

The mechanical stability of Langmuir–Blodgett multilayers

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Abstract

The properties and stability of confined Langmuir–Blodgett multilayers made of arachidic acid were investigated using the surface forces apparatus. Two different types of confined films were studied: one formed by bringing two separate LB films into molecular contact, the other formed by bringing one LB film into direct contact with mica. The measured thickness of confined material depends solely on the total number of trapped molecular layers (28 Å/layer). The force required to separate the substrates, however, depends on the type of contact made. More force (equivalent to a work of adhesion of 36 mJ/m²) is required to separate an LB film from mica than from another LB film (28 mJ/m²). Applied stress impacts the integrity of the LB multilayers; the films are particularly vulnerable to the combination of shearing and tensile stresses. Microscopic changes in film structure are sufficient to generate anomalous behavior at the macroscopic level, namely pinning of the contact region despite changes in load exerted on the deformable interacting bodies. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

One of the most appealing qualities of Langmuir–Blodgett (LB) films is their dimensionality. With little or no sacrifice in molecular-level control or order, tens to thousands of individual mono-molecular layers may be successively and successfully deposited to form a resultant LB film of significant thickness. It is this three-dimensional control that underscores the potential use of LB films in various scientific and technological applications [1]. The LB process offers not only the opportunity to create a material of well controlled thickness but also a scheme to amplify signals or responses associated with individual molecular layers.

Many LB film applications will likely require these

materials to be bounded not only by the substrate upon which they are built but also by an opposing surface. Relatively little is known, however, about the behavior and stability of LB films in this unnatural configuration. One key issue is the strength of adhesion of the multi-layered film to its bounding surfaces and how this compares to the strength of cohesion between the deposited layers. A related issue is the extent to which a film originally built upon one of the bounding surfaces equals that created when two thinner films are brought into contact. The latter, for example, might be more efficient to manufacture. In addition, the multi-layer thickness — a highly controllable parameter for unconfined films — may be less so for confined films. At a more basic level, it is important to determine whether the structure and integrity of a multilayered film remains intact during confinement. Such a configuration may impart both normal and shear stresses on the film, increasing the likelihood of structural damage and the loss of function.

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The surface forces apparatus (SFA) is an ideal tool for studying the properties of confined materials and the strength of adhesion between surfaces [2–4]. The device is designed to measure the distance dependence of forces acting between well-defined macroscopic surfaces separated by microscopic distances. Equivalently, the device can be used in the capacity of a ‘nanoscopic vise’ to confine thin films. An LB film built atop a smooth mica sheet can be gently brought into intimate contact with an opposing surface such as mica or another LB film. The film can then be exposed to varying amounts of stress by applying or removing normal forces with a series of springs and micro-stepping motors.

Perhaps the most powerful aspect of using the SFA for thin film studies is multiple beam interferometry (MBI) [5], an essential part of the SFA technique [6]. MBI allows for extremely accurate thickness and refractive index measurements, both of which provide insight into film structure. The interferometry is accomplished by making the two mica substrates and LB film between them part of a Fabry–Perot type interferometer. ‘Fringes of equal chromatic order’ (FECO) are generated by directing white light normally through the substrates. Conveniently, symmetrically designed interferometers with, for example, a thin film in the middle allow changes in film thickness and refractive index to be readily discerned. In particular, the wavelengths of even-order (‘even’) fringes are sensitive to both the film refractive index and thickness, while wavelengths of odd fringes are sensitive only to the latter. Comparing and contrasting the behavior of odd and even fringes gives us a powerful tool for investigating film structure and optical properties.

One of the first applications of the SFA was indeed to investigate the effects of shearing calcium stearate monolayers and multilayers trapped between mica surfaces [2,7]. Using an early version of the SFA (notably with advanced features like sliding capabilities), Tabor and Israelachvili found that neither monolayers nor multilayers were stable to shear forces; both showed visible signs of structural damage upon application of the shear force. Shortly after this, Briscoe et al. [3] extended this work to higher contact pressures and sliding velocities with similar results. More recently, Chen et al. [4] used the SFA to measure the elastic properties of surfactant and lipid monolayers. They report both the thickness and elastic modulus of several monolayers under compressive loads. Apart, however, from the early studies focusing specifically on sliding effects, the SFA has not been applied towards fundamental studies of confined multilayered films.

In this work we take advantage of the SFA to study effects of confinement on the simplest and most studied LB film, namely multilayers formed of a partially ionized fatty acid (arachidic acid). We address the

issues raised above and show that these multilayered materials are particularly susceptible to applied stress.

2. Experimental

Arachidic acid and subphase salts (BaCl_2 , KHCO_3 , and CuCl_2) were of the highest grade available, purchased from Sigma (St. Louis, MO) and used as received. HPLC chloroform and methanol for spreading solutions was purchased from Fisher (Pittsburgh, PA). Dipalmitoylphosphatidylethanolamine (DPPE) was purchased from Avanti Polar Lipids (Alabaster, AL) and used without further purification. Water used as a subphase in the depositions was produced by a Milli-Q unit and had a resistivity of $18 \text{ M}\Omega \text{ cm}$. The arachidic acid LB multilayers used in this study were prepared on freshly cleaved mica supplied by Mica New York (New York, NY). The Langmuir film balance and dipping device were automated and built by KSV Instruments of Finland.

Mica was freshly cleaved, cut with a hot platinum wire, and silvered with 480 \AA on one side by thermal evaporation. The surfaces were then glued, silver side down, to curved silica disks ($R \approx 1 \text{ cm}$). The first deposited layer was always DPPE, which is known to make an excellent quality monolayer on bare mica [8]. The phospholipid monolayer was deposited using the same conditions as Marra [8] and was allowed to dry for at least 10 min while changing to a salt subphase. Subsequent layers of arachidic acid were then deposited onto the DPPE-coated mica.

Arachidic acid LB films were deposited from an aqueous subphase containing 10^{-4} M BaCl_2 and $2 \times 10^{-4} \text{ M KHCO}_3$, and held constant at 20°C . The KHCO_3 buffered the subphase to a pH of 6.5. CuCl_2 was added to the subphase until its final concentration was $4 \times 10^{-7} \text{ M}$; this concentration has been shown to aid the deposition of large numbers of layers [9]. Monolayers were spread from an $\approx 1\text{-mg/ml}$ solution of fatty acid and chloroform, the latter being allowed to evaporate for 10 min before compressing the monolayer to 30 mN/m . Once this pressure was reached, the films were allowed 15 min to stabilize before conventional dipping commenced at a speed of 10 mm/min . At least 5 min elapsed between the upstroke and the downstroke to allow entrained subphase to evaporate and to enhance further transfer. Transfer ratios were always 0.95 to 1.02 as measured by barrier movement.

The LB coated surface was placed into the SFA with either an opposing, uncoated mica surface or a similarly coated LB surface and both surfaces were dried, out of contact, by evacuating the space within the SFA to $\approx 10 \text{ torr}$ using a vacuum system. The mica surface and/or LB film(s) were brought into molecular contact and the positions and shapes of the interference fringes were noted by recording them with a CCD-based opti-

cal detection system previously described by Levins and Vanderlick [10].

Experiments which we will call ‘JKR’ experiments, consisted of the following. First the load applied to the sandwiched films was gradually increased. Once a maximum force was reached, usually around 0.027 N, the motor direction was reversed, and the load was gradually decreased until the pull-off force was reached, causing the surfaces to jump apart. At various points during the loading/unloading cycle, CCD images were taken to record the shapes and positions of the interference fringes.

3. Results and discussion

Our experiments consisted of either an LB multilayer placed in contact with an opposing mica surface (denoted film/mica contact) or a multilayer placed in contact with an opposing LB multilayer (denoted film/film contact). The multilayers ranged in thickness between 4 and 26 arachidic acid layers and were always deposited atop a base layer of DPPE (on mica) for reasons noted in the previous section. The fatty acid layers making up the LB film are oriented in the classical head–tail/tail–head fashion. The last, top-most, layer of all deposited LB films is oriented such that the alkane tail projects outward, thus creating a hydrophobic surface. (Stable films having the polar head group projecting outwards can only be formed under water.)

As the gently curved substrates were brought towards one another in the SFA we always observed a jump from a short separation into flat adhesive contact, irrespective of the type of contact. (This mechanical instability — associated with the force measurement technique — is consistent with the existent of van der Waals attractive forces acting between the separated substrates.) The measured thicknesses of several confined LB multilayers, differing in the total number of deposited layers, are plotted in Fig. 1. A least squares fit to the data exhibits excellent linearity, especially when it is noted that both types of contact are represented in the plot, i.e. two 10-layer films in contact with each other yields the same total thickness as a single film of 20 layers in contact with an opposing clean mica surface. The slope of the least squares fit to the data yields the thickness per layer, $28.0 \pm 0.3 \text{ \AA}$, in good agreement with literature values for unconfined arachidic acid films obtained from AFM and X-ray reflectivity [11–13].

Although the two contacts (i.e. film/mica and film/film) behave identically with respect to total confined film thickness, the two types behave differently with respect to the force required to separate the surfaces from contact. The work of adhesion as derived from the force required to pull apart the

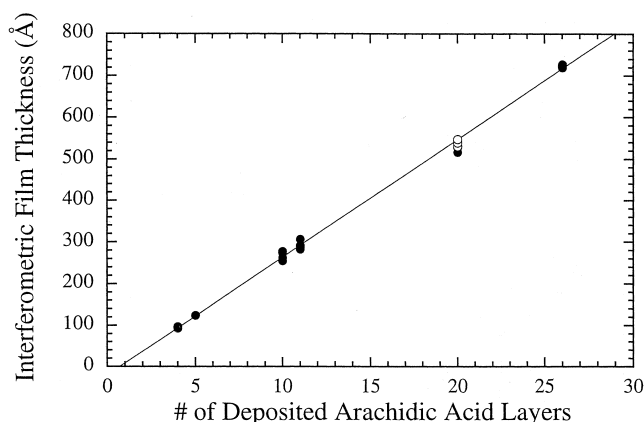


Fig. 1. Total interferometric thickness of several different LB multilayers of varying thickness. Closed symbols represent films which were built on one mica sheet and brought into contact with a bare mica sheet. Open symbols represent films which were built with half their total number of layers on each of two mica sheets and later joined by bringing the surfaces into contact.

multilayer/mica contact was found to be $36 \pm 5 \text{ mJ/m}^2$ (three trials). For sake of comparison we measured the adhesion between mica and DPPE (as deposited on mica) and found it to be 37 mJ/m^2 . The near equivalence of these adhesion values suggests that separation occurs at the multilayer/mica interface created by bringing the surfaces together, rather than at some interior interface within the film. (The other possibility is that failure occurs at the LB-created DPPC head-group/mica interface; this is unlikely as the interaction between the polar headgroups and mica is strong in comparison to interactions between methyl groups and mica. In addition this possibility would yield the unstable situation of exposed DPPC headgroups. Instead, what is seen experimentally is that a monolayer of DPPE can be repeated and reproducibly separated from an opposing mica surface.)

In contrast, the measured adhesion required to separate a film/film contact is $28 \pm 2 \text{ mJ/m}^2$, significantly less than the work required to separate film/mica and DPPE/mica contacts. As noted above, the similarity in adhesion between film/mica and DPPE/mica leads us to conclude that it is the SFA-made interface, the junction created by bringing the films together, which is broken during separation of the surfaces. Since the weakest interface should fail first, we can conclude that the interface which fails during film/film separation is, again, the SFA-made junction. Indeed our adhesion measurements for film/film contact are consistent with the force required to separate two hydrocarbon (methyl terminated) surfaces. Our value is, for example, the same as the adhesion measured between two DMPE monolayers as previously reported by Chen et al. [14].

Given that multilayer/mica contact fails at the multilayer/mica interface and not at an internal interlayer interface leads us to conclude that an SFA-made

hydrocarbon/hydrocarbon interface (associated with film/film contact) and a LB deposited hydrocarbon/hydrocarbon interface are not equivalent. This is certainly not evident when considering only the thickness measurements reported above. However, our adhesion results indicate that the hydrocarbon/hydrocarbon junctions formed during LB deposition must be stronger than any of the SFA-made interfaces we explored, including the hydrocarbon/hydrocarbon interface created by bringing two LB-coated surfaces into contact. Although we cannot quantify exactly how strong the coupling between the deposited layers is, we can at least say that it is greater than 36 mJ/m^2 , the adhesion energy of the multilayer/mica interface as measured in our experiments.

While both types of contacts could be reproducibly separated (each with a characteristic adhesion strength as reported above), the separation process itself caused irreparable and significant structural damage to *all* films. The damage is incurred near the periphery of the contact zone, as evidenced by placement of irregularities observed in both the odd and even interference fringes observed after separation. In no situation could we pull any two substrates apart from contact and reform contact without having to apply large external forces, further evidence that multilayered films are permanently damaged by the separation process. This result indicates that the LB multilayers are vulnerable to the tensile stresses which are present and greatest in magnitude at the boundary of the contact zone.

To explore the effects of stress more fully, we submitted multilayered LB films to loading/unloading 'JKR' experiments as described in Section 2. We found that increasing the load on a multilayer/mica contact always initiated structural changes to the film which were manifested in the interference fringes. The FECO from a typical loading/unloading cycle with a 10-layer arachidic acid LB film is shown in Fig. 2. Increasing force causes two irregularities in the even interference fringes to appear. The blemish at the top of the photo in Fig. 2b is always 'pointed' or triangular in shape and occurs just outside the contact zone (corresponding to the flat region of the fringes). The abnormality at the bottom of the photo in Fig. 2b usually appears somewhat further from the contact zone and looks like a discontinuity of slope or a 'step' in the fringe tails. During unloading (Fig. 2c), the triangular blemish at the edge of contact disappears, however, the irregularity in the tail region usually does not change and remains until the surfaces separate. While the behavior of the even fringes is very reproducible, during a select few experiments we also noted abnormalities, most pronounced at large applied loads, in the odd FECO as well.

It is possible to associate the observed interferometric response with a specific structural change to the LB

film arising from the loading process. In particular our results suggest that small shearing forces applied to the film induce a well-defined furrow (i.e. crease) to open up within the film. Since one of the surfaces in the SFA is mounted on a leaf spring, deflection of the spring associated with application of a normal stress also causes a commensurate small lateral displacement of one surface relative to the other. As the surfaces are pushed together, a small shearing force is thus directed toward the fulcrum of the leaf spring supporting the bottom surface, causing the lower surface to be pulled toward this fulcrum. The result of this displacement (much like that of an object moved laterally on a shag carpet) is the generation of a furrow in the film at the periphery of the contact zone furthest from the fulcrum of the leaf spring (top of photo, Fig. 2b). This gross 'defect' to the LB film can be seemingly healed by simply removing the shear force (Fig. 2c). On the other hand, at the same time the furrow is formed, the shear force causes a disordering, or pile up, of the LB film on the opposite side of the contact zone (bottom of photo, Fig. 2b); this structural defect cannot be reordered by removal of the shear force (Fig. 2c).

We discuss now more fully the interferometric evidence leading to the structural changes suggested above, which is also consistent with the shear-induced irregularities of the FECO reported by Israelachvili and Tabor [2,7]. Since we normally do not see irregularities in the odd interference fringes, we can rule out the possibility of a distinct change in separation and attribute the irregularities in the even fringes solely to a quantifiable refractive index change. The shift to a shorter wavelength in the 'pointy' blemish corresponds to a reduction in refractive index from 1.4885 (characteristic of an intact LB film) to 1.0160 (that of air). This is consistent with a furrow that penetrates the entire thickness of the original film. Additionally, the lateral maximum width of this blemish is approximately $2 \mu\text{m}$, which agrees well with our estimate of the deflection of the bottom surface toward the leaf spring fulcrum, approximately $1 \mu\text{m}$. Quantitative interpretation of the irregularities on the opposite side of the contact region is more difficult, since the size and shape of these blemishes vary from experiment to experiment. Since this abnormality is associated with a film disordering and/or pile-up, we expect the size and shape of this blemish to be very experiment-dependent. This was indeed the case; we often observed irregularly shaped 'steps' in the fringe region just outside the contact zone (the step sizes were generally uncorrelated with any multiple of layer thickness).

We also discovered that the structural changes to the multilayer induced by small amounts of shear (i.e. the opening of the film on one side with the corresponding disordering of the film on the other) have a dramatic impact on the size of the contact area during the

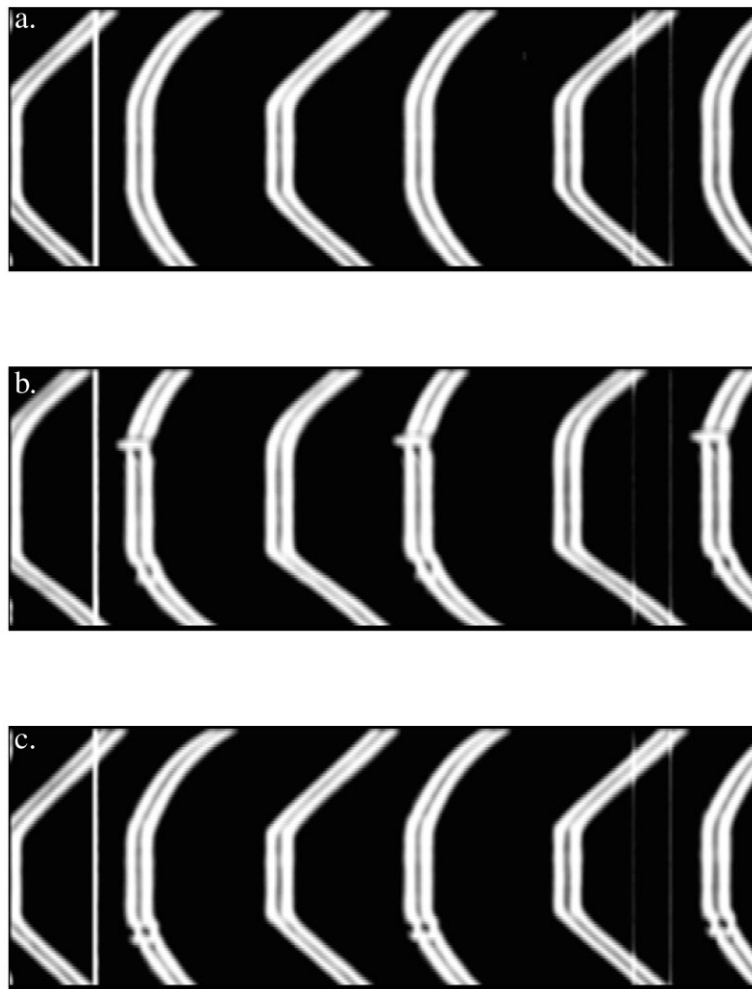


Fig. 2. Interference patterns generated during the loading/unloading of a 10-layer arachidic acid LB film. The vertical straight lines on the left and right are Hg reference lines, (a) FECO show no signs of damage upon initial contact. (b) Irregularities in the even FECO visible at maximum applied load (16 MPa). At the top edge of contact a fissure in the film has opened due to a shear force. Air fills this space, causing the shift to shorter wavelength. At the bottom edge of contact, the film becomes disordered, causing a discontinuity in the slope of the FECO tails. (c) Abnormalities in the FECO visible just before the surfaces separate. With the shear force removed, the fissure (top of photo) has closed, but the disordered region at the bottom remains until pull-off.

loading and unloading cycle. JKR theory [15] predicts that the contact radius should smoothly increase when the applied load is increased and reversibly decrease when the load is removed. Fig. 3 shows a comparison of the measured radius of LB/mica contact with that predicted by JKR theory. As is readily apparent, the area of LB/mica contact does not change as force is varied, in sharp contrast to the behavior predicted by theory. The nature of the structural changes induced in the film serves to pin the edges of the contact zone, preventing both its expansion and its recession. This is a dramatic effect given that microscopic changes in the structure of the ultra-thin coating serve to dictate the macroscopic behavior of the interacting bodies. We are unaware of any other such system which exhibits such a controlling influence on the deformation behavior of the contacting bodies.

Interestingly, while this phenomena was ubiquitous

and reproducible for all multilayer/mica experiments it was not the case for contact between two films. Some film/film loading experiments showed the signature irregularities in the even fringes, while other films appeared to remain unaffected. In no case, however, was the contact region ever totally pinned. Fig. 4 shows a loading and unloading cycle for film/film contact which demonstrated structural changes (as evidenced by the interference fringes). As the surfaces were compressed together, the increasing force caused the contact radius to grow, despite the appearance of irregularities at the periphery of the contact zone. As the force is removed, however, the structural changes incurred are sufficient to prevent the contact radius from decreasing, akin to the behavior observed with film/mica contact. Film/film contacts for which the LB multilayers show no evidence of rearrangement behaved in accord with JKR theory, as shown in Fig. 5. The con-

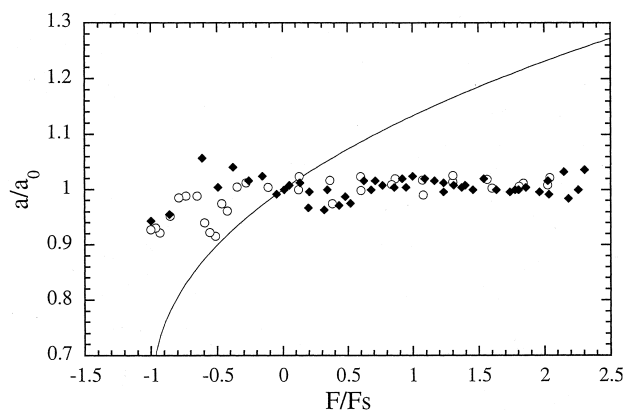


Fig. 3. A comparison between the contact radius growth for two multilayer/mica contacts (open and closed symbols) and JKR theory (line) is shown. The structural damage to the film is severe enough to pin the edges of the contact zone preventing it from expanding or receding.

tact area grows and diminishes as the loading is reversed (although a small hysteresis is observed). This behavior, in addition to the lack of irregularities in the interference fringes, provides strong evidence that it is indeed possible to create a situation where the LB film remains structurally intact despite the action of small shearing forces.

One can speculate on the cause of the difference in loading behavior between the film/film and film/mica contacts. The SFA-made hydrocarbon/hydrocarbon interface exhibits weak adhesion (28 mJ/m^2) which is measurably less than that of the film/mica interface (36 mJ/m^2). It is possible that this weak junction permits low friction sliding at the film/film interface reducing the possibility of shear induced damage. No such junction is available to film/mica contacts. On the other hand, the fact that all films exhibit damage when

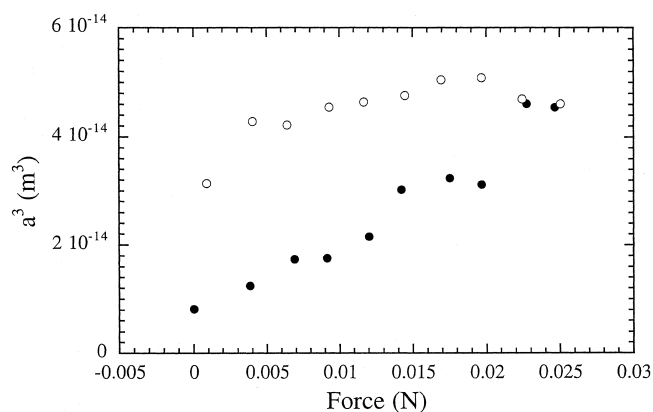


Fig. 4. Contact radius change during a loading/unloading cycle for a damaged film/film contact. The contact radius is scaled with that at no load (a_0) and the force applied is scaled by the magnitude of the pull-off force, F_s . In accord with JKR theory, the contact radius grows (closed symbols) as the load is increased, despite the defects in the film at the edges of contact. During unloading (open symbols), the contact radius remains relatively constant, inconsistent with theory.

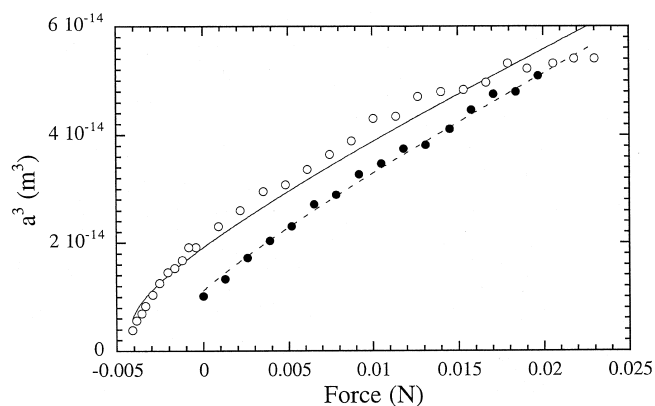


Fig. 5. Contact radius change during a loading/unloading cycle for an undamaged film/film contact. This type of contact behaves in agreement with JKR theory during loading (closed symbols) and unloading (open symbols). Parameters for the JKR fit of the unloading portion (solid line) are: effective elastic modulus, $K = 1.41 \times 10^{10} \text{ Pa}$ and adhesion energy, $\gamma = 27.03 \text{ mJ/m}^2$. The work of adhesion obtained directly from the pull-off force is 28 mJ/m^2 .

separated from adhesive contact, and that structural changes occur near the periphery of the contact zone, suggests that in general LB films are particularly vulnerable to the combination of shearing and tensile stresses.

Lastly, it is also interesting to compare the behavior of LB multilayers to the behavior of the DPPE base monolayer. A DPPE monolayer built atop a mica surface was brought into contact with an opposing mica surface. Attempts to separate and recontact these two surfaces were always successful, as surfaces repeatedly jumped into contact from a small separation. No irregularities in the interference fringes were ever observed, and JKR experiments on the monolayer system were always well behaved, as shown in Fig. 6 (interestingly the monolayer also exhibits a small hysteresis similar to

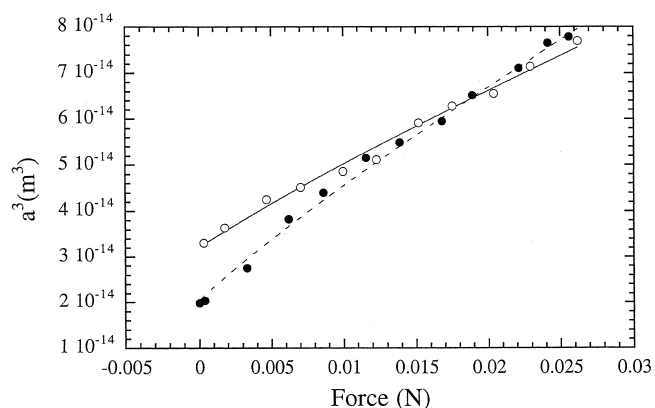


Fig. 6. Contact radius change during a loading/unloading cycle for a DPPE/mica contact. This type of contact also behaves according to JKR theory for both loading (closed symbols) and unloading (open symbols). Parameters for the JKR fit of the unloading portion (solid line) are: effective elastic modulus, $K = 1.90 \times 10^{10} \text{ Pa}$ and adhesion energy, $\gamma = 44.90 \text{ mJ/m}^2$. The work of adhesion obtained directly from the pull-off force is 37 mJ/m^2 .

that seen in Fig. 5). Chen et al. [4] subjected a DMPE monolayer to applied loads and also noted no signs of instability.

In short, it appears that in general the stability and performance monolayers is distinctly different from that of stacked monolayers in the form of LB films. While we did not pursue studies on films comprised of less than four arachidic acid layers, it would be interesting to examine the behavior of even fewer layers; however, the natural bilayer subunit of most LB films would ultimately pose practical limitations on this issue. Moreover, our aim was to investigate the specific nature of films comprised of multiple layers and not the asymptotic or possibly anomalous case of just a few layers. In this regard, we found that films comprised of only four layers display all behaviors ubiquitous to films of many layers.

4. Conclusions

Two different types of confined LB films were studied, one formed by bringing two individual films into contact and one formed by bringing mica into contact with a single film. The measured film thickness, as obtained from interferometry, depends only on total numbers of layers trapped between the mica sheets. This suggests little, if any, interdigitation or rearrangement when the exposed tail groups of individual films are brought into contact. With respect to total thickness, two halves appear to produce a whole. With respect to adhesion strength, however, this is not the case. Film/film contacts exhibit significantly less adhesion than film/mica contacts, which are, in turn, weaker than intra-film (i.e. interlayer) contacts.

A general and important result of our investigations is that the integrity of multilayered films is particularly susceptible to applied stresses. The lethal combination of shear and tensile stress, such as that found at the periphery of contact in our SFA experiments, causes identifiable and irrevocable damage to the LB multilayer. While the structural changes incurred are local

and microscopic, they are significant enough to impact the macroscopic deformation behavior of the interacting substrates; specifically, the damage prohibits any changes in size of the contact zone upon loading or unloading. The vulnerability to damage depends on which type of contact is established, and is probably related to the strength of adhesion between surfaces. While we did not attempt to quantify yield stresses per se, our experiments make clear that the tolerance to stress (especially shear) may limit many potential technological applications of LB films.

Acknowledgements

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