singular cases in which the

TABLE I. The mean value of the measured breakage time $\bar{t}_B$ and its accuracy $\Delta\bar{t}_B$ vs the strain τ and its accuracy $\Delta\tau$, for the different experiments at 19 ± 0.2 °C. N_T in brackets is the total number of events taken into account for the calculation of $\bar{t}_B$. t_1 is the time at which the stress was released in some experiments. The particular cases which are not included in the calculation of $\bar{t}_B$ are indicated. N_p is the number of measurements eliminated because penetration of a glass fiber was observed.

τ (10^{-4})	$\Delta\tau$ (10^{-4})	$\bar{t}_B$ (s) [N_T]	$\Delta\bar{t}_B$ (s)	t_1 (s)	Anomalous cases
3	0.4	4380 [18]	540	3000	2 plastic deformations, $N_p=6$
5.9	0.5	1710 [14]	245	1200	$N_p=5$
7.8	0.55	330 [17]	150	240	$N_p=3$
10	0.6	50 [17]	12	30	1 broken in 120 s, $N_p=2$
14.5	0.7	5 [18]	3.2		1 broken in 38 s and 1 in 170 s, $N_p=2$

time of breaking was very much larger than the mean value were also observed (Table I). They are probably due to a plastic deformation of these three rods. This would mean a strain less than the one calculated; these three values have not been taken into account. These anomalous cases were only observed for very low strain with very long breaking time and for very large strain. For long breaking times plastic deformation can be explained by an experimental artifact due to the evaporation of the water (see below). For large stresses it is possible that some rods succeed in reducing the stress by forming a multilayer locally (probably three layers).

The measured mean values $\bar{t}_B$ vs τ of Table I are plotted in Fig. 2(a). $\bar{t}_B$ increases only slowly for small τ values and Fig. 2(a) indicates a finite value of $\bar{t}_B$ for

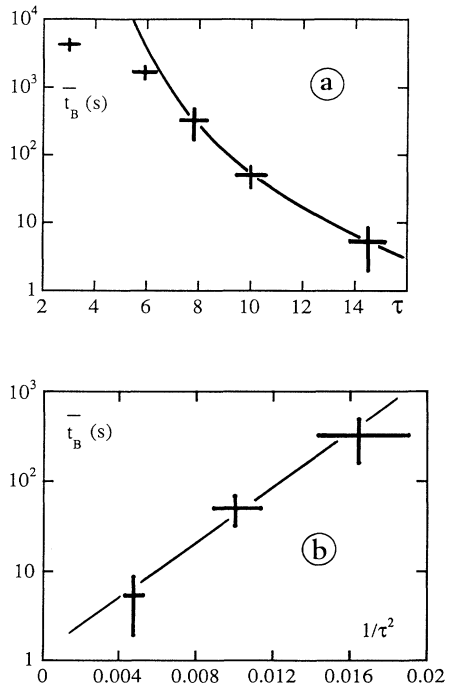

FIG. 2. The mean value of the breaking time $\bar{t}_B$ vs the strain τ on a semilogarithmic scale (a) and vs $1/\tau^2$ for the three measurements without experimental artifact (b).

$\tau=0$. A rod immobilized without strain between the three glass fibers was observed during 90 min to attempt to understand these surprising results. It appears that over long periods the evaporation of the water in the trough induces the sliding of the rod along the fibers. This breaks some pieces of the solid rod around the glass fibers. This experimental artifact induces the breaking or reduces the breaking time for low τ. This affects the result for $\tau=3\times10^{-4}$ and probably to a smaller extent for $\tau=5.9\times10^{-4}$. Consequently no threshold (if one exists) for the time-lag breaking can be deduced from these observations.

Pomeau recently proposed that the breaking results from the spontaneous nucleation of a crack [8] with a size above a critical size given by the Griffith critical condition [9] so that it can propagate. The probability of nucleation in two dimensions is proportional to $\exp(-p_0^2/\sigma^2)$ where σ is the stress in the material and p_0 a molecular pressure. This stress σ is proportional to the strain τ. The three shorter $\bar{t}_B$ are plotted in Fig. 2(b) versus $1/\tau^2$ on a semilogarithmic scale. The three points are on a straight line in agreement with the theory, but this theory does not explain the clearly defined breaking time.

The breaking time is temperature dependent. It was measured at three different temperatures for a strain $\tau=7.8\times10^{-4}$ [Fig. 3(a)]. It is plotted on a semilogarithmic scale in Fig. 3(b). In a naive model the slope of the straight line gives the energy of activation of the elementary process leading to the breaking [$\bar{t}_B \sim \exp(-E/k_BT)$]. One finds $E=2.7\times10^{-19}$ J.

In three dimensions time-lag breaking is observed on polycrystalline solids or glasses under the influence of the surrounding medium that creates small surface cracks and promotes their growth. This has been explained by a chemical attack of Si-O bonds by water molecules in glasses [10] and by stress induced corrosion in other materials [11]. We have verified that the breaking does not result from the degradation of the material due to the illumination (by changing the time of illumination and the intensity of the beam). Preliminary experiments were performed under a nitrogen flow. No change in the breaking time was observed. Breakage induced by the surrounding medium occurs at random depending upon

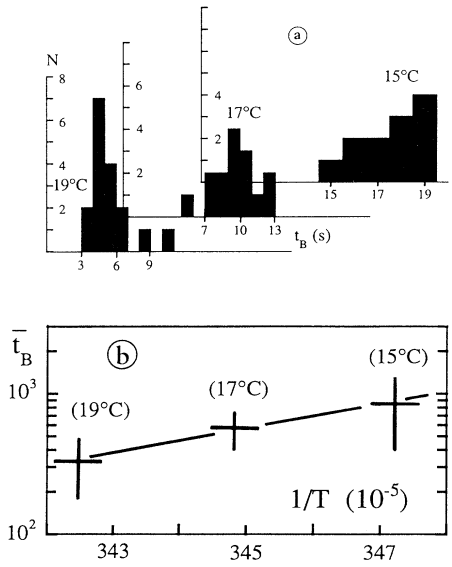

FIG. 3. The breaking time and the temperature T. (a) The experimental results for $\tau = 7.8 \times 10^{-4}$. (b) The mean value $\bar{t}_B$ of the breaking time vs $1/T$ on a logarithmic scale.

the initial surface of the material. In contrast our 2D material is a single crystal and the breakage time is clearly defined. The mechanism that induces the breakage is probably very different. The experimental inaccuracy $\Delta\bar{t}_B$ is only a fraction of the breakage time $\bar{t}_B$ and furthermore is consistent (Fig. 2) with simply the inaccuracy $\Delta\tau$ on the strain. The time t_B appears to be a surprisingly clearly defined function of τ.

The process that leads to such breaking is probably a large number N of elementary processes which appear at random with a Poisson law, the probability being proportional to $\exp(-t/t_0)$. A first model supposes a succession of elementary processes. If it is supposed that the elementary process number i takes place only when the elementary process number $i-1$ has taken place, the mean breakage time is Nt_0 and the width of the distribution of this time is $\sqrt{N}t_0$. A slightly different model supposes that the elementary processes are independent but that N elementary processes are needed to initiate the breaking. The experimental results on the dispersion are consistent with N to at least a few hundred. The dependence on temperature suggests that the elementary process is a thermal one. What is this elementary process? This migration of defects towards the region of largest stress would be a possibility [12], supposing that the density of defects is independent of the preparation of the crystals because they are at the equilibrium in the crystal or because they appear at the edge of the crystal under stress. However, this model implies plastic deformation before the breakage, which is not observed. Another possibility is suggested by the very anisotropic growth and optical properties of the solid domains [5,6]. The mechanical properties are probably also very anisotropic. The appearance of a solid domain melting under the effect of a bright light beam suggests that a solid domain is made of long fibers (Fig. 4), the molecular forces being very different in the direction of the length of a solid domain and in the perpendicular direction. Electron diffraction also suggests a fibrous structure at the molecular scale [6]. The elementary process could be the breaking of a fiber under stress, producing the progress of a crack from the edge of the domain. When the size of this crack reaches the critical size satisfying the Griffith critical condition, it propagates quickly. Experiments are in progress to test different possible mechanisms.

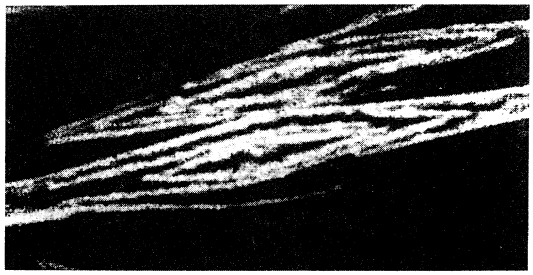

FIG. 4. Image of a needle-shaped solid domain partially destroyed by a strong illumination.

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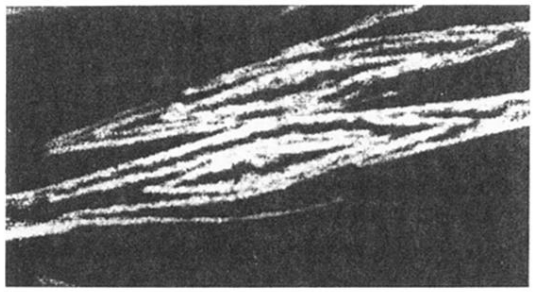

FIG. 4. Image of a needle-shaped solid domain partially destroyed by a strong illumination.