Elastic Properties of Langmuir-Blodgett Films

R. Zanoni, C. Naselli, J. Bell, G. I. Stegeman, and C. T. Seaton
Optical Sciences Center, University of Arizona, Tucson, Arizona 85721

(Received 18 August 1986)

The elastic properties of cadmium arachidate films, 11 to 401 monolayers thick, prepared on molybdenum and glass substrates by the Langmuir-Blodgett dipping technique, have been investigated by Brillouin scattering. Measurements of the dispersion of the guided acoustic waves with film thickness indicate an anomalously small ratio of the shear to the compressional elastic constants. Evidence for molecular reorientational fluctuations in the depolarized spectrum was also observed.

PACS numbers: 68.55.Pr, 62.65.+k, 78.35.+c

Langmuir-Blodgett (LB) films are unique because they are fabricated by dipping the substrate successively through a water surface containing an oriented monolayer film. The solid-state nature of the films has been established by electron diffraction,[1] x-ray scattering,[2] and scanning tunneling microscopy.[3] However, the fragile nature of these soaplike films suggests weak interlayer forces, and the high degree of orientation suggests anisotropic elastic properties. The compressional[4] and shear moduli[5] of a monolayer film spread on a water surface prior to deposition have been measured. However, only the coefficient of sliding friction between two LB films and the shear strength of the films have been determined experimentally[6] for deposited films. In this Letter we present the first experimental investigation of the elastic properties of LB films. We find them to be highly anisotropic, with shear properties reminiscent of smectic-*B* liquid-crystal media,[7] and we have observed depolarized spectra usually associated with molecular orientational fluctuations in a liquid. In addition, the large anisotropy leads to "bunching" of the guided acoustic waves.

Brillouin scattering has been used successfully to measure the elastic properties of surfaces and thin films for a number of years. In thin films, light is inelastically scattered from thermally excited acoustic phonons guided by the film. The spectral components are characterized by their frequency shift from the incident light frequency (the acoustic frequency Ω) and the change in the optical wave vector component parallel to the surface (which is equal to the parallel component of the acoustic guided-wave vector κ_p). The number of surface guided modes increases with film thickness (h), and their velocities depend on the product $\kappa_p h$, as well as multiple elastic constants of both the film and the substrate. There are essentially two orthogonal sets of guided acoustic modes, Sezawa waves (of which the Rayleigh wave is the lowest order) and Love waves, which in the present case are shear polarized with displacements parallel to the surfaces. By careful choice of scattering geometries and polarization of the incident and scattered light fields, it is possible to isolate various features of these acoustic modes and hence measure their dispersion relations (and the elastic constants).

The tandem Fabry-Perot interferometer used for frequency analysis of the scattered light was based on Sandercock's original design.[8,9] An argon-ion laser operating at $\lambda = 0.5145$ μm was the light source, and the Brillouin signal was detected with an FW130 photon-counting photomultiplier tube. An IBM PC servo controlled the tandem interferometer and recorded the Brillouin signal during the experiments.

The LB films used were formed from cadmium salts of the fatty acid arachidic acid, $CH_3(CH_2)_{18}COOH$, hereafter referred to as CdA. Film samples ranging in thickness from 11 up to 401 layers thick (27.8 Å per layer as measured by x-ray diffraction) were fabricated on both molybdenum and BK-7 glass[10] substrates with a Joyce-Loebel Langmuir trough. Standard substrate cleaning and deposition techniques were used.[11] The first layer was deposited with the hydroxyl group attached to the substrate, and successive layers were deposited with alternating orientations, commonly referred to as "*Y*" type.[12]

A typical Brillouin spectrum from the CdA samples is shown in Fig. 1. The polarized backscattering spectrum of a molybdenum substrate coated with 75 layers shows

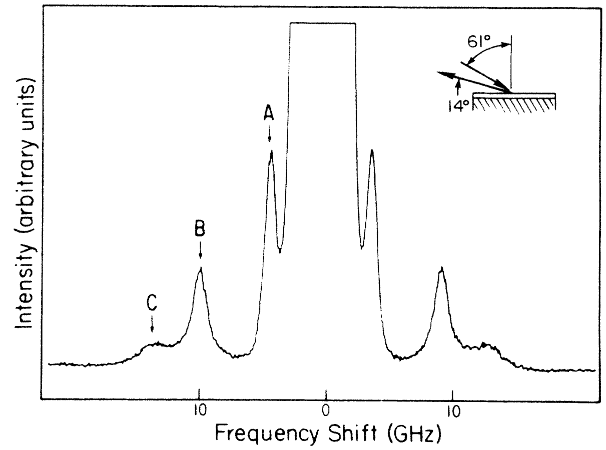

FIG. 1. Typical Brillouin spectrum of 75 layers of CdA coated onto a molybdenum substrate. The scattering geometry is illustrated in the upper right corner.

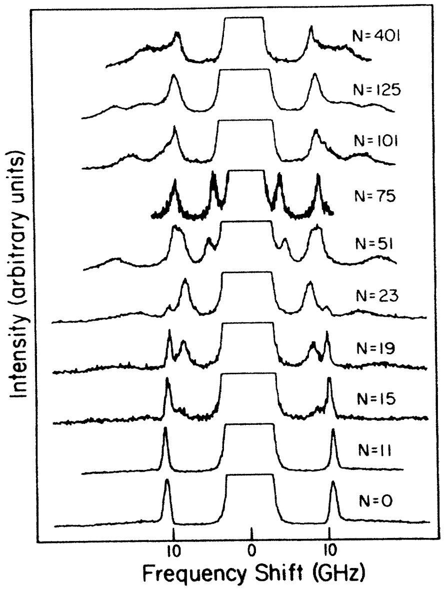

FIG. 2. Brillouin spectra of CdA film samples on molybdenum. The samples range in thickness from 11 to 401 monolayers thick.

three distinctive features arising from at least three guided acoustic modes. The peak corresponding to the smallest frequency shift is due to the Rayleigh wave. The velocity is obtained from the frequency shift and the scattering geometry (which gives κ_p). The variation of the Brillouin frequency shifts versus film thickness is illustrated in Fig. 2. In two separate experiments the elastic constants c_{33}, c_{44}, and c_{66} were measured, and the remaining constants c_{13} and c_{11} were obtained by a parametrized fit to an acoustical model of the LB film.

The value for c_{33} was obtained by observing backscattering at near normal incidence from longitudinal phonons in a 301-layer sample coated onto a BK-7 glass substrate. The angle of incidence of the incident light was 14°, and the scattered light was collected normal to the surface. A frequency shift of 23.6 GHz was measured for the longitudinal phonons traveling along a direction 4.5° from the surface normal. The sound speed of the longitudinal phonons is 3980 m/sec for an index of refraction of $n_0 = 1.525$.[13] We have measured the density of CdA films with Rutherford backscattering to be 1.32($\pm$0.06) g/cm^3. Therefore $c_{33} \cong 2.1\times10^{10}$ N/m^2.

The values of c_{44} and c_{66} were estimated by our observing guided Love modes in the LB film. *s*-polarized light at an angle of incidence of 60° was directed onto a 301-layer LB sample; the *p*-polarized scattered light was collected along the surface normal. No guided Love modes were observed as shown in Fig. 3. Since there are no clear features larger than 3 GHz it is possible to place limits on the values of c_{44} and c_{66}. The scattering angle within the film is 146°; therefore

$$c_{66}\sin^2\theta + c_{44}\cos^2\theta < 3.6\times10^9\ \mathrm{N/m^2},$$

where θ is the direction of the acoustic wave in the film. Here $\theta = 17°$, therefore $c_{44} < 4\times10^8$ N/m^2 and $c_{66} < 4.5\times10^9$ N/m^2.

With the values for c_{33} and c_{44}, the remaining elastic constants c_{11} and c_{13} can be obtained by a parametrized fit to a model of the Rayleigh-wave thickness dispersion data. The parametrized model of the Rayleigh wave velocity was constructed by modeling the LB film as a hexagonal film (symmetry axis normal to the surface) on an isotropic substrate. The calculated Rayleigh-wave dispersion curve, as well as dispersion curves for the higher-order guided-wave modes, is shown in Fig. 4 for comparison with experiment. Note the "bunching" of the guided-wave modes at velocities near the Rayleigh wave velocity of the free substrate. It is a direct consequence of the large difference between the shear and

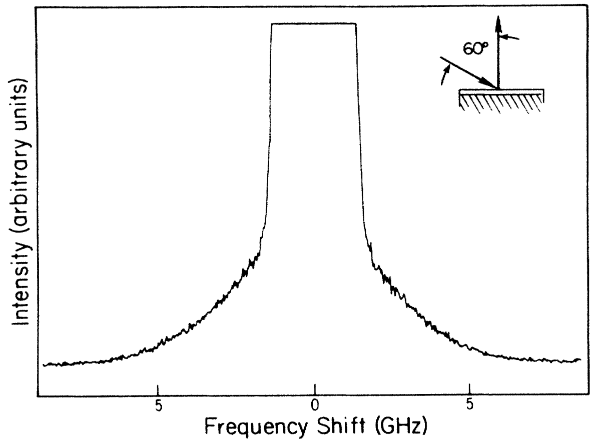

FIG. 3. Depolarized scattering from a CdA sample 301 layers thick. No phonon modes were observed larger than 3 GHz.

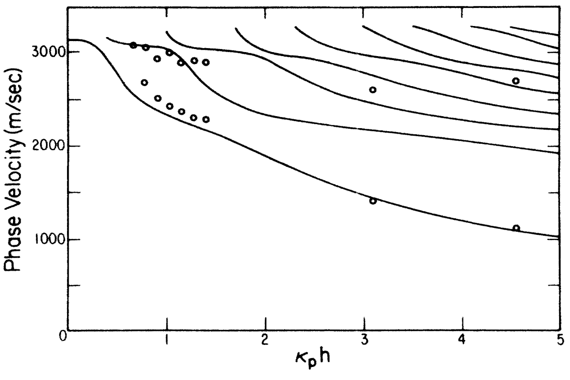

FIG. 4. Comparison of Brillouin scattering measurements with Rayleigh and Sezawa dispersion curves for a hexagonal film with $c_{33} = 2.1\times10^{10}$ N/m^2, $c_{13} = 1.0\times10^{10}$ N/m^2, $c_{44} = 4.0\times10^{10}$ N/m^2, and $c_{12} = 1.0\times10^{10}$ N/m^2 deposited on a polycrystalline molybdenum substate.

compressional elastic moduli, and is not obtained for isotropic films. It is scattering from two of these modes that gives rise to the remaining two peaks in Fig. 1. The value of c_{12} can be estimated from $c_{12}=c_{11}-2c_{66}$. Consequently, 0.2×10^{10} N/m$^2 < c_{12} < 1.1\times10^{10}$ N/m^2.

The frequency shifts of the Brillouin features were estimated with an error less than 2%. The largest error in estimating the phase velocity associated with a Brillouin feature was the scattering-angle measurement which was as large as 3%. Since the values of the elastic constants are interrelated more work must be done before reasonable errors can be assigned. The most significant error contributing to the elastic constants is the measurement of the film density which has been measured to within 5%.

No depolarized scattering was observed from Love waves; the spectrum is shown in Fig. 3. The long diffuse tails, which appear to be due to Brillouin features centered at or near zero frequency shift, may arise from molecular orientational fluctuations as in molecular liquids. The appearance of these features suggests that the individual long-chain LB molecules are undergoing orientational fluctuations inside the LB lattice, leading to a large damping of the shear waves polarized parallel to the layers.

These results show that the elastic properties of these LB films are highly anisotropic. The compressional constants are comparable to those obtained for oriented polymer films.[14] In contrast, the resistance to shear strains is small, as evidenced by the small shear elastic constants, much smaller than those observed in polymers. These properties are similar to results reported previously for smectic-*B* liquid crystals,[15] raising interesting questions about the similarities and differences between LB films and smectic-*B* liquid-crystal media. Similarly de Gennes has identified a solid form for smectic-*B* liquid-crystal media that appears to have similar properties to LB films.[16]

In summary, the elastic constants of LB-deposited films of CdA have been measured for the first time by Brillouin spectroscopy: namely $c_{44} < 4.0\times10^8$ N/m^2, $c_{66} < 4.5\times10^9$ N/m^2, $c_{11}\cong1.1\times10^{10}$ N/m^2, $c_{33}\cong2.1\times10^{10}$ N/m^2, $c_{13}\cong1.0\times10^{10}$ N/m^2, and 0.2×10^{10} N/m$^2 < c_{12} < 1.1\times10^{10}$ N/m^2. The shear elastic constant c_{44} is quite small for a solid film. There is evidence for molecular reorientation in the depolarized spectra of the CdA films.

This research was sponsored by the U.S. Army Research Office under Grant No. DAAG-29-83-K-0100.

---

[1] R. R. Nicklow, M. Pomerantz, and A. Segmuller, Phys. Rev. B **23**, 1081 (1981).

[2] A. Matsuda, M. Sugi, T. Fukui, and S. Izima, J. Appl. Phys. **48**, 771 (1977); T. Ohnishi, A. Ishitani, H. Ishida, N. Yamamoto, and H. Tsubomura, J. Phys. Chem. **82**, 1989 (1978).

[3] D. P. E. Smith, A. Bryant, C. F. Quate, J. P. Rabe, Ch. Gerber, and J. D. Swalen, to be published.

[4] K. C. O'Brien, J. Long, and J. B. Lando, Langmuir **1**, 514 (1985).

[5] B. M. Abraham, K. Miyano, S. Q. Xu, and J. B. Ketterson, Phys. Rev. Lett. **49**, 1643 (1982).

[6] B. J. Briscoe and D. C. B. Evans, Proc. Roy. Soc. London, Ser. A **380**, 389 (1982).

[7] P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974), Chap. 1, p. 15; O. Albrecht, H. Gruler, and E. Sackmann, J. Phys. (Paris) **39**, 301 (1978).

[8] J. R. Sandercock, in *Light Scattering in Solids III,* edited by M. Cardona and G. Güntherodt (Springer-Verlag, Berlin, 1982), p. 173.

[9] S. M. Lindsay, M. W. Anderson, and J. R. Sandercock, Rev. Sci. Instrum. **52**, 1478 (1981).

[10] Schott Glass Catalog, Duryea, Pennsylvania, 1985.

[11] R. Zanoni, Ph.D. dissertation, University of Arizona, 1986 (unpublished).

[12] G. Gaines, *Insoluble Monolayers at Gas-Liquid Interfaces* (Wiley, New York, 1966).

[13] J. D. Swalen, K. E. Rieckhoff, and M. Tacke, Opt. Commun. **24**, 146 (1978).

[14] D. B. Cavanaugh and C. H. Wang, J. Polym. Sci. **20**, 1647 (1982).

[15] O. Albrecht, H. Gruler, and E. Sackmann, J. Phys. (Paris) **39**, 301 (1978).

[16] de Gennes, Ref. 7.