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# Shear rigidity of spread stearic acid monolayers on water<sup>a)</sup>

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The effect of  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  ions and of  $p\text{H}$  on the two-dimensional shear modulus of stearic acid spread on a water substrate was determined. A large shear modulus was displayed by the films when the subphase contained  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  ions at the self-buffered  $p\text{H}$ . With  $\text{Fe}^{2+}$  dissolved in the subphase, the film displayed a viscous relaxation when strained but no residual stress was observed. No effect was observed with the  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ . Reducing the  $p\text{H}$  value in the subphase with the trivalent ions caused the shear modulus to disappear. The observations are interpreted in terms of hydrogen bonding.

## I. INTRODUCTION

It has long been known that compressed monolayers spread on water exhibit features in the diagram of surface pressure ( $\pi$ ) vs area/molecule ( $A$ ), which resemble phase transitions.<sup>1</sup> The  $\pi$ - $A$  diagram is very reproducible with a well defined system and similar features are displayed by numerous widely different compounds. Recently there has been a revival of interest in these systems, which was stimulated largely by the dislocation mediated theories of melting in two dimensions (2D) of Kosterlitz and Thouless<sup>2</sup> and of Nelson and Halperin.<sup>3</sup> Since the room temperature  $\pi$ - $A$  diagram of stearic acid has a discontinuous change of slope at  $20 \text{ \AA}^2/\text{molecule}$ , which separates two regions of the diagram into what have been called<sup>4</sup> liquid condensed and solid, it appeared that this would be an ideal system to study 2D melting. It is emphasized again that the phase assignments are not rigorous, as they were arrived at, in most cases, by indirect measurements such as viscosity.

The property that distinguishes a liquid from a solid is the presence in the latter of a shear modulus. The magnitude of the modulus also serves as an order parameter for the solid phase. Assuming that a solid phase in a 2D film of stearic acid exists, we then designed an experiment to measure the shear modulus which could serve as the signature for the liquid-solid phase transition.

## II. APPARATUS

A schematic drawing of the shear balance is shown in Fig. 1; this balance is incorporated in our high sensitivity wide dynamic range Langmuir balance<sup>5</sup> and we can thus measure the shear stress  $\sigma$  and surface pressure  $\pi$  simultaneously. The shear balance is constructed from a  $200 \mu\text{A}$  jewel bearing galvanometer. A shaft was attached to the meter pointer which extended both above and below the axis of the moving coil of the meter.

A vane of Pt was attached to the lower end of this shaft with its normal parallel to both the water surface and the meter movement axis to act as the force transmitter. The vane itself was partially immersed in the water; a shear in the film directed tangential to the vane would induce a rotation of the galvanometer coil. The upper part of the shaft was used to interrupt a light beam falling on a differential photodiode; the output of this diode was amplified and applied to the galvanometer coil to null the effect of the shear stress. This nulling current was then a measure of the shear stress. To induce a shear in the film, a pair of Pt vanes were located symmetrically on each side of the sensing vane (discussed above) with a separation distance small compared to the vane width. These vanes were attached to a common yoke and could be tangentially displaced as a unit. The yoke was mounted on a linear bearing which could be translated by means of a pressurized bellows. The displacement was accurately measured with a linear variable differential transformer. The sensitivity of the shear balance was determined by hanging weights on an arm which was also attached to the meter movement.

For the present study, the sensing (inner) vane and the translating (outer) vanes were, respectively, 19 and 30 mm wide. The inner vane must be shorter to avoid spurious effect resulting from changes in the meniscus as the translators are moved. The separation between the inner and outer vanes was 7 mm. The noise level (*vide infra*) of the measuring system corresponds to a force of  $\pm 10 \text{ mdyn}$  at the sensing vane. The detection sensitivity of the instrument is, then,  $\pm 2 \text{ mdyn/cm}$ .

## III. TWO DIMENSIONAL ELASTICITY THEORY

We shall review a phenomenological treatment of 2D elasticity and derive a few relations which will be used later.<sup>6</sup>

For a three dimensional isotropic solid, the free energy per unit volume due to an elastic deformation is given by<sup>7</sup>

$$F = \frac{1}{2} \lambda u_{ii}^2 + \mu u_{jk}^2, \quad (1)$$

where  $\lambda$  and  $\mu$  are the Lamé constants and  $u_{ij}$ 's are elements of strain tensor. If we restrict  $u_{ij}$ 's to contain only components in a plain normal to the 3 axis, Eq. (1)

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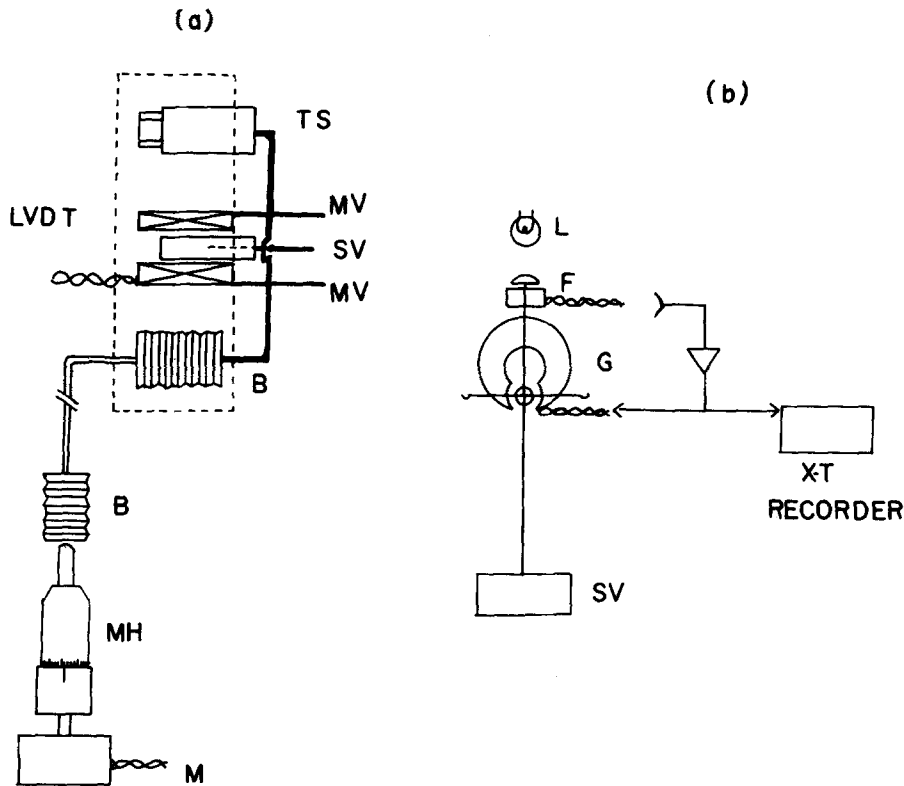


FIG. 1. (a) Top view of the shear balance assembly. M: motor; MH: micrometer head; B: bellows; MV: movable vanes; SV: sensing vane; LVDT: linear variable differential transformer; TS: translation stage. (b) Side view of the sensing system. SV: sensing vane; G: galvanometer; F: differential photodiode; L: lamp.

may be written as

$$F = \frac{1}{2} \lambda (u_{11} + u_{22})^2 + \mu (u_{11}^2 + u_{22}^2 + u_{12}^2 + u_{21}^2), \quad (2)$$

which we then reinterpret as a free energy per unit area with the appropriate change in the dimensions of  $\lambda$  and  $\mu$ . The components of the stress tensor are given by  $\sigma_{ij} = \partial F / \partial u_{ij}$ . Explicitly, they are

$$\sigma_{11} = (\lambda + 2\mu) u_{11} + \lambda u_{22}, \quad (3a)$$

$$\sigma_{12} = 2\mu u_{12}, \quad (3b)$$

$$\sigma_{22} = \lambda u_{11} + (\lambda + 2\mu) u_{22}. \quad (3c)$$

The modulus of (hydrostatic) compression (bulk modulus) is defined by

$$K = -A(\Delta\pi/\Delta A), \quad (4a)$$

where

$$\Delta A/A = u_{11} + u_{22},$$

and

$$\Delta\pi = \sigma_{11} = \sigma_{22}, \quad \sigma_{12} = 0. \quad (4b)$$

It follows from Eqs. (3) that  $u_{11} = u_{22}$  and thus

$$K = \lambda + \mu. \quad (5)$$

In terms of the modulus  $K$ , the free energy Eq. (2) can be rewritten as

$$F = \frac{1}{2} K u_{ii}^2 + \mu (u_{jk} - \frac{1}{2} \delta_{jk} u_{ii})^2, \quad (i, j, k = 1, 2). \quad (6)$$

The first term corresponds to the volume change and the second to the pure shear deformation. Since type of deformation can occur independently, each term of Eq.

(6) should be positive to be thermodynamically stable. Therefore  $K > 0$  (or  $\lambda > -\mu$ ) and  $\mu > 0$ .

The application of Eq. (5) to our experimental geometry requires some discussion. When the barrier is moved, say, in the 1 direction, there should be no film movement along the 2 direction, because the film is bounded by the trough walls. Therefore, for a small barrier movement, we have  $u_{22} = u_{12} = 0$ ,  $\sigma_{11} = \Delta\pi$ , and  $\Delta A/A = u_{11}$ . We define a uniaxial compression modulus  $K'$  through a similar relation as Eq. (4a): using Eqs. (3) we obtain

$$K' = \lambda + 2\mu = K + \mu. \quad (7)$$

In this case the stress in the 2 direction is  $\lambda u_{11} = \Delta\pi/(\lambda + 2\mu)$ , i.e., the stress is not hydrostatic and thus a finite shear stress is present. For compressions involving large  $\Delta A$ , in a solid film, it is expected that the shear stress would result in film fracture, dislocation nucleation, plastic flow, or some other mechanism which would relieve the strain and thus the hydrostatic modulus  $K$  would be applicable; however, for the case of small  $\Delta A$ , we expect to observe  $K'$ .

Our data in the following section show evidence for both of the above regimes. When compressing a solid film through a large  $\Delta A$ , a relaxation (pressure drop) is observed upon stopping the barrier. We interpret this as a relaxation of accumulated shear strain. Upon resuming the compression, the slope of the  $\pi$ - $A$  curve is initially steeper until  $\pi$  reaches the value it had before the compression was terminated, at which point the slope reverts to its original value; we associate the initial slope with  $K'$  while the final slope, on rejoining the  $\pi$ - $A$  curve, is associated with  $K$ .

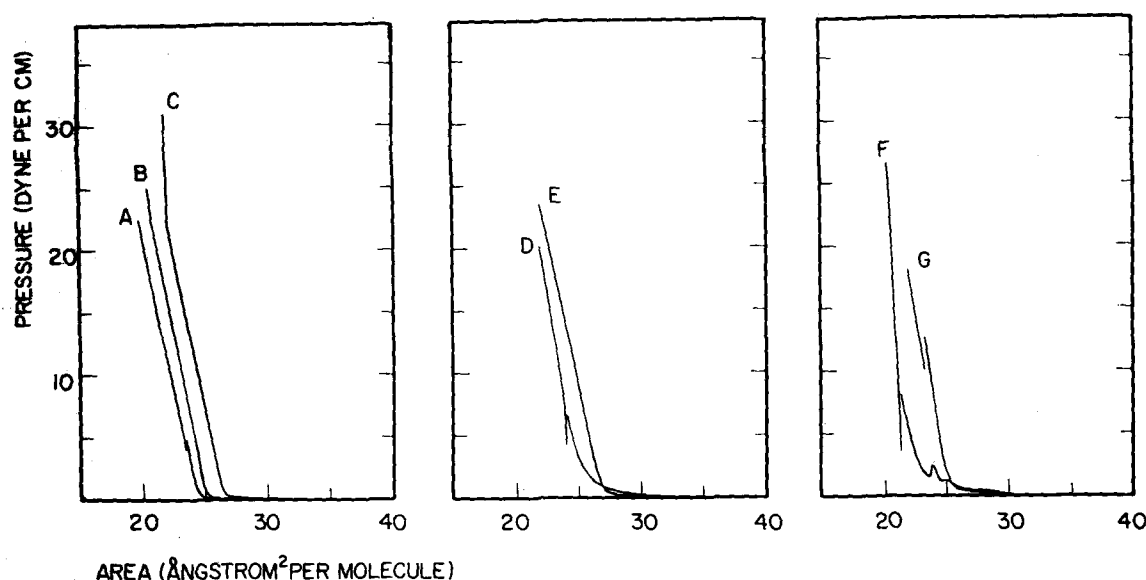


FIG. 2.  $\pi$ -A diagram of stearic acid monolayer on aqueous substrate of  $10^{-4}$  N solution of A:  $Mg^{2+}$ ; B:  $Ca^{2+}$ ; C: none; D:  $Al^{3+}$  (pH 4.6); E:  $Al^{3+}$  (pH 2.5); F:  $Fe^{3+}$ ; G:  $Fe^{2+}$ . The film was compressed at a rate of  $0.35 \text{ \AA}^2 \text{ molecule/min}$ . The discontinuity was due to the film relaxation while shear modulus measurement was performed.

#### IV. RESULTS AND DISCUSSION

In experiments on stearic acid spread on clean water we could detect no shear modulus in either of the two condensed phases [above and below the kink in Fig. 2(c)]; the same was true with stearyl alcohol and methyl stearate, both of which also display slope changes in their  $\pi$ -A behavior. At this point we enter a word of caution: it is always possible that a shear modulus exists in the limit of a vanishingly small shear, but that the threshold for nucleation of dislocations is so low that it lies below the detection sensitivity of our instrument. A second possibility is that in arriving at the final compressed state, a solid film would exist in such a highly fractured state as to consist of a large number of small diameter 2D platelets which are relatively free to slide around one another.

In our earlier experiments<sup>8</sup> a time dependent shear

modulus was detected which was somewhat irreproducible. This was traced to the presence of a small concentration of  $Al^{3+}$  ions which had leached out of the aluminum trough over a period of time ( $\sim 1$  day) through small pin holes in the paraffin coating. When plasticized paraffin films was substituted as a coating, the effect disappeared. The discovery of this transient shear modulus suggested we study the effect of various ions on the shear response.

Unbuffered  $10^{-4}$  N solutions were prepared from reagent grade calcium nitrate tetrahydrate, magnesium nitrate hexahydrate, Mohr's salt (ferrous ammonium sulphate), ferric nitrate hexahydrate, and aluminum nitrate nonahydrate to serve as the substrates for the stearic acid films. In addition to the five solutions above, an additional solution of  $Al^{3+}$  was prepared of the same concentration but buffered to pH 2.5 with HCl. The solutions and respective pH values are listed in Table I.

TABLE I. Summary of shear modulus measurements.

Ion	pH	$A (\text{\AA}^2/\text{molecule})$	$-Ad\pi/dA \text{ (dyn/cm)}^a$	$\mu \text{ (dyn/cm)}$
None	(5.4)			$< 0.2$
$Mg^{2+}$	5.4			$< 0.6$
$Ca^{2+}$	5.4			$< 0.2$
$Al^{3+}$	2.5			$< 1.5$
$Al^{3+}$	4.6	28.0	14.4 (72)	33.8
		24.0	100.0 (360)	49.3
		20.4	75.6 <sup>c</sup>	413.0
$Fe^{3+}$	3.8	28.2	1.7	1.8
		25.0	9.0 (18.9)	9.7
		21.3	245.0 (500)	47.2
$Fe^{2+}$	5.2			$< 0.3^b$

<sup>a</sup>The value for  $K$  is shown. When unambiguously measurable,  $K'$  is also shown in brackets.

<sup>b</sup>Residual shear modulus.

<sup>c</sup>Film begins to collapse.

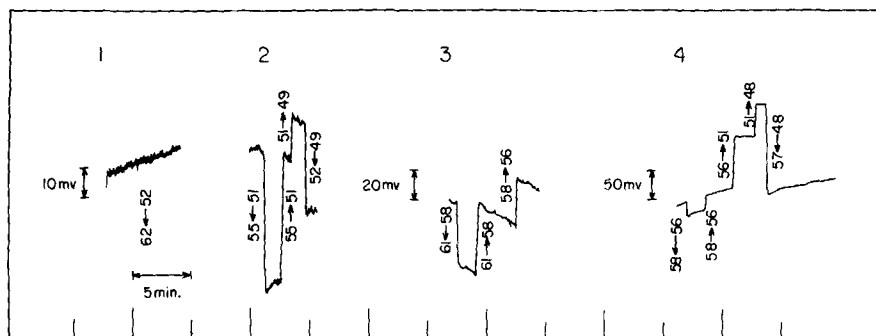


FIG. 3. Shear balance output for a stearic acid film on an  $\text{Al}^{3+}$  (pH 4.6) solution. The movable (outer) vanes were displaced stepwise and the restoring voltage needed to counterbalance the shear stress was monitored. 1 mV corresponds to 8 mdyn of stress. The position of the outer vanes is indicated by numerals (one unit corresponds to 4.6  $\mu\text{m}$ ) next to the trace, where the arrows show the direction of displacement.

The  $\pi$ - $A$  diagrams for stearic acid spread on pure water and on each of the above solutions are displayed in Fig. 2.

The film was compressed at a speed of  $0.35 \text{ \AA}^2/\text{molecule}/\text{min}$ . At a few points, the compression was stopped and shear measurement was made. During the measurement (15–20 min), the pressure dropped considerably in some cases. The discontinuities in Fig. 2 are due to this relaxation. Although the leakage around the barrier cannot be completely ruled out as the cause of the pressure drop, it should be noted that the pressure picked up as soon as the compression was resumed for the case of  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ . The relaxation thus seems to be due to a nonuniform stress resulting from uniaxial compression by the barrier as was discussed in the previous section.

In studying the shear property, we translated the outer vanes stepwise, inducing a strain in the film and observed the stress that developed at the sensing vane (see Fig. 1). A representative trace of the shear balance output is shown in Fig. 3. The above mentioned relaxation caused a tremendous drift of the shear balance as is evidenced in Fig. 3. We graphically subtracted the drift component to obtain the stress caused by the outer vanes. The numerals at the steps indicate the change of the LDVT output in mV; 1 mV corresponds to a 4.6  $\mu\text{m}$  movement. To calculate the shear modulus, we assumed that the stress field does not extend beyond the width of the sensing vane and ignored end corrections. The shear modulus thus calculated is shown in Table I along with both the area per molecule where the measurement was taken and the modulus  $-A d\pi/dA$  at the same point. As was discussed earlier, the moduli  $K$  and  $K'$  may be distinguished. In cases where the portion of the initial rise in  $\pi$  is clear enough so that the slope can be unambiguously calculated, we indicated this value in the bracket. A finite shear modulus was observed only with  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ , although a viscous relaxation was seen for  $\text{Fe}^{2+}$ . Note that reducing the pH of the  $\text{Al}^{3+}$  solution from 4.6 to 2.5 causes the shear modulus to disappear entirely. Although it is expected that  $K' - K = \mu$  [Eq. (7)], this relation seems to hold only at very low pressures. It is conceivable that, when the film gets rigid, nonuniform shear stress is not easily relieved and the force measurements  $\pi$  and  $\sigma$  may not reflect true thermodynamic properties of the film.

Langmuir and Schaefer<sup>9</sup> made studies of the effect of dissolved ions on various monolayer properties of

stearic acid and concluded that polyvalent ions had a profound effect, particularly aluminum. Although they discuss how shear modulus measurements could be made with their apparatus, they report no data. They did, however, present measurements of the effect of pH on the shear viscosity. The only actual shear measurement that appears in the literature was reported by Mouquin and Rideal.<sup>10</sup> They found a nonzero shear modulus ( $\sim 10 \text{ dyn/cm}$ ) for stearic acid on water. From our measurements, we must conclude that their water was contaminated.

The effect of various metal ions and of pH of the subphase on the  $\pi$ - $A$  relation has been studied previously<sup>11,12</sup>; our  $\pi$ - $A$  curves are generally in good agreement with these studies. Although no shear modulus measurement was performed, it is remarkable that the pressure rise at large area in the presence of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  ions was identified as an "expanded solid" phase.<sup>11,12</sup> Table I shows that the films are indeed solid. Wolstenholme and Schulman<sup>11</sup> also noted that the solid phase on  $\text{Ca}^{2+}$  and  $\text{Mn}^{2+}$  solutions is markedly different from the solid phase on  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  solutions. In the former, they inferred that the metal ions form disterate salts and that the molecules are pulled closer together. In the latter case hydroxy compounds of metal ions are formed and the hydrogen bonding provides a strong tie between neighboring molecules.

With this microscopic picture, the results of our shear modulus measurements can be understood as follows. The presence of hydrogen bonding can account for the fact that we only observe a shear modulus in solutions containing trivalent ions. Thus when the pH is lower than the value where hydroxide precipitation occurs, no shear modulus is observed; this corresponds to a pH of 4.2 for an Al solution. The lack of an observable shear modulus for the case of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions may be because the film has a very low yield stress or because it is in a highly fractured state as a result of compression. We tend to favor the latter explanation. In the absence of hydrolysis, the bonding is ionic in character; as a consequence, the film may not be able to mend itself of 2D cracks resulting from compression. The hydrogen bonds associated with the trivalent ions could better rejoin across compressional fracture lines. If this is the case, a melting of the 2D lattice following compaction should restore a macroscopically observable shear modulus. We shall search

for this effect in future experiments. In this respect, it is interesting to note that  $\text{Fe}^{2+}$  ions which form a monohydroxystearate behave intermediately as one might expect.

In summary, we have shown that ions capable of interacting through hydrogen bonding produce an observable 2D shear rigidity for spread monolayer films of stearic acid. This type of measurement is not only technologically important, but scientifically quite fascinating since one can vary the nature of intermolecular interactions, which is not readily achievable in a three dimensional state.

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