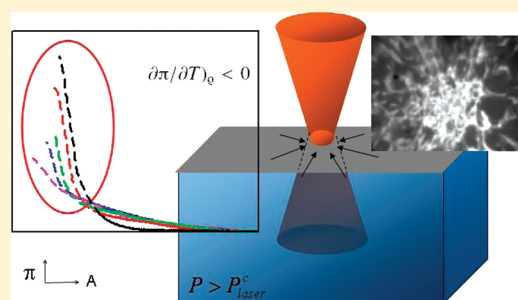


Dilatational Yielding of Solid Langmuir Monolayers

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ABSTRACT: In a previous work, Muruganathan and Fischer observed laser-induced local collapse of a methyl stearate monolayer. These experiments opened the possibility of studying the collapse mechanism in a highly controlled manner, since the laser intensity can be easily varied and collapse happens in a definite place (the laser focus). In this paper we extended the work presented by Muruganathan et al., describing the local yielding as an alternative pathway toward monolayer collapse competing with the global collapse of the monolayer. We first corroborated that the laser-induced collapse is a thermocapillary effect and afterward determined the threshold laser power necessary for the local pathway to win over the global collapse. We show that the laser threshold is determined more by the gradients in temperature and pressure than by the global pressure and temperature. We propose that the flow of material into the focus of the laser is observed after the yield stress of the monolayer is overcome. The higher the yield stress, the higher the temperature gradient that is necessary for the monolayer to yield. The local pathway opens only when the derivative of surface pressure with temperature is negative such that stress gradients point toward the laser focus and a sink of material is generated. In such a case we are able to give estimates of the dilatational yield pressure of the solid monolayer.



1. INTRODUCTION

In three dimensions we characterize solids and liquids as two distinct thermodynamic phases differing in their long-range order. More importantly fluids and solids exhibit different response to external shear stress. A solid deforms, while a liquid flows. We can convert a solid into a liquid and vice versa by phase transitions, where the external intensive variables such as the temperature and the pressure cross the phase transition line. The conversion of a solid to a liquid in this way we call melting. When we melt a solid, the liquid that is formed is at rest and not in an excited kinetic state. We may also convert a solid to a liquid by applying shear stress. The solid will undergo shear deformations under this stress up to a critical threshold, the yield stress. When approaching the yield stress, shear deformations diverge. Beyond the yield stress shear deformations grow as a function of time with a constant deformation rate. The material flows and has yielded to a liquid. The shear yielding of a solid is not an equilibrium phase transition but a kinetic process. We directly convert the solid to a kinetic flowing liquid. In three dimensions there is only one situation where a solid yields under the action of isotropic instead of shear stress. Under all normal circumstances mass conservation prevents a constant dilatational flow of material toward the center of a three-dimensional solid. Only the action of gravity can overcome the three-dimensional dilatational yield pressure by forming a black hole and letting any material constantly flow past the horizon into the interior of the hole where its final destiny is the collapse into the space time singularity.

Mass conservation still holds locally but no longer globally. The critical mass leading to gravitational collapse converts spatial coordinates that are independent of the time into time-dependent spatial coordinates and space yields.

For material existing in a quasi two-dimensional world mass conservation is not as strict and the curvature of the interface is not required for dilatational yielding. Surfactants living in the two-dimensional interface between adjacent three-dimensional phases may escape into the third dimension when conditions become too crowded at the surface. Indeed one can compress a solid monolayer using the barriers of a Langmuir trough exerting a constant surface pressure onto the monolayer resulting in a constant rate of compression and a constant expulsion of surfactants from the interface into the third dimension. As in three-dimensional solids, the yielding of the solid monolayer is not an equilibrium phase transition but a nonlinear kinetic process that must occur before the monolayer can locally collapse into the third dimension. What makes the yielding unique in a solid monolayer is the different dilatational instead of shear nature of the applied stress. The current work is a study of the local yielding of solid monolayers near a defined location on the monolayer. When we talk about a “solid” monolayer, we use the term solid with respect to the mechanical response to a steady

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stress being a steady deformation not a steady deformation rate. The use of the term solid in this mechanical way does not describe the thermodynamic hexatic order of the phase.

At this specific location we establish conditions favorable for monolayer collapse. The monolayer, however, will only locally collapse after a dilatational yielding threshold is overcome, allowing the monolayer to flow. The excess dilatational stress needed to finally force the monolayer to flow into the third dimension via the prepared collapse point allows us to quantify the yielding of the monolayer.

Surfactant monolayers at the air–water interface have been extensively studied as an interesting 2D system in apparent equilibrium states. These systems present different phase states depending on the temperature, lateral pressure, subphase composition, and nature of the monolayer-forming molecule. The monolayer is stable up to a characteristic rate-dependent pressure, called the “collapse pressure”. At this point, the external compression rate of the molecules can no longer overcome the rate at which molecules are expelled from the interface. The modes of collapse and the rate-dependent collapse pressure vary with the composition of the monolayer, with the subphase, and with the temperature,^{1–7} which also determines the morphology and material properties of the monolayer. Depending on the monolayer material properties, collapse of a 2D monolayer may lead to the formation of different 3D aggregates in the subphase, e.g., bilayer folds, vesicles, tubes, and micelles, etc. If these aggregates can readily respread at the interface upon decrease of the monolayer surface density, then the collapse is reversible; otherwise, it leads to irreversible loss of material from the interface. Collapse phenomena have been studied extensively using experimental techniques^{7–11} and theoretical models.^{2,4–7,12–16} The pathway from a 2D monolayer to a certain 3D structure, however, requires the transport of the monolayer toward the point of collapse. Until now much of the kinetic path toward collapse remains unclear. Pathways of the collapse of solid monolayers may reach collapse via the formation of cracks,^{1–4,17} via the shuffling of sheets on top of each other, or via the conversion of the solid monolayer into a liquid monolayer prior to collapse. In the latter case either melting¹⁸ or yielding enables the flow of the monolayer into the third dimension.

Muruganathan and Fischer¹⁵ observed laser-induced local collapse of a methyl stearate monolayer. On the basis of the assumption of a liquid monolayer, they predicted that locally heating a Langmuir monolayer at a surface pressure close to collapse with a focused IR laser induces the local collapse of the monolayer if the collapse pressure of the monolayer decreases more steeply with temperature than the surface tension of the pure water–air interface ($\partial\pi_c/\partial T < \partial\sigma_w/\partial T$). These experiments opened the possibility of studying the collapse mechanism in a highly controlled manner, since the laser intensity can be easily controlled and collapse happens in the laser focus. However, not all monolayer-forming molecules with $\partial\pi_c/\partial T < \partial\sigma_w/\partial T$ show laser-induced local collapse. For instance, some of us found that no local collapse could be observed in the case of dipalmitoylphosphatidylcholine (DPPC), dioleoylphosphatidylcholine, octadecanol and myristic and pentadecanoic acid monolayers, among others. The present work is a revision of the model presented in ref 15, starting with a detailed study of the methyl stearate laser-induced collapse. The results of this study first demonstrate that the laser-induced local collapse in insoluble monolayers is a thermocapillary effect. Second we show that as compared to global collapse there is a second threshold that must

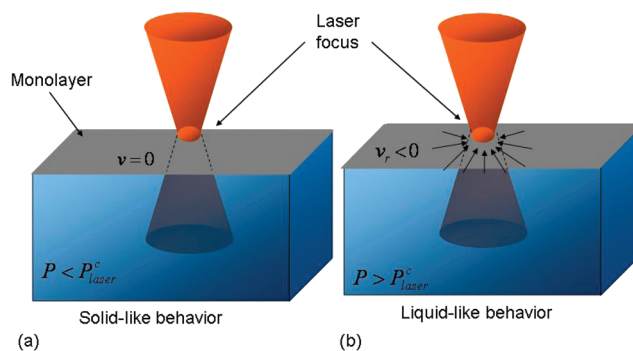


Figure 1. scheme of a monolayer locally heated by a laser. (a) $P < P_{\text{laser}}^c$, (b) $P > P_{\text{laser}}^c$. v is the flow velocity of the monolayer. A movie (yielding.avi) of the inward flow above $P > P_{\text{laser}}^c$ is shown in the Supporting Information.

be overcome prior to having laser induced local collapse. This threshold is accompanied by a conversion of the solid into a liquid monolayer. We show that the conversion differs from local melting and conclude that it must be local yielding. Lateral pressure versus area isotherms at a range of compression rates fast enough to prevent significant loss of material via collapse are performed. From these isotherms we determine the thermodynamic quasi equilibrium properties (a local minimum in the thermodynamic potential) of the monolayers when blocking the collapse. We measure the pyrobaric coefficient of a blocked monolayer which is the derivative of the surface pressure with the temperature of the monolayer at constant surfactant density. We show that local yielding of monolayers followed by local collapse correlates with a negative pyrobaric coefficient. From the pyrobaric coefficient we estimate the dilatational yield pressure. Only monolayers where the thermocapillary dilatational stress pushes the material into the laser focus with a strength exceeding the yield pressure choose the local collapse pathway in favor of the global collapse.

2. EXPERIMENTAL METHODS

2.1. Materials. The lipids were purchased from Avanti Polar Lipids (Alabaster, AL). All of the other surfactants were from Sigma Aldrich. Surfactant solutions were fluorescently labeled with 1 mol of 1,2-dihexadecanoyl-*sn*-glycero-3-phosphoethanolamine, triethylammonium salt (Texas Red DHPE) purchased from Molecular Probes (Eugene, OR, USA). The surfactants were dissolved in chloroform (about 1 mM) and spread at the air–water interface. The subphase was pure water (Millipore Milli-Q 18 M Ω cm) or solutions of CuSO₄·5H₂O (Merck).

2.2. Methods. A Nima and a KSV film balance were used for monolayer investigation. At least triplicate monolayer isotherms were obtained and averaged at a compression rate of 0.06 \AA^2 molecule⁻¹ s⁻¹ or higher. For each material, it was ascertained that increasing the compression speed produced no change in the isotherms and that reexpansion of the compressed monolayer led to no significant loss of material. Reproducibility was within a maximum of ± 1 mN m⁻¹ for the surface pressure and below ± 3 \AA^2 molecule⁻¹ for the molecular areas. The collapse pressure was determined as the highest lateral pressure reached during the compression process. The setup for studying collapse phenomena has been described in detail elsewhere.¹⁶ Briefly, it consists of a home-built Langmuir trough placed on the stage of an inverted

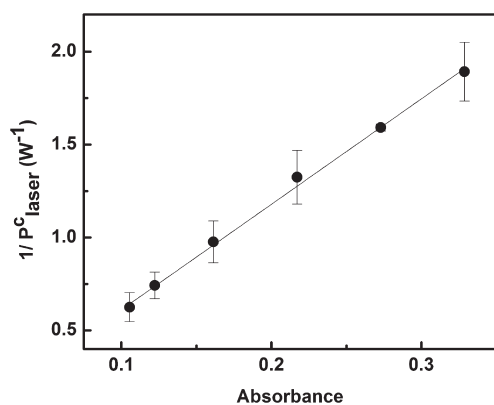


Figure 2. Reciprocal of the critical laser power in methyl stearate as a function of the absorbance of the aqueous CuSO_4 subphase at 1064 nm. The linear behavior shows that the laser-induced collapse is a thermocapillary effect.

fluorescence microscope (Zeiss-Axiovert 135) with a $100\times$ water immersive objective. The temperature of the trough can be controlled precisely. An IR laser beam ($\lambda = 1064$ nm, $P = 2$ mW to 2.7 W) was used to locally heat the monolayer in the focus of the objective. The light is partially absorbed by the subphase and heats the monolayer locally around the focus. In the previous work,¹⁵ it was observed that upon focusing an IR laser on a methyl stearate monolayer in the liquid condensed phase, at a laser power higher than a critical value of about 2 W, a radial flow of the surface toward the center sets in; see the scheme in Figure 1. Muruganthan and Fischer measured the flow quantitatively by following the characteristic texture of the monolayer as a function of time. Surfactant material aggregates into a three-dimensional structure in the hot spot that grows in radius due to a radial inward flow of the monolayer surrounding the aggregate.

3. THERMOCAPILLARY HEATING

In the present section we focus on determining the driving force of the laser-induced local collapse. To ensure that the phenomenon is driven by local heating and not by an optical effect, we performed experiments on subphases that contain CuSO_4 at different concentrations. The aqueous complex of Cu(II) absorbs light at 1064 nm according to the Lambert and Beer law, and thus, the subphase absorbance at the laser wavelength of 1064 nm linearly increases with the CuSO_4 concentration. Therefore, the absorbed power of the laser beam (P_{abs}) for a fixed laser power (P_{laser}) will increase linearly with the concentration in the subphase according to the following relation: $P_{\text{abs}} = P_{\text{laser}}(\text{Abs})r_w$, where r_w is the focal width of the laser which is about $1\ \mu\text{m}$ and Abs is the absorbance of the subphase at 1064 nm. We determined the minimum laser power that is necessary for observing the flow of molecules into the laser focus (P_{laser}^c). These experiments were performed with methyl stearate monolayers at $20\ ^\circ\text{C}$ and at a surface pressure near the collapse surface pressure $\pi = \pi_c - \Delta\pi$, $\Delta\pi \approx 1\text{--}5$ mN/m using subphases with increasing CuSO_4 concentrations. By collapse surface pressure we mean the highest lateral pressure reached in a compression isotherm registered at $-0.06\ \text{\AA}^2\ \text{molecule}^{-1}\ \text{s}^{-1}$ and at the indicated temperature. The isotherms of methyl stearate on the CuSO_4 solutions are indistinguishable from the isotherm on pure water (data not shown).

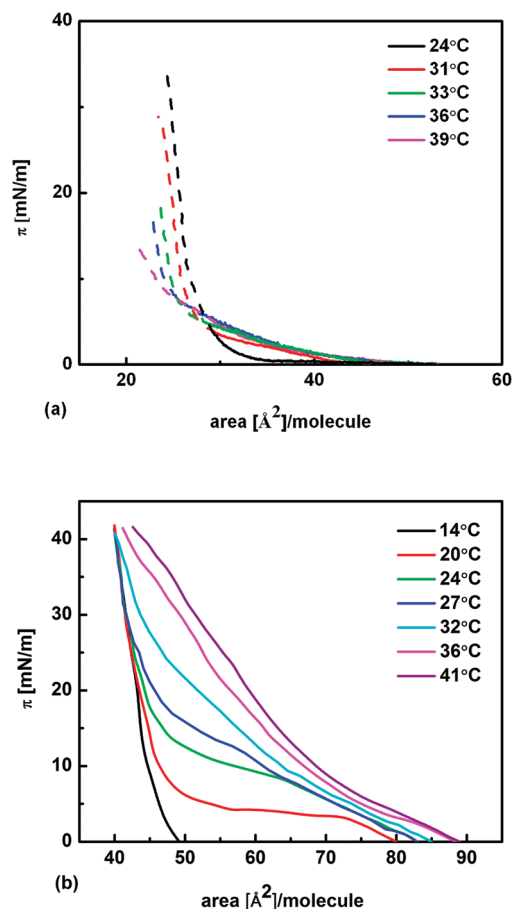


Figure 3. Surface pressure versus average molecular area compression isotherms for (a) ethyl stearate and (b) DPPC for the indicated temperatures at the air/water interface. In a, the isotherms are shown as dashed lines in the regions where $\text{pbc} < 0$. For DPPC $\text{pbc} > 0$ everywhere. The isotherms were recorded at a compression rate of $\dot{A} = -0.06\ \text{\AA}^2\ \text{molecule}^{-1}\ \text{s}^{-1}$.

Figure 2 displays the critical laser power as a function of the absorbance of the subphase at 1064 nm. The inverse of P_{laser}^c increases directly proportional with the absorbance, as it is expected if the process is purely driven by a local heating, since this means that the flow starts at a fixed absorbed power regardless of the subphase composition. Therefore the critical stress needed to yield the monolayer is a function of the temperature gradient only.

4. ISOTHERMS

In a liquid, a local temperature gradient will generate flow to keep the surface tension constant ($\nabla\sigma \approx -\nabla\pi = 0$). On the contrary, for a material in the solid state the density remains roughly constant $\nabla\rho = 0$ upon heating, and a local gradient of temperature will produce a pressure gradient that is proportional to $\nabla\pi = \left(\frac{\partial\pi}{\partial T}\right)_\rho \nabla T$. Local heating with the laser will hence move the local conditions from the global temperature and pressure to a locally different temperature and pressure that is connected to the global conditions via an isotherm if the monolayer is a liquid and along an isochore if the monolayer behaves like a solid. The heating results in a temperature increase of roughly 5 K/W of laser power.

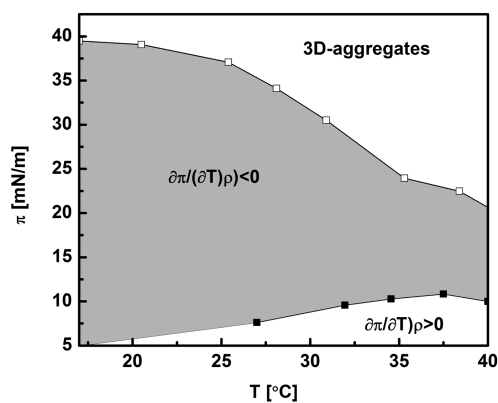


Figure 4. Collapse pressure diagram for ethyl stearate. The gray region indicates the region of negative pyrobaric pressure $\text{pbc} = \partial\pi/\partial T)_\rho < 0$: \square , collapse pressure π_c , determined at a compression rate of $\dot{A} = -0.06 \text{ \AA}^2 \text{ molecule}^{-1} \text{ s}^{-1}$; \blacksquare , the crossover pressure, π_{pbc} . The collapse pressure denotes the pressure where global collapse rates become comparable to the compression rate of the barriers. In most of the gray region global collapse rates are much lower than the compression rate of the barriers. Beyond the laser power threshold the local collapse rate is much faster than both the global collapse rate and the compression rate used in the isotherms. For this reason on the time scale of the local collapse the globally collapsing monolayer can still be considered as a quasi equilibrium monolayer.

Here we are interested in the change of pressure along an isochore, i.e., the pyrobaric coefficient $\text{pbc} = \partial\pi/\partial T)_\rho$. Parts a and b of Figure 3 show the pressure versus area compression isotherms for ethyl stearate and DPPC at various temperatures. In DPPC the pressure increases monotonically with increasing temperature at a constant area. For ethyl stearate two different regions exist: at large area pbc is positive, and at low area it becomes negative. For each temperature we may define a crossover pressure π_{pbc} where the behavior changes from a normal ($\text{pbc} > 0$) to an abnormal behavior ($\text{pbc} < 0$). A negative pyrobaric coefficient might be an artifact since the global collapse often occurs well before the collapse pressure obtained from the isotherm.¹⁹ A loss of material will lead to an underestimation of the apparent area per molecule. We therefore performed experiments where we measure the decrease of area due to the loss of material from the interface between the trough barriers as a function of time at constant pressure. These experiments indicate that the rates of global collapse in ethyl ester are small ($-\text{d}(\ln A)/\text{d}t < 10^{-4} \text{ s}^{-1}$) for temperatures below 30 °C and pressures below $\pi < 30 \text{ mN/m}$. In this region they can account only for a few percent of the negative pyrobaric coefficient. Hence at low temperatures and pressures below 30 mN/m the negative pyrobaric coefficient remains negative also when extrapolating toward high compressing rates were the monolayer compression rate strongly exceeds the global collapse rate. The rate of global collapse significantly increases when globally heating the monolayer or when approaching the rate-dependent collapse pressure π_c (compression rate $\dot{A} = -0.06 \text{ \AA}^2 \text{ molecule}^{-1} \text{ s}^{-1}$) of our isotherms. The phase diagram in Figure 4 displays the region of negative pyrobaric coefficient which lies between the rate-dependent collapse pressure and the crossover pressure (filled region). DPPC does not exhibit a negative pyrobaric coefficient.

We have performed local heating experiments in all materials at pressures close to the rate-dependent collapse pressure. We find that, for the monolayers that show laser-induced local

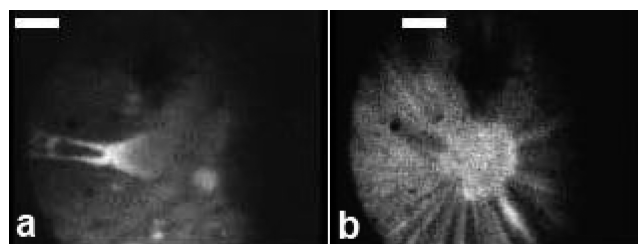


Figure 5. (a) Local melting of a methyl stearate monolayer observed at a global pressure and temperature of $\pi^\infty = 11 \text{ mN/m}$ and $T^\infty = 17 \text{ °C}$ at a laser power of $P_{\text{laser}} = 1.8 \text{ W}$. Inside the bright fluorescent melted liquid expanded phase, a liquid condensed island floats with the liquid expanded droplet past the liquid condensed surroundings, proving the liquid character of the liquid expanded phase. A movie (melting.avi) of the local melting is appended to the Supporting Information. Scale bar corresponds to $30 \mu\text{m}$. (b) Local yielding of a methyl stearate monolayer observed at a global pressure and temperature of $\pi^\infty = 24 \text{ mN/m}$ and $T^\infty = 25 \text{ °C}$ at a laser power of $P_{\text{laser}} = 0.5 \text{ W}$. Liquid condensed phase flows toward the laser focus exhibiting shear bands. Inside the focus the material agglomerates to form a three-dimensional aggregate. A movie (yielding.avi) of the local yielding is appended to the Supporting Information. The scale bar corresponds to $30 \mu\text{m}$. The scenarios seen in the two images proves that yielding is a process different from melting as well as that only yielding—not melting—is a pathway to local collapse.

collapse, the IR power threshold for the monolayer to flow toward the laser focus does not correlate with the proximity to the collapse point. Furthermore, an IR power threshold must be applied even for monolayers already at the collapse point. In some materials such as DPPC, we never reach a threshold where the monolayer flows into the center. All of this evidence points out that the pathway toward local collapse via the dilatational flow toward the laser focus is a different pathway to collapse than global collapse.

5. TIME SCALES

Once we overcome the threshold, the flow toward the laser focus is associated with dilatational rates of the order $-\nabla \cdot \mathbf{v} \approx \text{s}^{-1}$ (\mathbf{v} , the velocity of the flow) much faster than the global collapse rates, $-\text{d}(\ln A)/\text{d}t < 10^{-4} \text{ s}^{-1}$, measured in the isotherms under similar global conditions. This underlines the different physical nature of the local compared to the global collapse pathway. The heating with the laser locally removes the barrier that blocks this pathway at positions other than in the laser focus. The questions are hence: what is the physical nature of the barrier, and what is the physical process that removes it when we locally heat? When a local fluctuation leading toward a collapse instability at a specific site occurs, two scenarios of the progress of the instability with time are possible: The first possibility is the growth of the point of instability for example by the formation of cracks^{1–4,17} and a crack tip moving intermittently^{2,4} through the monolayer. Such a type of extension of the region of instability does not require the transport of material toward the point of instability since the location of instability—the crack tip—is moving toward regions of not yet collapsed monolayer material. It is a typical scenario of global collapse in a solid monolayer. The local heating with the laser if inducing a point of collapse instability is pinned to the point where one applies the heating. The instability does not move. If significant collapse is to occur at this point, noncollapsed material must be transported to the

local instability. This requires the monolayer to be liquid, not solid. The solidity of the monolayer prevents the flow toward the collapse point. When the molecules in the focus collapse and the monolayer remains solid, there is no further supply of collapse material and the local collapse remains a fluctuation. The laser heating must hence locally convert the solid into a liquid. The threshold to overcome is this local conversion to a liquid, a physical process that is quite independent of the collapse instability. This explains why local collapse is not observed in the laser focus, although global collapse might have already started elsewhere in the monolayer. The conversion from solid to liquid can in principle happen in two ways, i.e., via melting or via yielding. The following section discusses the differences of local melting versus local yielding.

6. LOCAL MELTING VERSUS LOCAL YIELDING

Phase diagrams of the monolayers studied in this work are well-known. It is possible to locally melt the monolayer if we are close to a liquid condensed/liquid expanded phase boundary. Figure 5a shows what happens if we locally melt the monolayer. A bright fluorescent droplet of liquid expanded phase appears in the laser focus surrounded by the unmelted liquid condensed phase. Prior to the melting we see a slight motion of the liquid condensed monolayer away from the focus. This is not surprising. The liquid expanded phase is less dense, and to acquire the lower density, the monolayer must flow away from the focus. In the Supporting Information we also supply a movie of the melting. In this movie the bright fluorescent droplet behaves like a liquid as we sometimes see liquid condensed islands in the liquid expanded phase floating with a velocity differing from the velocity of the liquid condensed phase surrounding the liquid expanded droplet. When locally melting the monolayer, we rarely observe a flow of the liquid condensed phase toward the focus. If we see it, it is orders of magnitudes weaker than the flow toward the focus observed for local yielding. Local melting strongly depends on the global temperature being close to the liquid condensed liquid expanded phase transition temperature. If we lower the global temperature, a higher laser power is needed to reach the phase transition temperature. At global temperatures 10 K below the transition temperature local melting is no longer observed since the power of our laser is insufficient to locally raise the temperature toward the transition temperature. We conclude that local melting is possible. Usually the lower density of the liquid expanded phase, however, suppresses the flow toward the laser focus and hence suppresses local collapse. Local melting is hence not the pathway to local collapse.

In Figure 5b and in a movie in the Supporting Information we show what happens when locally yielding the monolayer. If we locally yield the monolayer, the flow toward the focus starts at the threshold power and attracts material of the liquid condensed phase toward the central collapsing three-dimensional aggregate in the laser focus. This can happen in a region of the phase diagram far away $\Delta T > 10$ K from the liquid expanded phase. The region that starts to flow toward the laser focus in local yielding exhibits the typical texture observed in the liquid condensed phase with fluorescence microscopy, while flowing shear bands pointing radially inward distort this pattern due to the flow. There is, however, no evidence for the existence of a liquid expanded phase with uniform bright fluorescence as seen in the local melting. In contrast to local melting, the laser power threshold to induce the flow of the liquid condensed phase

toward the focus is almost independent of the global temperature and a proximity to a liquid expanded phase does not seem to play a role. Local collapse seems to be fairly independent of the global temperature. The local collapse flow increases with the temperature difference between the focus and its surrounding, showing that gradients in temperature are an essential ingredient of the phenomenon. This is very different from local melting, where the laser threshold is lowered with an increase in the temperature. We conclude that the laser threshold observed when locally yielding the monolayer is something different than a phase transition to the liquid expanded phase. All other denser monolayer phases are liquid crystalline hexatic phases that are all partially elastic as has been shown by rheological experiments of various groups.^{20,21} It is a conceivable idea that in an elastic (solid) material, the mechanical stress must overcome a threshold to force the material to flow. The importance of gradients rather than average global quantities point in the direction of mechanical gradients.

7. PYROBARIC COEFFICIENT, LOCAL YIELDING, AND LOCAL COLLAPSE

To force the solid monolayer to yield and then flow into the center of the focus, the stress gradient must point from the periphery toward the focus of the laser. This requires the surface pressure in the solid monolayer to decrease with temperature and brings us back to the pyrobaric coefficient. We analyzed the effect of local heating monolayers composed of different molecules and found that, for monolayers with $d\pi_c/dT < d\sigma_w/dT$, wherever the value of pbc is negative at pressures lower than the collapse pressure, local collapse is observed. On the contrary, for $pbc > 0$ neither local yielding nor local collapse is observed at any laser power. In Table 1 we summarize the regions in pressure and temperature that we tested and where local yielding followed by local collapse is observed (for monolayers with $pbc < 0$) or not observed (for monolayers with $pbc > 0$).

On the basis of the assumption that the monolayer behaves as a liquid, Muruganathan and Fischer in their work¹⁵ claimed that only one condition is required for local collapse. They showed that if the collapse pressure decreases with increasing temperature with a slope smaller than the change of the surface tension of the bare air–water interface with temperature ($d\pi_c/dT < d\sigma_w/dT$), then local heating by a laser beam will lead the molecules at the monolayer to acquire a three-dimensional structure.

However, this is not the only condition that should be fulfilled in the case of monolayers that behave like a solid, since they will not flow easily. To confirm this idea, we analyzed the effect of local heating of monolayers prepared with different surfactants; the results are summarized in Table 1. As an example, we found that monolayers of DPPC do not show a flow of material inside the laser focus for any laser power on either water or CuSO_4 solutions. On the contrary, ethyl stearate shows collapse when it is submitted to a local heating.

The force density (i.e., the tension gradient) is directed toward the focus or away from it if the tension in the focus is higher or lower than in the colder periphery, respectively. The former situation supports collapse of the monolayer, while the latter prevents it. The monolayer will hold until a critical pressure gradient is reached in which it will yield and will start to flow. This will happen when the stress gradient $\nabla\sigma = -\nabla\pi = -pbc\nabla T$ is directed toward the focus. Since the monolayer is considered to be solid before yielding, the density can be approximated as

Table 1. List of the Analyzed Monolayer-Forming Molecules with the Corresponding Sign of the Pyrobaric Coefficient and the Tested Ranges of Pressure and Temperature, Where We Observed or Did Not Observe the Local Yielding Followed by Local Collapse^a

surfactant	laser-induced local collapse	surface pressure range (mN/m)	temp range (°C)	pbc
methyl stearate	yes	8–33	20–35	<0
methyl arachidate acid	no	any pressure	20–35	>0
ethyl stearate	yes	24–27	20–35	<0
hexadecanol	yes	5–50	20–35	<0
octadecanol	no	any pressure	20–35	>0
dimiristoylphosphatidylcholine	no	any pressure	20–35	>0
distearoylphosphatidylcholine	no	any pressure	20–35	>0
dipalmitoylphosphatidylcholine	no	any pressure	20–35	>0
dioleoylphosphocholine	no	any pressure	20–35	>0
dioleoylphosphatidylglycerol	no	any pressure	20–35	>0
myristic acid	no	any pressure	20–35	>0
pentadecanoic acid	no	any pressure	20–35	>0

^a A negative pyrobaric coefficient seems necessary to force the monolayer to locally collapse into the IR-laser focus.

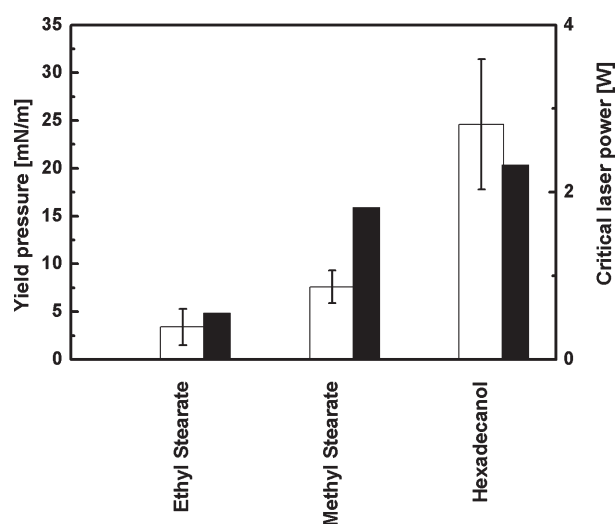


Figure 6. Yield pressure and critical laser power for ethyl stearate, methyl stearate, and hexadecanol monolayers at 26 °C on water subphases. White bars are the yield pressure and correspond to the left scale while black bars are the critical power and correspond to the right scale. The computation of the yield pressures relies on the separation of time scales between local collapse, compression of the barriers, and global collapse. This separation of time scales holds very well for monolayers at room temperature. Surfactants are ordered in a sequence of increasing difficulty to induce local collapse.

constant. In that situation, the pressure inside the focus is

$$\pi_{\text{focus}} = \pi_{\infty} + \int_{r_{\infty}}^{r_w} dr (\text{pbc}) \nabla T$$

where π_{focus} and π_{∞} are the surface pressure at the laser focus and far away from it, respectively. We assume the pyrobaric coefficient $\text{pbc}(\pi, T)$ to be roughly constant. We also neglect systematic errors in the measurement of the pyrobaric coefficient arising from the fact that beyond the equilibrium spreading pressure the molecules escape to the third dimension and thus, the number of molecules at the interface changes with time. At

collapse, the global pressure π_{∞} assumes the value of the collapse pressure, π_c , and thus $\pi_{\text{focus}} \approx \pi_c + (\text{pbc})\Delta T$.

The product of the pyrobaric coefficient with the increase in temperature in the focus $(\text{pbc})\Delta T$ is the excess pressure that pushes the monolayer from outside the laser focus into it. The same product at the laser threshold $(\text{pbc})\Delta T_{\text{critical}}$ is the maximum pressure that the solid can withstand without flowing, and therefore we will define the yield pressure as $\pi_{\text{yield}} = -(\text{pbc})\Delta T_{\text{critical}}$. Due to the neglect of the global collapse rate in the derivation of the yield pressure, we systematically overestimate the magnitude of the yield pressure.

In Table 1 we show the sign of the pbc for each material that we analyzed. All of these materials show $d\pi_c/dT < d\sigma_w/dT$. As expected, only the monolayers with negative pyrobaric coefficient $\text{pbc} < 0$ ($\pi_{\text{yield}} > 0$) show inward flow of material to the laser focus. We quantified the yield pressure π_{yield} for these monolayers at 26 °C and at a surface pressure near the collapse point of each of them. The temperature gradient in the illuminated region of the monolayer can be calculated according to $\Delta T = T(r) - T_{\infty} = \alpha P_{\text{laser}} r_w / 2\pi\kappa r$.¹⁸

Here T_{∞} is the temperature far away from the hot spot, $\alpha = 0.1 \text{ cm}^{-1}$ is the adsorption coefficient of water at the wavelength of the IR laser, and $\kappa = 0.6 \text{ W/mK}$ is the heat conductivity of water. The partial derivative occurring in the definition of the pyrobaric coefficient $\text{pbc} = \partial\pi/\partial T|_{\rho} \approx (\pi(T_1) - \pi(T_2))/(T_1 - T_2)$ is approximated by replacing the derivative with finite differences computed from the isotherms at different temperatures (T_1 near T_{∞} and T_2 near $T(r)$). Figure 6 shows the yield pressure and the critical laser power for monolayers of ethyl stearate, methyl stearate, and hexadecanol at 26 °C and a surface pressure near the collapse of each monolayer. We note that a linear viscoelastic response of the material to thermocapillary stress cannot explain the experimentally observed threshold. A linear viscoelastic material described by a frequency-dependent shear or compression modulus would always result in doubling of the speed of flow with doubling of the dilatational stress. This is not what we observe. Here at low stress, no flow is observed and the material starts to flow only after a threshold not related to the thermodynamic phases is overcome. The phenomenon might be explained with other nonlinear viscoelastic relations between

stress and strain but not with linear constitutive relations. We believe that yielding is the simplest nonlinear viscoelastic model describing our experiments. We do not explain in a microscopic way why the material resists flow at low stress; however, Iñes-Mullol and Schwartz²⁰ have also shown that the coupling of the tilt and bond orientation in a tilted hexatic phase leads to elastic torques that prevent a reorientation of the tilt at insufficient stress.

It is not clear what is the chemical reason for some of the materials to exhibit a negative pyrobaric coefficient that finally enables the local collapse pathway. This question will be an important point for understanding the connection between chemical structure and local collapse behavior.

8. CONCLUSIONS

In this paper we extended the work presented by Muruganathan and Fischer.¹⁵ Beyond a critical laser threshold a new pathway toward the collapse of the monolayer into the focus opens via the dilatational yielding of the solid monolayer. This pathway differs from the global collapse because contrary to global collapse the location of instability is at rest and the monolayer must flow toward the fixed laser focus. We have shown that gradients in surface pressure yielding the solid and generated during laser-induced heating represent a more important determinant of the local collapse than phase transitions between thermodynamic equilibrium phases. Stress gradients yielding the monolayer must be directed toward the laser focus to support the flow into the collapse point at the laser focus. This requires a negative pyrobaric coefficient. Among a variety of monolayers of different chemical composition, we found three monolayers with a negative pyrobaric coefficient. Only in monolayers with $d\tau_c/dT < d\sigma_w/dT$ and negative pyrobaric coefficient a laser threshold for local collapse could be reached. Beyond the laser threshold the dilatational rate of the local collapse pathway exceeds the global dilatational collapse rate and the local collapse becomes the dominant pathway toward collapse. The laser threshold together with quasi equilibrium pressure versus area isotherms allows us to estimate the dilatational yield pressure in monolayers with negative pyrobaric coefficient.

■ ASSOCIATED CONTENT

S **Supporting Information.** Movies of the local melting (melting.avi) for a monolayer of methyl stearate at 17 °C and 11 mN/m and of the local yielding (yielding.avi) with inward flow of material for a monolayer of methyl stearate at 25 °C and 24 mN/m (real times and the real sizes for these movies, 20 s (30 frames/s) and $240 \times 180 \mu\text{m}^2$, respectively). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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