Shear Modulus Measurements on Classical Monolayer Systems

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The responses to shear of monomolecular films of stearyl alcohol ($C_{18}H_{37}OH$) and nonadecanoic acid ($C_{18}H_{37}COOH$) spread on water were studied as a function of density. A static shear modulus appears at a phase transition, previously assigned as the liquid-solid transition. The value of the modulus, however, is several orders of magnitude lower than the Kosterlitz-Thouless prediction.

In this Letter we report the first observation of a static shear modulus exhibited by a monomolecular film spread on cation-free water. A monomolecular film spread on water has many features that make it a nearly ideal, model two-dimensional (2D) system with which to test the theories of melting in 2D.[1-3] On the average, the interaction between the film and the substrate is uniform, thereby eliminating or minimizing the complications that arise from commensurate/incommensurate ordering encountered with solid substrates. Further, the thermodynamic state of the 2D system is defined through the easily determined surface-pressure–specific-area diagram (π-A). The surface pressure, π, is defined as the difference between the surface tension of clean water and of film-covered water; the specific area, A, is the area per molecule. Numerous substances have been spread on water and the π-A diagram, which is interpreted as the 2D equation of state, has been determined. A typical diagram, obtained with stearyl alcohol, is displayed in Fig. 1. Most straight-chain fatty acids and alcohols as well as a very large class of other substances produce similar curves. The distinctive feature is the kink (B in Fig. 1), which signals a second-order transition according to the Ehrenfest criteria. In the conventional interpretation the kink is assumed to be a liquid-to-solid transition, progressing from low to high density. It is quite tempting, then, to identify this feature with the melting transition discussed by Kosterlitz and Thouless,[1]

Halperin and Nelson,[2] and Young.[3]

We have recently designed an apparatus for measuring the static and the dynamic responses of films to an applied shear stress and have employed it to study monolayer systems. The most important characteristic of the new device is
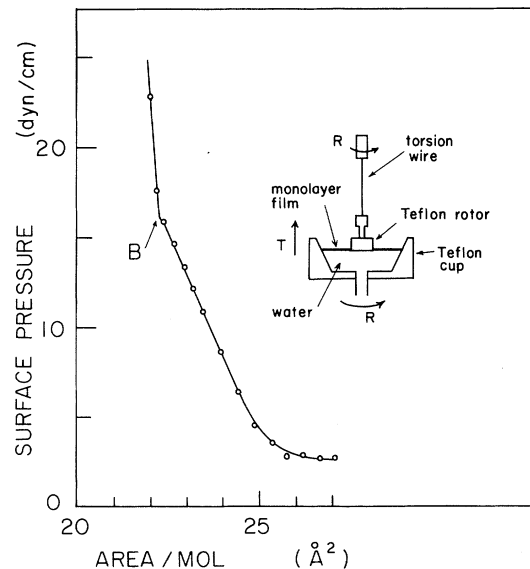

FIG. 1. π-A diagram of stearyl alcohol film at 24 °C. Inset: schematic diagram of the experiment. Either the top of the torsion wire or the Teflon cup can be rotated (R) to shear the film. The cup can be translated upward (T) while maintaining the film level and thus compresses the film.

centrosymmetric construction (Fig. 1, inset), which ensures that the film is hydrostatically compressed with no obstructions over the entire area. Although the apparatus will be described in detail elsewhere,[4] a brief description follows. A Teflon cup with sloping sides contained the water (acidified to pH 2.7 with HCl), on the surface of which the film was spread. The film was compressed by withdrawing water from the bottom while raising the cup to maintain the water level at a fixed elevation. A capillary-wave generator/detector system[5] which did not touch the water surface enabled us to determine the surface tension, and hence the surface pressure. A small Teflon rotor suspended by a fine torsion fiber just touched the water. The fiber was fastened to an axle which could be twisted in increments of 0.27°; independently the cup could be continuously rotated by ± 10° with a resolution of 0.03°. The rotational motion of the rotor was detected with a laser beam reflected from a mirror, which was part of the rotor assembly, onto a position-sensing photodiode.

The dynamic shear response of a film was studied by monitoring the free oscillations of the rotor following a single 0.27° twist of the fiber. The quasistatic shear response was studied by measuring the angular displacement of the rotor resulting from the slow rotation of the Teflon cup through a small angle.

A complete analysis of the motion in the nonsteady state for all values of the viscosity and rigidity is very complex. However, the analysis is relatively simple for the quasistatic case and for a dynamic response with a small shear modulus or viscosity.[4,6] The data we shall discuss later fall in either of these cases. We assume that the shear response of a film can be described by a linearized 2D elastohydrodynamic equation with a complex rigidity coefficient $\mu = \mu' + i\omega\mu''$, where μ' and μ'' are the shear modulus and shear viscosity, respectively.[7]

The results of our investigation are summarized in Table I. Typical data from the quasistatic measurements are shown in Fig. 2. Since a relaxational behavior is evident, a model involving a single relaxation time, τ, was used to fit the data; the fitted curve is also shown in Fig. 2. With this model, the complex rigidity can be written as

$$\mu' = [\mu_0 + \mu_\infty(\omega\tau)^2]/[1 + (\omega\tau)^2]$$

and

$$\mu'' = [\mu_\infty - \mu_0]\tau/[1 + (\omega\tau)^2],$$

where μ_0 and μ_∞ are the zero- and infinite-frequency shear moduli, respectively. μ_0 and μ_∞ are presented in Table I for the quasistatic case. The nonzero μ' has been observed for the first time in these films. We wish to emphasize that only a quasistatic measurement, as was done here, can unambiguously show a nonzero μ'. In the dynamic measurements a very large $\omega\mu''$ relative to μ' masks the latter, which probably accounts for the failure of others[8] to observe a shear modulus.

TABLE I. Summary of shear parameters.

| | Stearyl alcohol | | | | | | Nonadecanoic Acid | | |
| | (ω~0) | (ω~1.34/sec) | | (ω~8.60/sec) | | | (ω~0) | (ω~1.37/sec) | |
π	μ' [a]	μ'	μ''	μ'	μ''	π	μ'	μ'	μ''
1.0	~0	1.1	2.5			1.4	~0	~0	1
2.7	~0			26	11	3.4	~0	~0	1
7.5	~0			20	10	20.1	~0	1.5	4.5
11.1	~0	1.6	7.0			Kink			
13.0	~0			26	10	32.2	0.6 (1.2)		
Kink						34.1	0.5 (1.1)	1.7	21.7
15.9	0.3								
16.3		5.8 [b]	14.2						
17.9	0.4			44	28				
19.5	0.5 (1.5) [c]	8.4	24.9						
20.9				37	27				

[a] μ' in 10^{-3} dyn/cm and μ'' in 10^{-3} dyn sec/cm.
[b] Error in μ' in the dynamic measurement is $\sim 0.1\omega\mu''$.
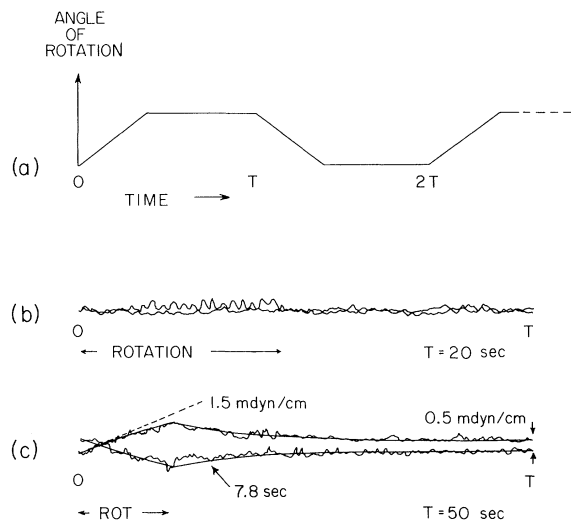[c] μ_0 and μ_∞ (in parentheses) for the quasistatic measurement ($\omega \sim 0$).

FIG. 2. Stress in the stearyl alcohol film in response to the cup rotation [shown in (a)], (b) at $\pi = 13.0$ dyn/cm and (c) at $\pi = 19.5$ dyn/cm. In (b) and (c), eight traces from clockwise and counterclockwise rotations are averaged and superimposed so that the residual stress ($\sim\mu_0$) is clearly seen. The smooth curve in (c) is a fit using a single-relaxation-time ($\tau = 7.8$ sec) approximation.

The appearance of a finite μ' is clearly correlated with point B in Fig. 1, the so-called liquid-solid transition. However, the magnitude is several orders of magnitude smaller than the Kosterlitz-Thouless (KT) value calculated for 300 K and 20 Å^2/molecule, i.e., 10^{-3} dyn/cm instead of 225 dyn/cm. The possibility that we were observing a mechanical artifact was excluded by deliberately misaligning the rotor slightly with respect to the cup center and finding no effect on the modulus. A linear stress-strain relationship also confirmed that, within the torque range employed, $(0.2-1)\times10^{-3}$ erg, we had not stressed the film beyond the yield point.

Anomalously strong dispersion and softening of the shear modulus at low frequency has been observed in freely suspended liquid-crystal films.[9] These effects were attributed to large-scale motion of defects. That view was supported in part by the rapid quenching of the dispersion as the temperature was lowered.[10] For the case of the monolayer films studied here, we believe the small shear modulus to be an inherent property of the films rather than due to defect motions because the modulus is very weakly density dependent (or the equivalent, pressure dependent) which is unusual for any process requiring an activation energy. Furthermore, when disper-

sion is taken into account, the calculated μ' remains small in the high-frequency limit. Although the resolution of the dynamic measurements is poor with a concomitant large error in μ', a worst-case estimate using a single relaxation process that is consistent with our data yields a relaxation time $\tau \sim 0.02$ sec and $\mu' \sim 2$ dyn/cm in the high-frequency limit. This value is still much smaller than the KT value.[1]

The small magnitude of the modulus might suggest a liquid-hexatic[2] transition rather than a liquid-solid transition. However, a simple calculation shows that this is not the case. On minimizing the Frank free energy[11] of the hexatic phase and by assuming a strong anchoring (the bond orientation held rigidly at the wall), our data yield $K_A \sim 4\times10^{-4}$ erg for the Frank elastic constant; whereas the value predicted just below the isotropic-hexatic transition is, according to Ref. 11, $K_A \sim 72k_B T/\pi \sim 10^{-12}$ erg. Our value, again, differs by several orders of magnitude. It is interesting to note that a similar value is obtained for a Frank constant of a 2D analog of the ordinary 3D nematic liquid crystals[12] if scaled to a monolayer thickness.

The molecules studied here are by no means pointlike. A large number of rotational and configurational degrees of freedom are contained in the alkyl chains and the associated entropy must be ultimately removed on compression to a solid phase. Therefore, it should be pointed out that the phase transition that we are concerned with here could be of a quite complex nature involving the coupling between the chain ordering and the positional ordering.

In summary, we have observed for the first time a nonzero shear modulus in monomolecular films on a cation-free water substrate. The magnitude of the modulus, however, is much smaller than predicted by theory. There may be some ambiguity in defining the nature of the high-density state; however, that ambiguity can only be resolved through structural studies, e.g., x-ray diffraction. The current work is, nonetheless, being expanded to a large number of materials in order to gain a greater understanding of the phase transitions in these films.

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Resolution of New Structure in the Collective-Mode Spectrum of ³He-B

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A high-resolution acoustic impedance technique has been used to investigate the real squashing, $J = 2$, mode in ³He-B. For a magnetic field perpendicular to the sound propagation direction, six components have been observed. The two center states appear to be a splitting of the $J_z = 0$ mode. This new splitting is observed to be dependent on T/T_c, pressure, and/or frequency, but is independent of magnetic field. In $H \cong 0$, additional features have been observed which can be associated with dispersion-induced mode splitting.

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The properties of superfluid ³He are well described by p-wave pairing with an order parameter given by a 3×3 complex matrix.[1,2] Various collective modes exist and are associated with temporal oscillations of the matrix components about their equilibrium values. Zero-sound experiments have played a fundamental role in the detailed study of these collective modes of the order parameter.[2,3] In superfluid ³He-B, a classification of the collective modes according to total angular momentum, J, is appropriate.[4] Two $J = 2$ collective modes have been found to couple to zero sound, the squashing mode[5] and the real squashing mode (rsq mode).[6] The $J = 2$ nature of the rsq mode has been verified in a pulsed-ultrasound experiment where the mode was observed to split linearly with magnetic field into five components[7] that can be assigned magnetic quantum numbers $J_z = 0, \pm 1, \pm 2$. The coupling strength of these states to zero sound is predicted[7,8] to depend on the sound propagation direction $\hat{q}$, the applied magnetic field $\vec{H}$, and the $\hat{n}$ texture.[9]

In this Letter we report the observation of new structure in the rsq-mode spectrum through the use of a high-resolution acoustic impedance technique. We have observed six components in a magnetic field perpendicular to the sound propagation direction. The two center states appear to be a splitting of the $J_z = 0$ mode. This new splitting is observed to be dependent on T/T_c, pressure, and/or frequency,[10] but is independent of magnetic field after some threshold field is applied. In addition, predicted[11] splittings at nonzero momentum q in small magnetic fields ($H \leq 3$ mT) have been observed for the first time.

Our measurements were performed in a cell mounted on a copper nuclear demagnetization cryostat capable of operation down to 0.4 mK. Two X-cut, 12.7-MHz transducers separated by a 4-mm path length were used to perform measurements at 38.2 MHz around 1 bar and 63.8 MHz around 5 bars.[12] As described previously,[6,13] temperatures in the ³He were determined with a resolution of 0.1 μK from the susceptibility of

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