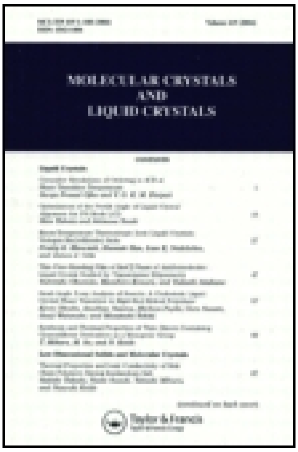

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MECHANICAL PERTURBATION APPLIED ON FREELY SUSPENDED SMECTIC FILMS

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Abstract We apply a mechanical perturbation in the plane of the smectic layers of a free standing film by the means of modulation of the film's length. Experiments have been performed on films of different thicknesses in the liquid-like, hexatic and crystal-like smectic phases present in 7o.7. We show that the meniscus is crucial for understanding the mechanical properties and that the tilt angle of the molecules in the SmG phase is one more degree of freedom for the film to respond to the perturbation.

INTRODUCTION

Free standing films have been studied extensively in the last twenty years[1], but little work has been done on the mechanical properties of these films. To complete previous work done on film's tension[2,3], shear constant and viscosity[4,5], we have developed a new experimental set-up that applies a mechanical strain to the film. A periodic motion is generated by a piezo-electric element on one side of the film holder (the frame) so that the film will be alternatively expanded and compressed in a direction parallel to the plane of the smectic layers. This allows the investigation of the elastic properties of the film. We find an expected crystal behavior of the SmB phase as well as an unexpected role of the tilt angle θ of molecules in the SmG phase. We also find experimental support for the assumption[6] that a free standing film can not be considered as independent of the meniscus that connects it to the frame.

METHOD

The effects of a mechanical perturbation on a free standing film are detected through the deviation of the resonant frequency $\Omega_{n,m}$ of the vibrating film. For a rectangular film submitted to a (n,m) transverse vibrating mode, $\Omega_{n,m}$ is given by the equation:

$$\Omega_{n,m} = \pi\sqrt{\frac{\tau}{\rho}}\cdot\left[\left(\frac{n}{x}\right)^2+\left(\frac{m}{y_o}\right)^2\right]^{1/2} \tag{1}$$

where τ stands for the total tension of the film in dyne/cm, ρ is the two dimensional density of material involved during the motion in g/cm^2, y_o is the constant width and $x(t) = x_o + x_a * e^{i\omega t}$ is the length of the frame modulated at frequency ω and amplitude x_a around the equilibrium position x_o. The mechanical perturbation $\Delta x(t) = x(t) - x_o$ is held at a frequency ($\omega \sim 1$ Hz) much smaller than the actual transverse resonant frequency of the film ($\Omega_{n,m} \sim 700$ Hz).

The 2D density ρ has contributions from both the density of the liquid crystal compound ρ_{LC} and the density of the gas surrounding the film ρ_{air}. For a film of thickness 100 layers, the contribution of the air is predominant ($\rho_{air} \sim 10^{-3}$ g/cm^2 versus $\rho_{LC} \sim 3\ 10^{-5}$ g/cm^2) such that ρ can be considered as a constant during the perturbation process[7].

The side motion of the frame induces a deviation in the tension of the film and generates a flux of molecules between the meniscus and the film to restore the equilibrium state. This process happens at the same frequency ω as the perturbation $\Delta x(t)$, but a relaxation time is needed for molecules to flow from the meniscus that leads to a phase-shift between the response signal and the perturbative signal. A detailed analysis done in reference [7] gives an expression of the relaxation time $t_{rel} = \dfrac{N_o}{\alpha * \kappa^{-1}\rho_o}$ where N_o and ρ_o are the unperturbated number of molecules and density of the film, α is a positive constant in dyne*seconds and κ^{-1} is the elastic constant parallel to the smectic layers in dyne*cm/g. We established in a previous experimental work that t_{rel} depends on the smectic phase, from 2 seconds in the liquid-like SmA, SmC phases to about 10 minutes in the crystal-like SmB, SmG phases.

The modulation of the side affects $\Omega_{n,m}$ via x(t) and the tension τ leading to a periodic modulation $\delta\Omega(t)$ of the resonant frequency. We measure the amplitude of $\delta\Omega(t)$ and its phase-shift relative to the perturbative signal to obtain information on the elastic behavior of smectic films parallel to the layers, as well as on the relaxation mechanism that allows molecules to flow between the meniscus and the film.

EXPERIMENTAL SET-UP

The experiment consists of three main parts described in reference [7]. First is a film holder (the frame) installed inside an oven to ensure temperature regulation better than ± 0.01° C. One side of the frame is mobile and connected to a piezoelectric element (see Fig. 1). The piezo modulates the length of the film $\Delta x(t)$ with an amplitude x_a that can range from 1 μm to 20 μm and a frequency ω between 1mHz to 20 Hz. The dimensions of the film at rest are $y_o = 0.71$ cm and $x_o = 0.73$ cm, approximately. The oven stands on top of an inverted microscope to observe the film during a run and a top window allows a laser or light beam to be sent to the film. The exact number of layers can be measured by a method presented in reference [8].

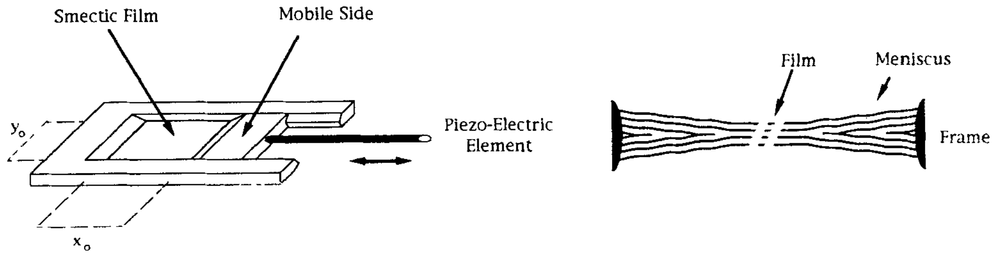


Figure 1: Schematic of the frame with a section of the film and the meniscus.

The second part of the experimental set-up induces and detects the (1,2) transverse vibrating mode of the film[9]. An electrostatic excitation is applied to the film by means of four electrodes set a few μm from the film. A He-Ne laser beam is used to measure the resonant frequency $\Omega_{n,m}$ of the membrane by the condition $\Phi = 90$ degree where Φ is the phase-shift of the reflected laser signal relative to the electrostatic signal sent to the electrodes. The value of $\Omega_{n,m}$ depends on the thickness of the smectic film as well as on the temperature (see reference [10] for a more detailled discussion) and ranges usually from 600 Hz to 800 Hz for a film thickness of 2000 to about 5 layers, respectively. We call Ω_T the resonant frequency of the film at temperature T when no mechanical perturbation is applied.

When a perturbation is applied to the film, the resonant frequency $\Omega_{n,m}$ oscillates about Ω_T due to the motion of the side. We detect this modulation $\delta\Omega(t)$ through the linear response of the phase $\Phi(t)$. During all the perturbation measurements, the frequency of the electro-static excitation is kept constant at the eigen-frequency value of the non-perturbated film Ω_T. The phase Φ is therefore periodically modulated around $-\pi/2$ and a lock-in detector provides the amplitude A_Φ of this modulation and the phase-shift D_Φ between the phase $\Phi(t)$ and the perturbation signal $\Delta x(t)$ (see Fig. 2).

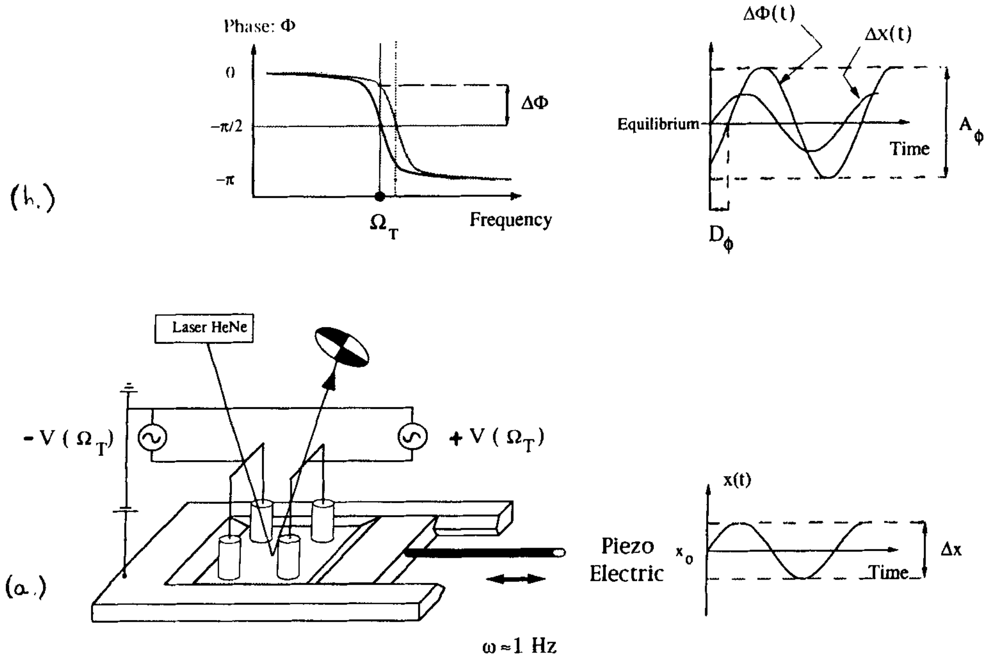


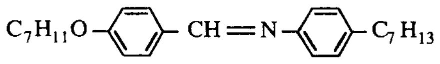
Figure 2: Parts of the experimental set-up. (a) Frame with the four electrodes; (b) detection of $\Omega_{n,m}$ and of the parameters A_Φ and D_Φ.

As the resonance frequency Ω_T is strongly dependent on the actual temperature of the film, we detect Ω_T at each temperature increment before performing the perturbation measurement.

RESULTS

We examine the compound 4-n-heptyloxybenzylidene-4-n-heptylaniline (7o.7) with bulk phase sequence and chemical structure given below.

$$\text{Crys} \xrightarrow{33.0^\circ\text{C}} \text{SmG} \xrightarrow{51.0^\circ\text{C}} \text{SmB} \xrightarrow{65.4^\circ\text{C}} \text{SmC} \xrightarrow{70.5^\circ\text{C}} \text{SmA} \xrightarrow{83.0^\circ\text{C}} \text{N.} \xrightarrow{84.0^\circ\text{C}} \text{Iso.}$$



SmB and SmG phases are crystal-like with the molecules' long axis perpendicular to the plane of the layers in SmB, and tilted to the normal of the layers in the SmG phase. In reference [9], Sirota et al. have shown using X-ray measurements that the 7o.7 phase sequence is strongly dependent on the film's thickness and that two tilted hexatic phases SmI and SmF appear between the SmB and SmG phases for sufficiently thin films. Molecules are tilted towards their nearest-neighbours in SmI and towards their second nearest neighbours in SmF.

Results can be summarized by three curves that show the characteristic behavior of films subjected to a mechanical perturbation. The temperature calibration of the presented graphes are shifted in comparaison to Sirota's measurements, but the temperature range of each smectic phase coincides.

Figure 3 shows the amplitude of the phase modulation A_Φ for a 204 layers thick film with a side excitation of frequency 4 Hz and amplitude 100 mV which corresponds to a displacement Δx_{max} of ± 1.05 μm. When cooling from 76° C, the film first undergoes the SmA to SmC phase transition not visible on the curve, but then an increase of 100 times can be observed when passing the SmC to SmB transition at 67° C. At the untilted SmB to tilted SmG phase transition (57° C on our graph), the film has a large drop in the amplitude A_Φ which is unexpected because both phases are crystalline-like. The value of

A_Φ in the SmG phase is similar to the liquid-like phases. We believe that this is due to the tilt angle θ of the molecules as we will discuss later. The film shows a similar behavior when cooling with a hysteresis at the SmB/SmG transition temperature of about 3 degrees which is typical for such materials.

Figure 4 shows the amplitude A_Φ and the phase-shift D_Φ of the resonance phase modulation relative to the side excitation $\Delta x(t)$ for a run made on a 13 layer film with a short SmB temperature range. For such a thickness, the following phase sequence is expected on cooling with our temperature calibration[9]: SmA –[67°C]→ SmC –[64°C]→ SmB cryst. –[61°C]→ SmI –[58.8°C]→ SmF –[48.6°C]→ SmG . We start the cooling run with a mechanical excitation of 100 mV and a frequency of 4 Hz to avoid creation of holes in layers as is frequent in the SmB phase. We increase the amplitude of the side's motion to 300 mV ($\Delta x(t) \sim \pm$ 3.16 μm) to obtain a better signal/noise ratio once the SmB temperature range is passed. Both runs are displayed on the graph with the amplitude data of the 100 mV excitation multiplied by a factor of 3 to be comparable with the 300 mV run. One can observe the expected increase in A_Φ at the liquid-like to crystal-like transition temperature as well as the decrease at the SmB/SmG transition. A factor of 2 between the liquid SmC and the crystal SmG phase is now detectable in A_Φ on this run. The transition SmI to SmF that should be observed at 58.8°C is not detectable. But 10.2°C below, the hexatic SmF to crystalline SmG phase transition can be observed in A_Φ around 48.5°C.

On figure 5, we display a run on a 9 layer film with a side excitation of frequency $\omega = 2$ Hz and amplitude x_a = 500 mV (± 5.53 μm). The film should have an expected phase sequence using our temperature calibration given by: SmA –[67°C]→ SmC –[64°C]→ SmI –[59.2°C]→ SmF –[48.2°C]→ SmG and a 'direct' liquid-like to hexatic phase transition can be studied. The graph shows the SmC to SmI transition to be a bit lower than expected: 61.9°C. Again the SmI to SmF transition is not seen except perhaps for a slight change of the slope in the continuous increase of A_Φ around 58 °C. The hexatic SmF to crystal SmG transition is apparant in this run. A jump corresponding to a 35% increase in A_Φ as well as a bump in the phase-shift D_Φ happen at 42.7°C on both the cooling run and the heating run with no significant hysteresis.

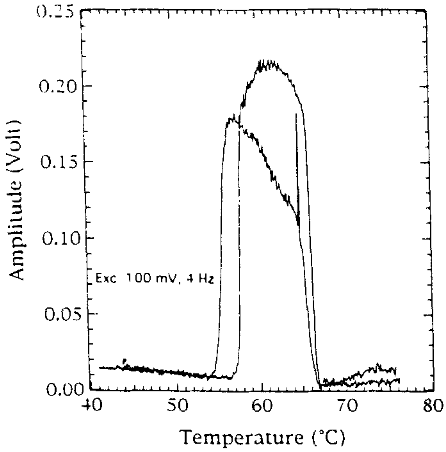


Figure 3: Curve obtained from a 204 layer film with a large crystal SmB phase. Excitation applied: [4 Hz, 100 mV ~ ± 1.05 µm].

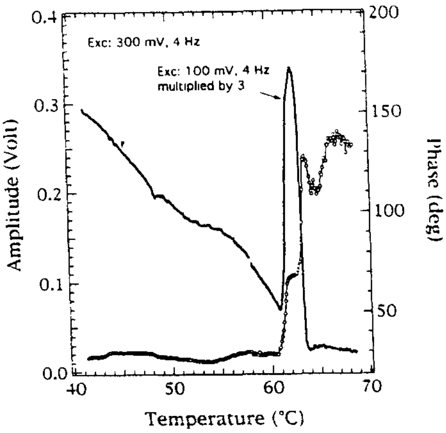


Figure 4: Two runs made on a 13 layer film. Excitation applied: [4 Hz, 100 mV] through SmB; [4 Hz , 300 mV] then. The amplitude data of the first run are multiplied by 3.

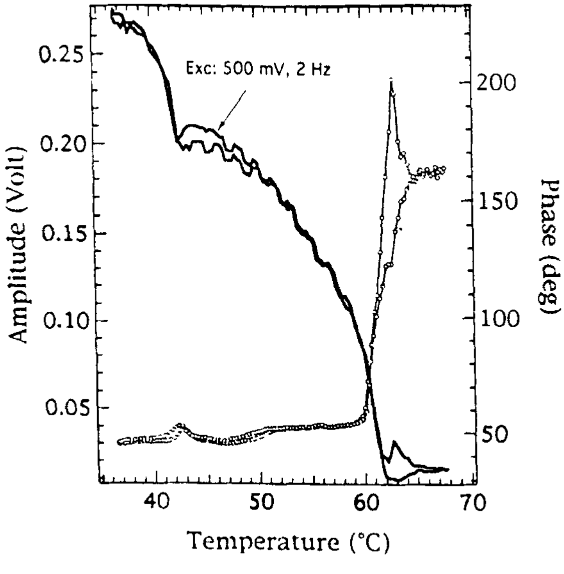


Figure 5: Run on a 9 layers film with 'direct' liquid-like to hexatic phase transition.

In all cases the phase-shift D_Φ between the phase modulation $\delta\Phi(t)$ and the side excitation signal $\Delta x(t)$ shows a jump of 90 degrees at the liquid to crystalline (or hexatic) phase transition.

DISCUSSIONS

The three important phenomena observed on our experimental data are first the increase in the amplitude's modulation A_Φ by a factor of 100 at the liquid SmC to crystal SmB phase transition; second the drop of A_Φ at the untilted crystal SmB to tilted crystal SmG phase transition and finally the 90 degree change of the phase-shift D_Φ between the phase modulation $\delta\Phi(t)$ and the perturbating signal $\Delta x(t)$ at both the liquid-like to crystal-like and liquid-like to hexatic phase transition.

Value of the amplitude A_Φ

The increase of A_Φ at the SmC to SmB transition can be explained in light of the meniscus that connects the film to its support (see Fig. 1). The meniscus has a volume much larger than that of the film and thus it acts as a reservoir of molecules for the membrane. The exchange of molecules is characterized by a relaxation time t_{rel} that we measured to be less than 2 seconds in SmA and SmC liquid phases and about 10 minutes in SmB and SmG crystal phases. When the film and the meniscus are in a liquid-like phase, t_{rel} is comparable to the inverse frequency ω of the mobile side (~1 second) and a flux of molecules can be established to limit the modulation of the tension such that the amplitude A_Φ stays small. In the SmB and SmG temperature range the meniscus is 'frozen' to exchanges because the relaxation time of the crystal-like phases is much longer than the inverse frequency of the side. The tension is then highly modulated by the perturbation. In the smectic B phase, the system has no way to counter the length's modulation and we get an important increase in the amplitude's modulation A_Φ for the phase signal in comparaison to the SmC phase.

An effect of the 'frozen' meniscus can be seen optically when heating the film back to the SmC phase with no applied perturbation. If the heating rate is fast enough, we observe tiny islands nucleating across the film at the SmB/SmC transition. At this temperature, the 2D density should undergo an important decrease[12] that can not be adsorbed by the frozen meniscus. The system responds to this frustration by exploring the third dimension and creating partially new layers in order to reduce its 2D density. We call this the 'constellation' effect as it resembles a clear night sky.

When entering the SmG phase temperature range, we expect the same order of magnitude for the amplitude of $\delta\Phi(t)$ as in the SmB phase because of the relaxation time t_{rel}. Instead we see an important decrease in the amplitude A_Φ, reaching the value obtained in the liquid-like phase because the tilt angle θ of the molecules in SmG can be seen as one more degree of freedom for the system to respond to the perturbation. When the meniscus is 'frozen', the modulation of the side leads to a modulation of the nearest neigbhoors center of mass distance D and of the in-plane inter-molecular distance L that defines the equilibrium state. But the inter-molecular distance L can be kept approximatively constant during the side modulation by increasing the tilt angle θ as shown in Fig. 6. In the untilted SmB phase, the intermolecular distance must vary with the modulation. By compensating the perturbation $\Delta x(t)$ with the modulation of the tilt angle θ, the film's tension τ changes little and the amplitude A_Φ is much less than that in the SmB phase. We have not detected yet the hexatic surface melting that effects the surface layers a few degree above the actual phase transition of the interior layers as seen

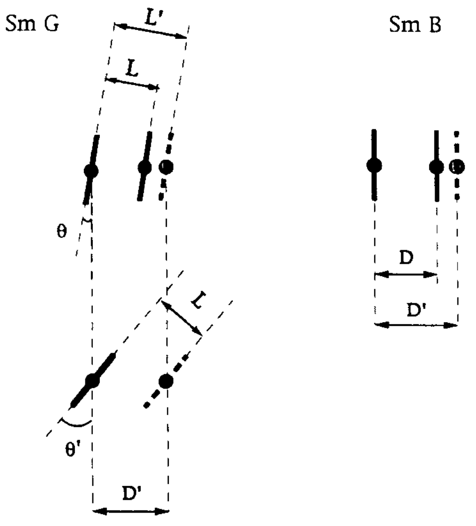


Figure 6: Molecules submitted to a horizontal expansion of the center of mass distance D. The inter-molecular distance L can be kept constant in SmG by increasing the tilt angle θ.

in thin films of 7o.7 by E.B. Sirota[11]. But further investigations are in process. Also, for every film's thickness we investigated, we were never able to observe a significant change in A_Φ or D_Φ at the SmI to SmF phase transition. A change in the direction of the tilt angle θ might not be detected by our experimental set-up.

Value of the phase-shift D_Φ

The last point we would like to discuss is the 90 degree change in the phase-shift D_Φ of the phase modulation $\delta\Phi(t)$ relative to the side excitation signal $\Delta x(t)$. This occurs at the liquid-like to crystal-like as well as liquid-like to hexatic phase transition and it can be understood through the ideas developed in reference [7].

In the aforementioned article [7], we make an expansion of the resonant frequency of a free standing film around the tension τ and the displacement x(t) using the expression (1) For a square shaped frame with a small oscillating displacement $\Delta x(t)$ relative to the rest length x_o, the modulation $\delta\Omega(t)$ of the resonant frequency is given by:

$$\delta\Omega(t)= \Omega_o A \left(\frac{1}{1-iE} - \frac{B}{A}\right) \frac{x_a}{x_o} e^{i\omega t} \qquad (2)$$

where Ω_0 is the unperturbated resonant frequency, $A = \kappa^{-1}\rho_0/2\tau_0$, $E = (\omega\, t_{rel})^{-1}$ and $B = 1$. Around the resonance $\delta\Phi(t) = \mu{*}\delta\Omega(t)$ where μ is a measured negative value, and equation (2) leads to an expression for the measured quantities A_Φ and D_Φ when defining $\delta\Phi(t)$ to be equal to $A_\Phi\, e^{iD_\Phi} e^{i\omega t}$.

$$A_\Phi = \left| \mu\ \Omega_o A\ \frac{x_a}{x_o} \sqrt{\left(\frac{1}{1+E^2} - \frac{B}{A}\right)^2 + \left(\frac{1}{1+E^2}\right)^2} \right|$$

$$D_\Phi = arctg\left(\frac{A{*}\,E}{(A-B) - B{*}\,E}\right) \qquad (3)$$

The limiting cases show that at high frequency the system responds in phase with the perturbation and the amplitude of the phase modulation A_Φ is given by equation (4a). In equation (2), the ratio B/A can be neglected because it stands for the 'pure' contribution of the side modulation Δx(t) and is estimated to be at most 2% of the response signal. At low frequency, the system is in quadrature to the perturbation and its amplitude is given by equation (4b).

$$A_\Phi = \left| \mu\ \Omega_o A \left(1-\frac{B}{A}\right) \frac{x_a}{x_o} \right| \quad (4a) \qquad A_\Phi = \left| \mu\ \Omega_o A\ \frac{x_a}{x_o}\ \omega\ t_{rel} \right| \quad (4b)$$

The high frequency case corresponds to a mode in which molecules can not follow the external excitation and no exchange of molecules between the film and the meniscus is possible. This is similar to the physical case when the meniscus is 'frozen' in a crystal-like smectic phase and so the limiting case shows that the tension responds in phase with the external perturbation Δx(t). When the meniscus is in a liquid-like smectic phase, there is an analogy possible with the low frequency limiting case because molecules can easily flow between the meniscus and the film and the system responds in quadrature to the perturbation. A 90 degree change of the phase-shift D_Φ then occurs at both the SmC/crystal SmB and the SmC/hexatic SmI phase transition because in each case the meniscus undergoes a SmC/SmB bulk-like transition due to its large volume whatever the thickness of the film is. Therefore we see that D_ϕ provides an understanding of the process of exchange of molecules between the meniscus and the film.

Conclusion

We show that the meniscus plays a crucial role in understanding the mechanical properties of smectic films and that the film and the meniscus should be taken as a whole entity. We also show that the tilt angle of the crystal SmG phase is an additional degree of freedom for the film to respond to a mechanical perturbation.

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