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Optical studies of low-dimensional phase transitions

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Abstract

Optical techniques such as ellipsometry and Brewster angle and fluorescence microscopy have considerably enhanced our understanding of the physics of thin films. We discuss a few recent results obtained by these techniques. In the domain of wetting phase transitions, ellipsometry experiments have revealed that long range forces can split the classical first order wetting transition into two transitions: a first order transition followed by a second order or critical wetting transition upon increasing the temperature. For Langmuir films, a single molecular layer of an insoluble amphiphilic at the free surface of water, the properties of a number of condensed phases have been studied using Brewster angle and fluorescence microscopy. Unexpected and surprising results have been obtained for both the fracture properties and the melting of two-dimensional crystals.

Résumé

Les techniques optiques telles que l'ellipsométrie, la microscopie à l'angle de Brewster et la microscopie de fluorescence ont permis d'améliorer considérablement nos connaissances sur la physique des films minces. Nous discutons quelques résultats récents obtenus avec ces techniques. Dans le domaine des transitions de mouillage, des mesures ellipsométriques ont montré que les forces à longue portée peuvent dédoubler la classique transition de mouillage du premier ordre: lorsque la température croît, une transition du premier ordre est suivie d'une transition du deuxième ordre, dite aussi transition critique. Dans le domaine des films de Langmuir, c'est à dire de films constitués d'une seule couche de molécules amphiphiles insolubles à la surface de l'eau, les propriétés d'un grand nombre de phases ont été étudiées par microscopie de fluorescence ou par microscopie à l'angle de Brewster. Des résultats surprenants et inattendus ont été obtenus à la fois sur la fracture et la fusion de cristaux bidimensionnels.

1 Introduction

Much progress has been made in understanding the physics of thin films over these last years. For a large part, this is due to both the increasing interest in matter confined in two dimensions and the development of new experimental techniques allowing for more detailed experiments. In this paper, we will limit ourselves to studies of thin films on

liquid surfaces. The use of these liquid 'substrates', having no structure in the plane of the film, simplifies experiments considerably, since the roughness of solid surfaces and its crystalline order pose additional experimental challenges.

Among the techniques that caused much progress in the study of thin films is X-ray surface scattering. These experiments can now be performed with high intensity X-ray beams which allows one to obtain information on the structure within the plane of monomolecular films on a molecular scale [1]. The structure along the normal to the film can also be probed using either X-ray or neutron reflectivity [1].

In spite of the enormous progress that has been made in these fields, optical techniques remain very powerful tools with several advantages. The optical experiments are low cost, making it possible to study systems on a very long time scale, much longer than what is reasonably possible with X-rays or neutrons. The oldest optical technique for the study of surfaces, ellipsometry [2], is very sensitive to refractive index variations in the interface region. This technique is consequently well adapted, for instance, to the study of wetting phenomena which do not necessitate to resolve the structure of the film in the plane of the interface. In section 2 below, we will report some ellipsometry observations of the surprising wetting behaviour of alkanes on water.

When resolution in the plane of the interface is necessary, on the other hand, Brewster angle microscopy introduced in 1991 [3,4] and recently improved [5] allows for obtaining direct images of films as thin as monolayers with a resolution in the plane of the interface of better than $1\mu\text{m}$. Moreover, this technique allows one to obtain information on the optical anisotropy within the film, i.e. the molecular orientation within a monolayer. Some examples of Langmuir monolayers studied by Brewster angle microscopy will be given in section 3.

Fluorescence microscopy, introduced in the beginning of the 1980's [6] and improved recently [7] offers similar possibilities but necessitates the introduction of a fluorescent impurity in the film. The two additional drawbacks of this technique are that, first, the molecular orientation observed with this technique is that of the fluorescent impurity, not that of the molecules that constitute the film [8] and that, second, dense and organized phases expel the fluorescent impurities and are consequently more difficult to study than for instance with Brewster angle microscopy. In section 4, we report on a study of the mechanical and melting properties of two-dimensional crystals by fluorescence microscopy. For the system under study, however, the molecules of the two-dimensional crystal are themselves fluorescent and therefore no fluorescent impurity has to be added to the system, thus avoiding the drawbacks of classical fluorescence microscopy.

2 Wetting : first and second order surface phase transitions

If one considers a liquid droplet on a substrate, one generally distinguishes two possible situations. If the sum of the liquid-substrate and the liquid-vapor interfacial tension is larger than the substrate-vapor interfacial tension, the droplet will have a contact angle between 0 and 180° , a situation called partial wetting. On the other hand, the situation may arise that the sum of the liquid-substrate and the liquid-vapor surface tension equals the substrate-vapor surface tension. The contact angle will then be zero and the droplet will spread out to form a uniform film that covers the whole substrate surface: the li-

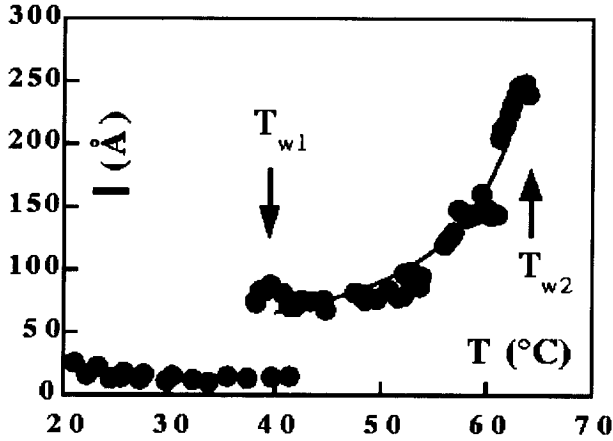


Fig. 1. Wetting of hexane on brine (water and salt : 1.5M NaCl). The thickness of the alkane film as a function of the temperature, as deduced from ellipsometry experiments. T_{w1} is the temperature of the first order wetting transition and T_{w2} is the temperature of the critical wetting transition.

liquid completely wets the substrate. The transition between the partial wetting and the complete wetting state is usually studied as a function of temperature. Up to recently, this surface phase transition was believed to be always of first order, with a discontinuous jump in the thickness of the adsorbed film at the wetting temperature T_w . From a theoretical point of view, this implies that there is a discontinuity in the first derivative of the surface free energy with respect to the temperature [9]. Experiments have confirmed the generic first-order nature of the wetting transition by observing a large hysteresis in the vicinity of the transition temperature, together with the existence of metastable surface states [10–12].

Studying the wetting behaviour of alkanes on water, we have recently shown that the situation can be more complicated than the scenario sketched above. Specifically, we have demonstrated that the long-range van der Waals forces can split the first order wetting transition into a succession of two transitions. This implies that, instead of two surface states (partial and complete wetting), there are three possible surface states. The result of the study of the wetting behaviour of hexane at the brine (salt water) / air interface as the substrate is shown in Figure 1 [13]. Increasing temperature, the first transition at a temperature denoted T_{w1} is clearly of first order, as is evident from the discontinuous jump and the hysteresis. Upon increasing the temperature even further, upon approach of the temperature T_{w2} , a completely continuous (and reversible) divergence of the layer thickness is observed. Thus a continuous or critical wetting transition takes place at the interface.

The first transition is between the partial wetting situation (microscopic film) at low

temperatures and a situation where a mesoscopic film is present on the brine substrate. This mesoscopic film coexists with a droplet of excess liquid, a situation commonly referred to as pseudo-partial wetting [14]. This first order transition can be understood as an incomplete (or frustrated) first order wetting transition. Above T_{w1} the short range forces induce a wetting transition, which in the usual situation would lead to an infinitely thick film (complete wetting). However, in the hexane-brine system, the net effect of the long-range (in the sense of an algebraic decay at large distances) van der Waals forces is an attraction between the two interfaces bounding the wetting layer. This effective attraction between the two interfaces prevents the layer to grow to an infinite thickness: the film remains mesoscopic. Above T_{w1} , increasing temperature even further, the Hamaker constant which quantifies the net effect of the long range forces, decreases and eventually changes sign. The Hamaker constant (and consequently the attraction between the two interfaces) vanishes at a temperature T_{w2} , where the thickness of the film diverges in the experiment. Below T_{w2} , the film thickness is given by the minimization of the surface energy, which for film thicknesses much larger than a typical molecular size, can be written as:

$$V(l) = A'(T - T_{w2})/l^2 + B/l^3$$

where $A = A'(T - T_{w2})$ is the Hamaker constant which vanishes (linearly) at $T = T_{w2}$, and B/l^3 (with $B > 0$) is the next term in the development. It is necessary to retain this second term, since the first one becomes very small. Minimizing the energy, the film thickness increases and diverges continuously as $T = T_{w2}$ is approached according to $l \simeq B/[A'(T_{w2} - T)]$ to become macroscopic at T_{w2} . Thus, a second order or critical wetting transition occurs at T_{w2} which is consequently referred to as the critical wetting temperature.

The second order or critical wetting transition was first observed at $T_{w2} = 53^\circ\text{C}$ in a study of the wetting behaviour of pentane on water [15]. In this system, no evidence of a first-order transition could be obtained at the lowest temperature the experiments could go to, 0°C . A theoretical estimate of the first-order transition temperature gives $T_{w1} \simeq -30^\circ\text{C}$ [16], in qualitative agreement with the experimental result. A slightly different system was used in order to be able to observe the succession of the two wetting transitions: the wetting of hexane on brine. A longer alkane was used since longer hydrocarbon chains have, in general, higher wetting temperatures. This allowed us to shift T_{w1} within the experimental window of observation. Salt was added to increase the refractive index of the water. As the leading term in the Hamaker constant is the refractive index difference between the alkane and water, this allows for a controlled decrease of the Hamaker constant of the system. Consequently, T_{w2} could also be shifted in the experimental window from the high-temperature side; without salt the critical wetting temperature is too close to the boiling point of water to be able to perform experiments. The critical wetting temperatures T_{w2} measured on both the pentane/water and the different hexane/brine systems are in very good agreement with the temperature at which, if one performs the calculation of the Hamaker constant, the effective attraction between the two interfaces vanishes, thus confirming the new wetting scenario described above.

The experiments described above took several years to perform. The problem is that the long range forces which stabilize the thickness of the mesoscopic film in the pseudo-partial

wetting state are very weak. One of the consequences is that the equilibrium film thickness is very difficult to reach; at each temperature, we typically had to wait for a week before stable values could be obtained. For this reason, the choice of ellipsometry which was used as the experimental technique in this study, is probably the most appropriate technique to study the evolution of the film thickness with temperature.

3 Two-dimensional phase transitions in Langmuir films

Water-insoluble amphiphilic molecules deposited at the surface of water form a monomolecular film : one part of the amphiphilic molecule is hydrophobic and stays on the surface of the water while its other, hydrophilic, part is immersed in the water. These molecules can be compressed strongly in the plane of the interface by decreasing the total surface area using movable barriers. This is because strong hydrophilic forces maintain the molecules on the surface of the water. At high surface pressure Π , the film becomes metastable and collapses, i.e. the film undergoes a mechanical instability, and multilayers can appear. However, a number of amphiphilic molecules allow for surface pressures higher than $\Pi = 50mN/m$ before collapse occurs. Noting that the thickness of the film is $h \simeq 20\text{\AA}$ (the length of a typical amphiphilic molecule), one can calculate the corresponding three dimensional pressure in the film, $p \simeq \Pi/h$. This pressure then reaches values larger than $p = 3.5 \times 10^7 N/m^2$ (350 bars) without collapse occurring.

Just like is done in three dimensions, thermodynamic studies of films, i.e., matter confined in two dimensions can be performed, yielding the phase diagram of an amphiphilic molecule forming a monolayer. The thermodynamic variables are temperature, area per molecule (corresponding to the molecular volume in three dimensions) and surface pressure (corresponding to the pressure). The area per molecule A is deduced from the number of molecules deposited at the surface and the total area of the film; the surface pressure Π is deduced from the force per unit length exerted by the film on one of the movable barriers.

As an example, Figure 2 gives the generic (but simplified) phase diagram for fatty acids ($\text{CH}_3 - [\text{CH}_2]_n - \text{COOH}$), in which the acid group $-\text{COOH}$ is hydrophilic and the hydrocarbon tail $\text{CH}_3 - [\text{CH}_2]_n -$ is hydrophobic). This phase diagram is remarkably rich. For low surface pressures and low surface density (large area per molecule A), one finds a two-dimensional gaseous and a two-dimensional liquid phase. These are disordered phases equivalent to the three-dimensional gaseous and liquid phases. At high surface pressure and density two different crystalline phases, i.e. phases with (quasi-) long range positional and orientational order are observed, analogous to three dimensional crystals. In the CS crystalline phase the long axis of the amphiphilic molecule is vertical to the surface, whereas in the L'_2 phase it is tilted. Between the crystalline phases and the liquid and gas phases, a large number of other phases are observed: three tilted phases L_2 , L'_2 , O_v and two non-tilted phases S and LS in the simplified phase diagram). These phases are mesophases with a long range orientational but a short range positional order; consequently these are very similar to one layer of a smectic phase observed for liquid crystals in three dimensions. However, the plane of the monolayer, contrary to what is the case for a smectic layer, is not a symmetry plane since the water imposes the same orientation to each molecule (the polar head in the water and the tail in the air).

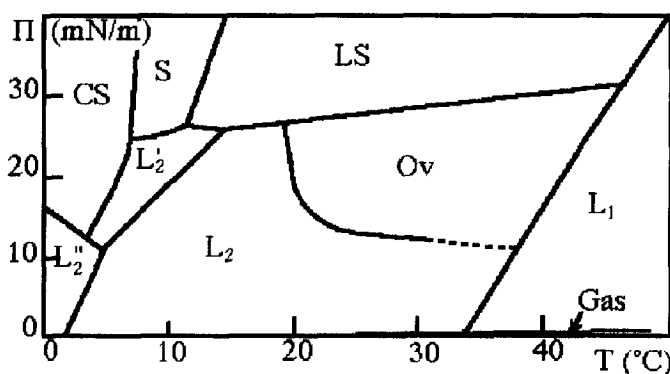


Fig. 2. Generic and simplified phase diagram for Langmuir films of fatty acids. The temperatures (and surface pressures) indicated on the phase diagram are for behenic acid on water at pH=2

The structure on a molecular level and the ordering within these phases have been studied extensively by X-ray surface scattering [1]. On a more macroscopic scale (larger than $1\mu\text{m}$), fluorescence microscopy and Brewster angle microscopy yield images of domains when phase coexistence is observed, and reveal the orientation of the molecules within the phases; also the defects in the orientation can be observed [8] (Figure 3). These new developments have allowed for detailed studies of the properties of two-dimensional phases, in particular the physics of the two-dimensional mesophases.

4 Mechanics, fracture and melting of crystals in a Langmuir monolayer

Here, we focus on the properties of a macroscopic two-dimensional single crystal, allowing for macroscopic experiments. In two dimensions, thermal fluctuations destroy the long range positional order. The resulting quasi long-range order observed in two-dimensional crystals is characterized by a (very slow) algebraic decay of the positional correlations. This probably explains why crystalline two-dimensional phases of compounds such as fatty acids or fatty alcohols contain too many defects to obtain macroscopic single crystals. Surprisingly, some compounds, such as the NBD-stearic acid we consider here, are able to form single crystals of macroscopic size, typically $1\text{mm} \times 20\mu\text{m}$. In the following, we first describe the phase diagram of the compound, after which we describe the mechanical and fracture experiments; finally, we study the melting of these crystals.

4a. Phase diagram of NBD-stearic acid

An isotherm (surface pressure Π as a function of area per molecule) at $T = 20^\circ\text{C}$ of a monolayer of pure NBD-stearic acid [or 12-(N-methyl)-N-((7-nitrobenz-2-oxa-1,3-diazo-4-yl) amino) octadecanoic acid] is shown in Figure 4 [18,19]. One observes a first order phase transition characterized by a coexistence plateau and a hysteresis: in the plateau region, the surface pressure during a compression is slightly larger than the surface pressure during the decompression.

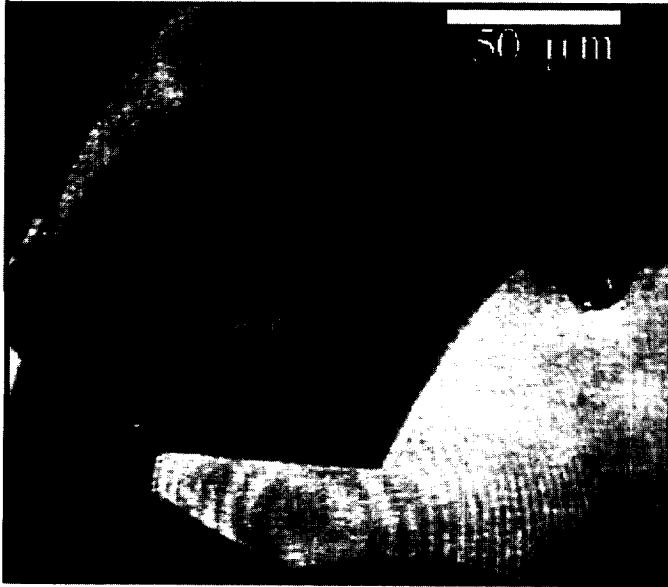


Fig. 3. Example of an image of a tilted mesophase obtained with the Brewster angle microscope (L'_2 phase of hexadecanoic acid). The surface density is homogeneous. An analyser in the microscope allows to observe the surface optical anisotropy resulting from the tilt of the molecules. Line defects limit regions of uniform tilt azimuthal direction (regions of uniform grey level).

The NBD-group is a fluorescent group covalently attached to the amphiphilic molecule. When illuminated with blue light, the NBD-group emits orange light. This allows one to observe the monolayer directly by fluorescence microscopy. Figure 5 shows such an image of the film, obtained in the plateau region of the isotherm i.e., at two-phase coexistence. The molecules of NBD-stearic acid were deposited on the water surface at a low surface density. Subsequently, by a very slow compression the surface density was increased to that of the plateau region. Fluorescence microscopy reveals the existence of rectangular bright domains in a dark phase. These bright domains move but do not deform when a slight air stream passes over the film, indicating that the dark background phase is fluid. The bright domains are, in fact, solid as was demonstrated by means of micro-mechanical experiments described below. Moreover, both X-ray and electron diffraction have shown that the dense phase is crystalline having a quasi long-range positional order [20,21]. In addition, analysis of the fluorescence of the solid phase and of the polarization of the reflected light when the film is illuminated with red light (to avoid fluorescence) indicates that the fluid phase is disordered (a two-dimensional liquid phase), while the domains of solid phase are single crystals [18,19].

The surprisingly large contrast observed between the solid phase and the liquid phase by fluorescence microscopy is explained by the difference of the configuration of the molecules in the liquid phase and in the crystal. In the liquid phase, the area per molecule is large ($> 83\text{\AA}^2$) and the molecules lie flat at the surface of water. In fact, the NBD group is

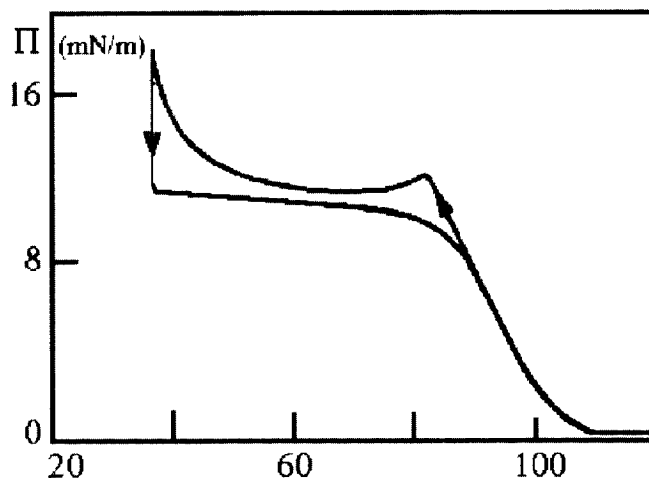


Fig. 4. Isotherm at 20°C of a monolayer of NBD-stearic acid (surface pressure Π as a function of the area per molecule in \AA^2). A hysteresis is observed in the plateau region where the values of Π measured increasing A are larger than those obtained by decreasing A

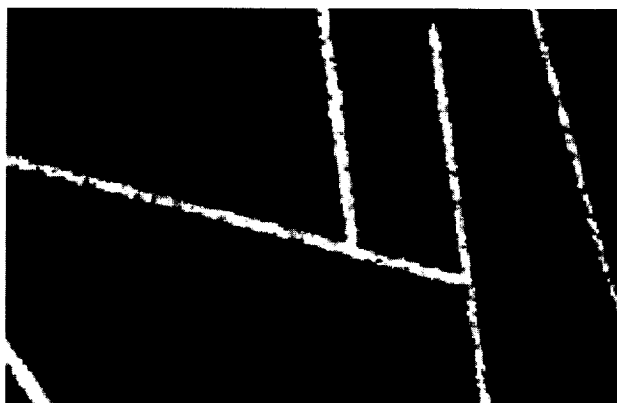


Fig. 5. Image of a film of NBD-stearic acid obtained in the plateau region by fluorescence microscopy. In this layer, the length of the crystals was 0.8mm and their width was $10\mu\text{m}$.

rather polar, and thus acts as a second hydrophilic group: in the liquid phase the two polar groups are immersed in water. In contact with water, the fluorescence of the NBD groups is quenched; consequently the 2d liquid phase does not fluoresce and appears as the dark phase on the images. In the solid phase, the area per molecule is about three times less; the long axis of the molecules are perpendicular to the surface. The NBD groups are out of water and a large fluorescence is observed for the solid phase. The thickness of the crystals (one molecule) was verified by ellipsometry experiments [18].

In conclusion, in a Langmuir film of pure NBD-stearic acid one obtains macroscopic single two-dimensional crystals in equilibrium with a two-dimensional liquid phase of the same compound. The observation of a coexistence plateau in the isotherms, as well as the large change in area per molecule at the liquid-solid transition indicates that the observed liquid-solid transition is strongly first order.

4b. Mechanical properties and fracture of a single two-dimensional crystal

The rectangular shape of the crystals and their macroscopic length, of the order of one mm, allows for mechanical experiments.

Measurement of the Young's modulus. Stresses were applied to single crystals using three parallel glass fibres (diameter $10\mu\text{m}$) piercing through the surface of the water perpendicularly. A single crystal can be introduced between these fibres. Two of them are fixed at a distance of 1mm with respect to each other. These maintain the two extremities of one side of the crystal in place. The third fibre can be moved and is used to apply a force to the middle of the crystal, on the other side. In this way, a classical three-point flexion experiment is obtained. The surface of the glass fibres is silanized such that the wetting angle with the surface of water (covered with the Langmuir film) is 90° , in order for the glass fibres do not deform the surface of the water by capillary rise on the glass fibres. The force applied to the crystal can be deduced directly from the deflection of the middle glass fibre, having calibrated its force constant. The deformation can be obtained directly from the fluorescence images. The plot of the deformation of the crystal versus the applied force is linear and reversible: no hysteresis is observed (Figure 6). The crystal is thus perfectly elastic; no plastic deformation is observed within the accuracy of the experiment. From the slope of the force-deformation curve, knowing the dimensions of the crystal, the two dimensional Young's modulus can be obtained: $E_{2d} = (3660 \pm 1300)\text{mN/m}$ [22].

The Young modulus is measured on a single crystal in equilibrium with its liquid, i.e. at its melting point T_m . According to the theoretical prediction deduced from the initial ideas of Kosterlitz and Thouless [23-26] of melting by dislocation unbinding, the Young's modulus at the melting point for a two-dimensional crystal is

$$E_{KT} = 16k_B T_m / A$$

where k_B is the Boltzmann constant. With $A=33\text{\AA}^2$ and $T_m = 300^\circ\text{C}$, one obtains $E = 630\text{mN/m}$, a value 6 ± 2 times smaller than the measured value. This means that the melting starts at a temperature much higher than that predicted by theory of melting by dislocation unbinding. This confirms in fact that the melting in our case is strongly first order: the melting is not induced by dislocation unbinding, which would lead to a continuous melting transition.

Fracture. A very surprising observation made during these experiments is that the 2d-crystals under the stress applied with the three glass fibres break after a certain delay. Subsequent experiments reveal that the delay time t_B is a steep and well-defined function of the stress τ . The initial crack appears at a time t_B , after which it propagates quickly. The experimental results revealed that a plot of the natural logarithm of the mean value $\langle t_B \rangle$ versus $1/\tau^2$ yields a straight line over three decades in time (Figure 7) [27] :

$$\langle t_B \rangle \sim \exp(\tau_0/\tau)^2$$

This behaviour is in agreement with the predictions of Griffith [28] who calculates

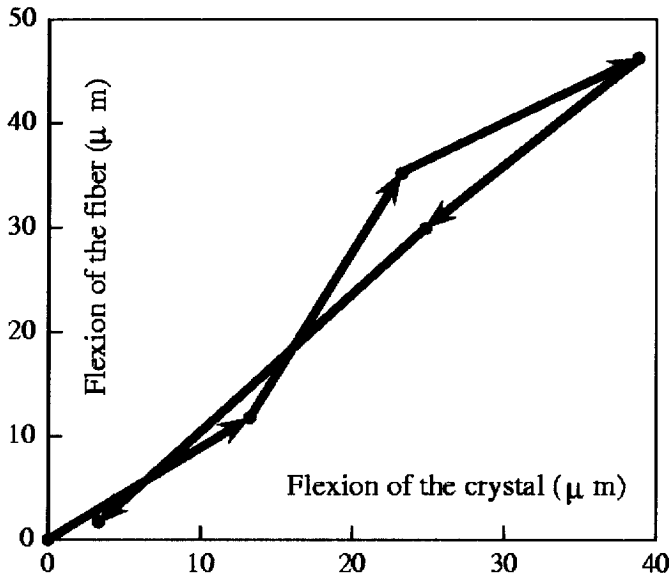


Fig. 6. Bending of the middle glass fibre (proportional to the force applied to the crystal) as a function of the flexion of the two-dimensional crystal. The same results are obtained when increasing or decreasing the stress.

the energy barrier to nucleate a crack in a two-dimensional crystal from homogeneous nucleation theory. In this picture, the energy barrier to overcome before a crack can grow is due to the fact that new surface (line in 2d) needs to be created. The energy gain upon fracture of course is the elastic energy stored in the volume (surface) that is liberated; assuming an activated process, this leads to the observed dependence of the breaking time on the stress. This indicates that the observed fracture is not due to a defect motion in the crystal but to the nucleation of cracks. A possible exception occurs at the highest stresses; here a fraction of the crystals breaks instantaneously. However, the fracture does not result from the nucleation of a single crack as is supposed in the model of Griffith. If this were the case, the distribution of t_B 's for a given force would be a Poisson distribution (i.e., an exponential) contrary to the well-defined time of breaking observed in the experiment (Figure 8). The macroscopic breaking of the crystals thus probably results from the nucleation of a large number of micro-cracks.

In conclusion, we observe the nucleation of a fracture in the two-dimensional crystals. The fracture initiates on the borders of the bended crystals, opposite to the third, mobile fibre. As the nucleation process appears to be well described by homogeneous nucleation theory, one may infer that there are no (or very few) defects present in the long borders of the crystals or that these defects do not play any role in the fracture process.

4c. Melting of the two-dimensional crystals

The melting of the 2d-crystals prepared at room temperature can be achieved by de-

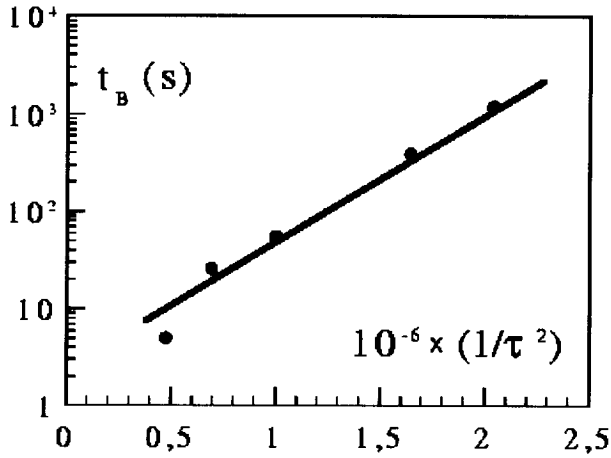


Fig. 7. Mean value of the delay time t_B (on a logarithmic scale) versus $1/\tau^2$. τ is the relative elongation of the borders of the bended crystal and is proportional to the stress.

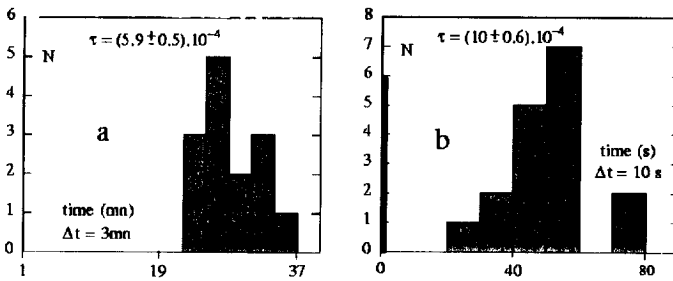


Fig. 8. Statistics of the breaking time (a) for a low strain ($\tau = 5.9 \pm 0.5 \cdot 10^{-3}$) and (b) for a somewhat higher strain ($\tau = 10 \pm 0.6 \cdot 10^{-3}$). For the highest strains one observes the apparition of an instantaneous rupture.

compression or by heating. A completely different process which induces the melting is illumination with blue light at a high intensity. The melting starts after illumination at constant intensity for a time t_m . Subsequent experiments show that the melting results from a chemical reaction with the oxygen in the air: at fixed light intensity, the melting time t_m decreases with increasing oxygen content in the air above the monolayer (Figure 9). Moreover, this chemical reaction is reversible: when the illumination is stopped just before the melting appears, the crystal loses the 'memory' of the illumination in about 10 minutes. A possible interpretation of the reason for this third method to melt the crystals is that a photochemical reaction creates impurities in the crystal. The presence of these

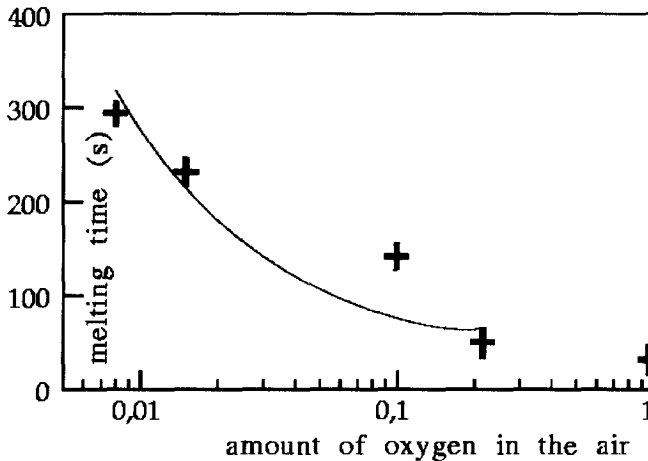


Fig. 9. Melting time, defined as the time of illumination (for a fixed light intensity) necessary to initiate the melting as a function of the amount of oxygen in the air above the crystal (volume fraction).

impurities will translate the liquid-solid transition line in the phase diagram, just as in freezing-point depression.

An important point is that the same behaviour is observed, independently of which of the three processes is used to melt the crystals. As already noted above, the melting is not a dislocation unbinding process. However the melting of these 2d-crystals shows very unexpected characteristics and some of them demonstrate that dislocations do, in fact, play a fundamental role in the melting process. The most important of these observations are [29]:

1 - The melting by heating, decompression or illumination of a single crystal starts everywhere in the crystal or along the small borders. However, when the crystals have melted, strips of $2\mu\text{m}$ width along the long borders of the initial crystal resist to the melting (it takes about 15 minutes to melt the inside of a crystal for a temperature increase of 1°C ; however, an increase of 10°C is required to melt the borders in a similar time). (Figure 10)

2 - When two crystals have grown into each other, which is sometimes observed in the experiment, a grain boundary is present. Along such a grain-boundary, the melting occurs almost instantaneously, a long time before the melting of the inside of the crystals starts.

3 - When a crystal is subjected to a bending stress, using the three glass fibres, the melting starts along the neutral line of the stress, the middle of the crystal (Figure 11).

4 - The same observation, the melting along this neutral line, is also observed when the crystal is subjected to a stress, and subsequently melted by illumination a short time after the stress has been relaxed. However, if the crystal is illuminated more than three minutes after the stress has been released, the melting appears everywhere in the crystal, except again in the two strips along the long borders.

5 - When a crystal is broken in two along a line parallel to the long borders, the two

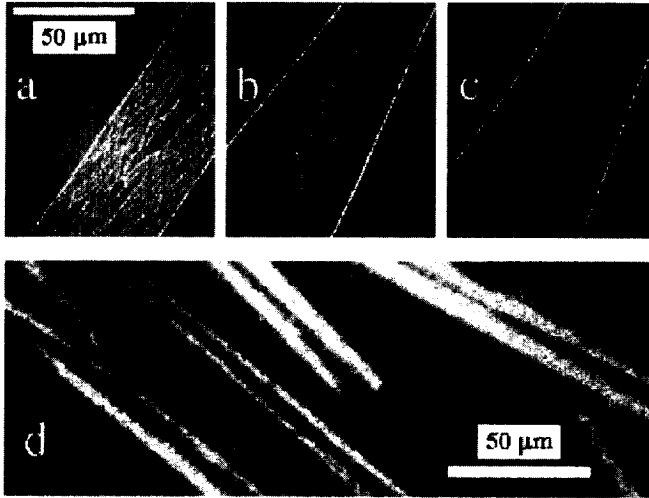


Fig. 10. (a-c) Three images showing the evolution of the melting by illumination. d) melting by heating. For both cases, the long borders resist to the melting.

newly created borders do melt, provided the crystal is illuminated immediately after the fracture. The two old borders do not melt again. If we wait about 20 minutes between the breaking in two of the crystal and the illumination, two strips along the new borders resist to the melting (Figure 13).

Observations 2, 3 and 4 reveal the important role of the defects in the melting. Along a grain boundary, i.e., an array of dislocations, the melting is very rapid. From thermodynamic considerations one would expect to observe exactly the contrary to observation 2: as the melting relaxes the stress (and consequently lowers the free energy), it should be easier to nucleate the liquid phase at the points of maximum stress [30]. In the experiment, the contrary is observed: the neutral line is in fact the region in the crystal where the stress is minimal, and the melting starts here. Consequently, one cannot look at the formation of the liquid phase as being due an energy barrier (determined by the homogeneous nucleation of the liquid phase) that has to be overcome. In the crystal under a bending stress, dislocations that are present in the crystal will move in order to accommodate the stress. In a stressed crystal the so-called Peach-Koehler force acts on the dislocations [31]. Considering only the climb of the dislocations, depending on their position and orientation, half of the defects are rejected out of the crystal from the borders, whereas the other half moves towards the neutral line. As the melting of the stressed crystal starts here, one again observes that the melting appears first where there is an accumulation of dislocations. Observation 4 confirms that the effect of the stress on the melting is not a direct one; even in the absence of stress the crystal has a 'memory' of the applied stress. The suppression of the stress suppresses the Peach-Koehler force; after a delay t_m which is a characteristic time for the diffusion of the dislocations away from the neutral line towards the rest of the crystal, the melting again starts everywhere in the crystal (except along the long borders).

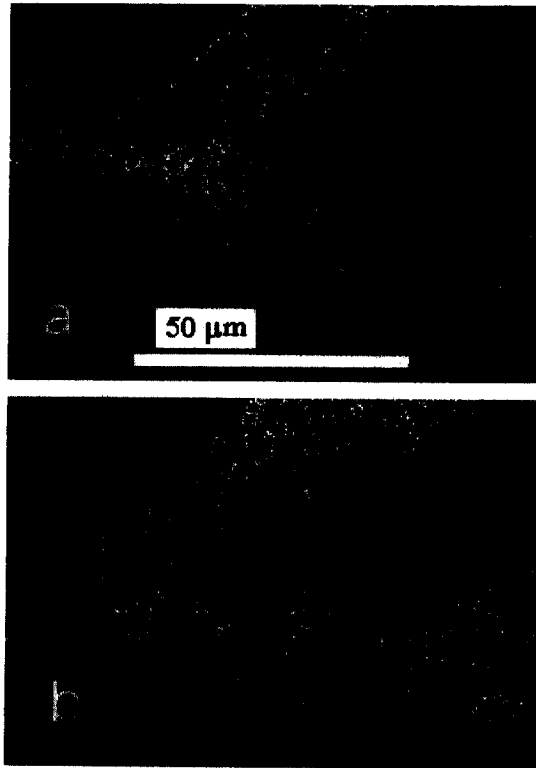


Fig. 11. (a) Two crystals grown into each other, indicating the presence of a grain boundary. (b) upon illumination, the melting appears first along the grain boundary.



Fig. 12. A crystal subjected to a stress is melted by illumination a short time after the stress has been released. The melting starts along the neutral line.

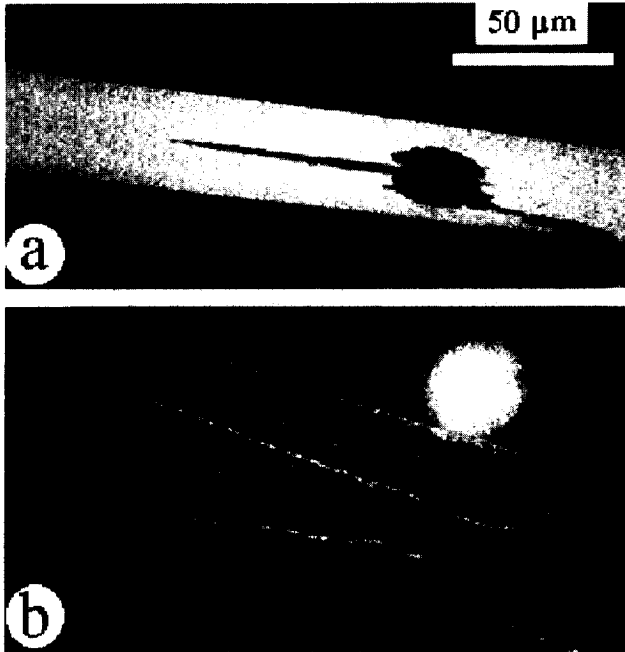


Fig. 13. (a) A crystal is broken in two along a line parallel to the long borders. (b) 20 minutes later, the two new borders resist to the melting.

In the light of these considerations, observations 1 and 5 suggest that dislocations are rejected from the strips along the long borders of the crystal. If the concentration of dislocations is small, the nucleation of the liquid phase should be more difficult. This is supported by the results from the fracture experiment. The observation of a delay before fracture is compatible with the theory for the (homogeneous) nucleation of cracks, which implies that no defects are present in the border where the fracture initiates. A possible mechanism for the removal of dislocations in the vicinity of the border of the crystal is that the effective interaction of the dislocations with the boundary can be expressed as an interaction with their image dislocations. This interaction leads to a removal of the defects from the boundary region. However, the large distance of interaction observed in these experiments ($2\mu\text{m}$) remains a puzzle. It is worthwhile noting that the large anisotropy of the crystal probably plays an important role in this behaviour: the experiments indicate that the dislocations are rejected from the long boundaries but not from the short ones, which melt in the same fashion as the rest of the crystal, or even more rapidly.

In conclusion, the melting of the two-dimensional single crystals of NBD-stearic acid is not driven by dislocation unbinding. This can be concluded from the observation that the melting temperature is six times larger than what would be expected for dislocation unbinding. However, the dislocations do play an important role in the melting process: the melting is strongly first order and the liquid phase is formed by heterogeneous nucleation, with the dislocations as nucleation centres. As the long borders of the crystal appear to have a very low concentration of dislocations, the liquid phase can not nucleate here,

and the borders resist to melting. Such a behaviour has never been observed in three dimensional crystals which in generally start melting at their free surface. This observation is all the more surprising, since the two-dimensional crystals are in equilibrium with their liquid phase. In principle, there is thus no energy barrier for the formation of the liquid phase, since no new solid-liquid 'interface' needs to be created.

5 Conclusion

Optical techniques, such as ellipsometry, Brewster angle and fluorescence microscopy are well-adapted for detailed studies of low-dimensional systems and their phase transitions. We have discussed these techniques giving a few examples of experiments which would be very hard or impossible to perform using other experimental techniques such as X-ray or neutron scattering. For the wetting behaviour of alkanes on water, ellipsometry experiments have revealed a surprising subtlety in the usual picture of wetting transitions: instead of one transition that is discontinuous, a succession of two transitions can be observed, the second of which is continuous. In the study of Langmuir films, monomolecular layers of amphiphiles on the free surface of water, Brewster angle microscopy has allowed detailed studies of the phase behaviour of fatty acids, revealing a large number of two-dimensional phase transitions that have their analogy either in three-dimensional atomic systems, or in liquid crystalline phases found in three dimensions. Finally, fluorescence microscopy on two-dimensional crystals shows that the melting and fracture properties can be quite different from what happens in three dimensions. The generally accepted conclusion that in two dimensions defects play a more important role than in three dimensions seems to be borne out in the experiments; however, the specific way in which the defects intervene appears to be much more subtle than has been anticipated so far.

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