Scanning Force Microscopy Characterization of Viscoelastic Deformations Induced by Precontact Attraction in a Low Cross-Link Density Gelatin Film

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Scanning force microscopy (SFM) is used to investigate novel perturbation/response phenomena in a soft polymer network. Topics addressed include (i) the volume of film affected by tip-sample contact and (ii) the time-evolving residual signature of this contact. An outward deformation of nanometer-scale, soft, hydrated gelatin films is induced by the close proximity of the SFM tip. A domelike defect is created, centered at the site of approach and exceeding the tip-sample contact zone in diameter by as much as 3 orders of magnitude. The stretching of the film changes the stiffness of the polymer network and its frictional character. A precise correspondence of height and frictional force is quantified in histograms of the number of image pixels versus height or frictional force, and as a function of lateral distance from the center of approach. Relaxation of the dome is observed on a time scale of minutes with stretched exponential time dependence, consistent with a distribution of relaxation times. Film age also affects the size of the doming region: an increase to a maximum volume is observed, followed by a decrease to nanometer scale dimensions with age. This apparently reflects competing increases of long and short-range order that determine film cohesion. Five stages of gelatin film aggregation are experimentally distinguishable, differing in the extent of cohesion generated by progressive intermolecular coordination (e.g., crystallinity).

1. Introduction

Scanning force microscopy (SFM) is well-known as a tool for imaging atomic- or molecular-scale structures.\(^1\)\(^,\)\(^2\) More noteworthy on soft materials, however, is the sensitivity of SFM to local viscoelasticity and tribology.\(^3\)\(^-\)\(^4\) These attributes enable careful investigations of nanoscale mechanical perturbation/response, and the potential to image residual changes in structure and/or properties.\(^6\)\(^-\)\(^10\)\(^-\)\(^2\)\(^5\) SFM studies of residual effects in organic materials can be grouped into two categories, which we term “manipulation” and “transformation”. The former only addresses the movement of material,\(^6\)\(^-\)\(^7\)\(^-\)\(^9\)\(^2\)\(^0\)\(^-\)\(^2\)\(^4\) whereas the latter additionally exploits the capabilities of SFM to sense changes in material properties.\(^8\)\(^-\)\(^10\)\(^-\)\(^2\)\(^5\) The present study falls into this second category, along with much of our earlier work.\(^8\)\(^-\)\(^10\)

Forces exerted between approaching surfaces can have an enormous impact on the bimaterial interface formed upon contact.\(^2\)\(^6\) For a rigid-asperity-on-soft-film system, the relevant “interface” is more than simply the boundary

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of minutes to hours. 

In soft materials, molecules may rearrange in response to forces exerted at the molecular level.26 One possible result is the outward deformation of one or both contacting surfaces in response to attractive forces. In the present study we probe a photographic-gelatin network film, at an intermediate stage of cohesion, that deforms outwardly toward an approaching SFM tip. Remarkably, the frictional response and stiffness of the deformed film are modified, toward lower friction and higher stiffness compared to the surrounding unmodified film. These modified properties apparently derive from the stretching of molecules in amorphous regions.

Our previous studies of perturbation/response have tracked residual effects in gelatin films over a time interval of minutes to hours.8-10 In the present study we again encounter relaxation in this dynamical time frame, reflecting a nonequilibrium state attained during the initial deforming event. Thus the system cannot be understood solely in terms of quantities from equilibrium thermodynamics, i.e., interfacial and elastic energies, but also additionally exhibits viscoelastic (nonequilibrium) behavior.

2. Experimental Details

Aqueous gelatin solutions of 10−3 to 10−2 wt % were prepared by slowly heating (2 h) a 1 wt % mixture of gelatin (Kind and Knox photographic grade) in distilled/deionized water (DW) to 45 °C, followed by dilution with DW at 20 °C to the desired concentration. Freshly cleaved muscovite mica (Union Mica Corp.) substrates were rinsed in DW, immersed in the aqueous gelatin solution (immediately after its preparation) for 3 h, rinsed in a DW bath, removed such that residual water sheeted off, covered, and allowed to dry slowly overnight at 20 °C in moderate humidity (25% < RH < 50%). SFM imaging and measurements were performed within 24 h, and repeatedly during a period of weeks, primarily with the Nanoscope III (Digital Instruments, “DI”). Additional humidity-dependent measurements were performed with PicoSPM (Molecular Imaging), which employs an O-ring sealed glass chamber to control the sample environment. (Humidified or desiccated air was circulated through this chamber, where relative humidity (RH) was controlled automatically to within ±2%.)

Topographic and frictional force as well as topographic and force modulation images were simultaneously collected at constant (mean) cantilever deflection using triangular microfabricated 100 μm cantilevers (nominal spring constant = 0.58 N/m) with pyramidal Si3N4 tips purchased from Digital Instruments. Force modulation images, i.e., images of the cantilever modulation amplitude in response to Z modulation of the cantilever support (via a piezoelectric oscillator), were collected at a driving modulation amplitude of several nanometers and frequencies of 20−22 kHz. The DI 1231 and 2043 J scanners with lateral/vertical scanning ranges of approximately 150/5 μm were used. The total load or “contact force” (Fc) was in the 50−1000 nN range depending on the amount of gelatin contaminating the tip (discussed in the results). Choosing a fast-scan direction perpendicular to the primary cantilever axis enables friction-actuated cantilever torsion.

Procedures were executed to verify that correspondences between height and friction were not instrumental artifacts due to coupling of the normal deflection and twisting of the cantilever. Although a steep surface produces torsional effects in addition to frictional forces,8 such effects were negligible in the present study because variations in surface height were minimal.

Conversely, a huge frictional force may exert a large enough drag on the tip (especially if scanning up a slope) to deflect the cantilever downward. This is expected to yield an artificial image of lower surface elevation; then a region of lower friction by comparison appears higher in elevation. We tested for such effects in two-phase gelatin films where the friction coefficient differs by as much as a factor of 5 between the two-phase regions.5 We varied the loading force, and thereby the frictional force, through a large range and observed no appreciable change in the relative elevations imaged in topographic mode. On the films of present interest, differences in friction on different surface regions are much smaller than on the two-phase films used in the abovetest, so we assume that the coupling of frictional forces with measured height in the images analyzed here is negligible. The same results indicate that differences in modulation amplitude (force modulation) that herein correlate with local friction do not yield identifiable differences in the measured elevation, i.e., height artifacts.

3. Results

3.1. Stages of Film Aging. We introduce our observations within the context of aging in gelatin films.27 Films prepared as described above exhibit dramatic aging effects for approximately the first 2 weeks following preparation, described below with the aid of Figure 1. Here we present topography/friction images (left/right) of four successive, transient film stages (A through D). In stage A, which lasts at most 2 days, the film is completely unstable with respect to lateral scanning of the SFM tip. Film morphology changes between successive images. We display this effect in Figure 1a by imaging a 5 × 5-μm region following repeated raster scanning of a 3 × 3-μm region. In the smaller 3 × 3-μm region (upper left) the effect of the additional scanning can be observed by comparing to the surrounding region. Under lateral scanning, gelatin tends to aggregate and in some locations form “bands” perpendicular to the fast scan axis. (This phenomenon has been reported in other SFM studies of polymer films.20-23) On gelatin these agglomerates exhibit lower friction than relatively unperturbed film portions. Thus the polymer is extremely susceptible to perturbation by the SFM tip, as well as accumulation on it.28

The second characteristic film stage (B) is exemplified in Figure 1b. A previously raster-scanned, 5 × 5-μm region was imaged over a 10 × 10-μm region. Upon raster scanning, the film does not agglomerate laterally as in Figure 1a but rather becomes raised relative to the surrounding film and exhibits correspondingly lower friction. Force modulation images (not shown) further indicate greater stiffness in the modified film. Accumulation of polymer on the tip remains rapid. This behavior is observed typically for several days but generally lasts less than 1 week.

Upon reaching stage C at several days of age, the films no longer exhibit raising under shear. However, following the approach and contact of tip to film a raised circular region of reduced friction is imaged, centered at the point of approach.29 This is exemplified in a 40 × 40-μm image, Figure 1c. Notably, the raised circular region has diameter as much as 3 orders of magnitude larger than the estimated tip-sample contact diameter. Accumulation of polymer

(27) Aging effects are prevalent in many physically associating polymeric systems and are commonly known to gelatin technologists, in applications such as photographic media.

(28) The latter indeed is manifest as an observed increase in tip-sample adhesive (pull-away) force the longer a given tip has been used to image the film. Subsequent scanning electron micrographs of such tips verify the presence of polymer, forming a “collar” that presumably enlarges the contact zone.

(29) Generally, this also is observed in stage B. Imaging the modified circular region is complicated, however, by the perturbations of lateral scanning during that stage.
on the tip is usually slow or negligible on an experimental time scale of hours. Stage C is the focus of the present study; the above observations will be elaborated in the following sections. With additional aging on the scale of days, quantitative rather than qualitative changes are generally observed: the lateral range of circular perturbation decreases. Figure 1d is a $10 \times 10 \mu m$ image containing an outward deformation of approximately $0.5 \mu m$ in diameter, observed upon approach and contact at 15 days of age. No accumulation of polymer on tip was observed. We term this state of the film stage D. Though primarily differing quantitatively, we choose to distinguish stage D from C because the submicron lateral extent of the deformation is within roughly 1 order of magnitude of the estimated tip–sample contact area, and thus not a starkly delocalized phenomenon as in stage C. Stage D typically is entered at approximately 1–2 weeks of age. Upon reaching stage E at 2–3 weeks of age, none of the perturbative effects of stages A through D are observed.30

**3.2. Phenomenology of Circular Perturbation.**

Large circular regions of raised height and reduced friction like that in Figure 1c can also be imaged in force modulation mode. In Figure 2 we present a topography/stiffness (left/right) image ($13 \times 13 \mu m$) that displays the qualitative result: the modified circular region approximately 10 \( \mu m \) in diameter is imaged as greater cantilever modulation amplitude in response to \( Z \) modulation of the cantilever support, i.e., enhanced stiffness. Note that the region nearest the center is additionally raised in height/stiffness; this is frequently observed following repeated approach–withdrawal cycles, as performed prior to collecting the image in Figure 2.

The bulk of our detailed investigations of the circular deformations focus on frictional images.32 We wish to quantify the frictional force on deformed circular regions such as that in Figure 1c, in particular to compare it to structure-related variations in friction observed in our earlier studies.8–10 Figure 3 contains a typical friction loop acquired over a 100-\( \mu m \) scan line, passing through the center of a deformed region. The difference of the lateral force exerted during left-to-right versus right-to-left scanning quantifies the relative frictional force on the deformed versus unperturbed regions. From these data we find that the frictional force is reduced by approximately 30\% relative to its value prior to deformation.

We wish to analyze carefully the correspondence between surface height and friction. To do this, we have

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**Figure 1.** Topography/frictional force images (left/right) of four successive, transient stages during aging of thin gelatin films. (a) Film is completely unstable with respect to lateral scanning of the SFM tip. Under lateral scanning, gelatin tends to aggregate in some locations. Agglomerates exhibit a lower friction than relatively unperturbed film portions. This behavior lasts at most 2 days beyond the time of film preparation. (b) Film becomes raised relative to the surrounding film and exhibits correspondingly lower friction. This behavior is observed for several days but generally lasts less than 1 week. (c) Upon approach and contact of tip to film, a raised circular region of reduced friction is imaged, centered at the point of initial approach, with a diameter as much as 3 orders of magnitude larger than the contact diameter. Little or no effect of lateral scanning is observed. This stage is entered at several days of age and typically lasts until 1–2 weeks of age. (d) Qualitatively like (c) but the lateral extent of the deformation is within 1 order of magnitude of the estimated tip–sample contact area. This stage is entered at approximately 1–2 weeks of age and lasts approximately 1 week. Beyond this time no residual perturbative effects are observed.

**Figure 2.** Topography/stiffness (left/right) image ($13 \times 13 \mu m$) that contains a raised circular region approximately 10 \( \mu m \) in diameter, centered at the site of initial approach, with correspondingly enhanced stiffness.

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31 When present and imaged in friction mode, this smaller region is correspondingly reduced further in friction.

32 These images can be acquired more quickly than force modulation images, particularly important when monitoring time-dependent changes (section 4). Further, frictional images do not suffer from the nonlinearity of the piezoelectric scanner. This is a significant problem in large (tens of microns) topographic images with a \( Z \) range of only a few nanometers.
developed algorithms to convert images into “annular histograms”, i.e., the number of image pixels within incremental friction force intervals as a function of distance from the deformation center, depicted in Figure 4a for the case of a typical friction image. The black circles demarcate the boundaries of circular annuli, each of which is converted to a friction force histogram. In Figure 4b we analyze height and friction images of a representative deformation. Height and friction histograms are plotted with abscissas oriented vertically and positioned horizontally according to the distance from the center of the deformed region. The topography and friction profiles rendered by each set of histograms are analogous to a single radial scan originating at the center of the deformed region, but integrated over all azimuthal directions, i.e., 360°.

Profiles rendered in the above fashion tend to average out the noise as well as a variable image background. The result is the ability to quantify with improved precision the deformation diameter, height, and friction reduction. In particular we find that at distances just beyond 2 μm from the center of the circular region analyzed in Figure 4b, both the height and friction profiles begin to depart slightly from the constant values maintained at smaller distances (dashed lines at left). The extent of this departure increases with increasing distance in precisely proportional amounts for height versus frictional force. At 4-μm distance both quantities rapidly change, as evidenced by broad histograms; this distance corresponds to the edge of the circular deformed region seen qualitatively in the images. Both quantities approach the values of the surrounding unperturbed film (dashed lines at right) quite gradually, not attaining these values until 5.5-6 μm from the deformation center. Thus the perturbed film region extends substantially farther from the initial approach site than is apparent by simply viewing the images or examining a single scan profile.

We have compared the deformation due to a single approach with that due to multiple approach—withdrawal cycles. In Figure 5 we present representative frictional images (40 × 40 μm) acquired with the same tip on the same film during a single imaging session. The image in Figure 5a contains a circular region approximately 10 μm in diameter exhibiting lower friction and was captured immediately after a single approach of tip to sample. Figure 5b displays a similar region approximately 15 μm in diameter, obtained immediately after two approach—withdrawal cycles (and final approach). Figure 5c contains such a region approximately 18 μm in diameter, obtained after several tens of approach—withdrawal cycles executed rapidly in “force-displacement” mode. Figure 6 quantifies images from Figure 5 in the form of annular histograms such as those in Figure 4b. The bottom set of data derive from the image of Figure 5a (single approach), while the top data correspond to Figure 5c (many approach—withdrawal cycles). Most notable is the fact that the maximum friction reduction in each deformed region is approximately constant; i.e., the signal along the vertical axis does not change appreciably with cycling. Instead, the effects of repeated approach—withdrawal are almost exclusively lateral.

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(33) In many cases, instrumental drift during image acquisition results in an image of a slightly elliptical modified region.

(34) The image background is related to interference between laser light reflected from the cantilever and that from the sample mounting hardware (the sample is transparent). One expects this to contribute to images whether the tip is in contact with the sample, and indeed this is observed.

(35) The breadth is of course a function of the width of annular rings chosen. Decreasing this width increases the lateral resolution of changes in height or friction but also degrades the signal/noise.
The modulus of gelatin is a strong function of water content. Assuming that the size of the deformed region is dependent on modulus, we expect that its size also should be affected by water content, the latter a function of humidity. We have investigated this on films in stage D of aging, i.e., exhibiting submicron deformations. Representative topography/friction images of 2×2-μm regions are shown in Figure 7 following multiple approach–withdrawal cycles in each case, operating at relative humidities (RH) of (a) 4% and (b) 42%. At RH = 4% we find no certain evidence of deformation or friction reduction, whereas at RH = 42% there is obvious outward deformation and friction reduction. This observation demonstrates that films that have progressed beyond the point of yielding outward deformations can be forced to do so by water plasticization.

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Figure 5. Dependence of the size of a modified (deformed) circular region on repeated cycles of approach–withdrawal, as seen in frictional force images: (a) one approach (no withdrawal); (b) three approaches (two withdrawals); (c) several tens of approach–withdrawal cycles.

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3.3. Relaxation Dynamics. All of the images of circular deformation in sections 1–3 were acquired immediately after the perturbing event. The question arises whether a metastable state has been achieved or if instead the excited state relaxes to an unstressed state. In Figure 8 we present the time evolution of two typical circular deformations (a and b), as seen in frictional images. Both deformations resulted from repeated approach–withdrawal cycles, as produced the deformation of Figure 5c. Figure 8a contains six 40×40-μm images (extracted from 100×100-μm images) collected immediately after the deforming process (upper left, "time

Figure 6. Quantification of the images in Figure 5 as annular histograms. The bottom set of data derive from the image of Figure 5a (single approach), whereas the top correspond to Figure 5c (numerous approach–withdrawal cycles).

Figure 7. Humidity dependence of topography/friction images (left/right) of a 2×2-μm region of a film at stage D of aging, following multiple approach–withdrawal cycles: (a) RH = 4%; (b) RH = 42%. Only at RH = 42% is there outward deformation and friction reduction.

Figure 8. Time evolution of two typical circular deformations (a and b), as seen in frictional images. Both deformations resulted from repeated approach–withdrawal cycles, as produced the deformation of Figure 5c. Figure 8a contains six 40×40-μm images (extracted from 100×100-μm images) collected immediately after the deforming process (upper left, "time
We observe a slight increase in apparent diameter of the deformation zone, together with an increase in its frictional signature (brightening). This effect is seen more starkly over a longer time scale in the 40 × 40 μm images of Figure 8b. In addition to the time = 0 case, images were collected only at elapsed times of 7, 14, 23, 34, and 47 min. Though not shown, time-dependent changes in the height of the deformed regions track the frictional changes seen in Figure 8. Thus the “dome” in the film collapses with time while its perimeter propagates outward.

Figure 9 contains representative frictional histogram profiles derived from three of the images in Figure 8b, corresponding to time = 0, 7, and 47 min (bottom to top). These data quantify both obvious and subtle effects contained in the images as follows.

1. The depressed frictional signal observed at time = 0 relaxes toward its higher initial value by an amount that is greatest near the deformation center. For example, after 47 min the frictional signal relaxed by approximately 60% in the centermost annulus but only 50% in the annulus located 4.2 μm from the center.

2. The “visual deformation perimeter”, indicated with vertical lines in Figure 10, increases with elapsed time. (39) We define this perimeter as the radial distance at which the mean value of the frictional histograms varies most rapidly with distance (essentially an inflection point).

3. The “ultimate deformation perimeter”, defined as the distance beyond which the histograms are centered on the dashed lines (unperturbed), remains nearly constant at 13–14 μm over the 47-min time interval investigated. The radial movement of the visual deformation perimeter presumably is driven by lateral stresses in the region beyond the visual limit (but within the ultimate deformation perimeter).

Observation 1 indicates different relaxation times depending on the distance from the deformation center. We examine the functional dependence on time in greater detail in Figure 10. The data derive from the images in Figure 8b and correspond to (a) the centermost annulus and (b) the annulus located 4.2 μm from the deformation center. We plot the time dependence of the frictional signal normalized to its value at time zero, δF(t), to its value at time zero, δF(0). The bars denoting the data are centered vertically at the mean value obtained from each histogram; the bar height is equal to 2 times the standard deviation. In each graph we superimpose best fits of the data to two functional forms: an exponential decay exp(−t/τ) (dashed line) and “stretched” exponential exp(−(t/τ)β) (solid line). The values obtained for the fitting parameters are (a) τ = 21 min for both the

(38) Here the tip was removed from the imaged region following acquisition of each image (and re-engaged far away prior to collecting the next image). In some cases we collected images at similar time intervals but allowed the tip to raster scan continuously over the imaged region during intermediate times. No significant difference was observed in the time evolution of images whether the region was continuously scanned. Thus we identify the changes of Figure 9b as intrinsic and dynamical, i.e., not due to the scanning process.

exponential and stretched exponential, $\beta = 0.46$, and (b) $\tau = 32$ min for the exponential and 46 min for the stretched exponential, $\beta = 0.37$.

4. Discussion

4.1. Aging Network Structure. Gelatin forms triple-helical ("crystalline") physical cross-links under the driving force of collagen-fold renaturation; this process is described by more than one rate constant, the slowest requiring months or even years.\(^{(41)}\) We assign the evolution in mechanical integrity observed in Figure 1 to these slow aging processes. In stage A the films exhibit poor adhesion of film to substrate and weak lateral cohesion within the film. This apparently reflects a low degree of both short (i.e., crystalline) and long range (i.e., network) order. The latter suggests that a cross-linked network, or in the vocabulary of percolation theory,\(^{(42),(43)}\) an "infinite cluster", has not yet formed. Finite-sized "clusters" presumably exist; their signature may be the scan-induced formation of agglomerates seen in stage A. We attribute lowered friction on these agglomerates to increased molecular orientation, i.e., crystallinity, which we expect to yield lesser viscoelastic dissipation (friction) based on previous work.\(^{(8)-(10)}\) At the same time some small units, perhaps individual molecules, are susceptible to accumulation on the SFM tip.

We tentatively describe stage B as percolated, i.e., linked together as a network and thus possessing a degree of long range order, but of low cross-linking density, i.e., little short range order. The result is a soft, rubbery character and the presence of small clusters not yet linked to the infinite network (free to accumulate on the tip). Attractive forces between tip and sample apparently cause the film to stretch vertically and perhaps undergo delamination from the substrate. Vertical film stretching presumably induces a degree of molecular orientation, hence stiffening the film, making it less dissipative during subsequent lateral scanning.

At stage C the film possesses substantial long-range order (as manifest in the huge circular deformations), plus enough short range, crystalline order to provide sufficient cross-link density for the rubbery state. The volume of material involved in the interaction with the SFM tip is maximized at this stage, presumably by a balance of these two levels of order. A sharply diminished accumulation of gelatin on the SFM tip suggests that most molecules are part of the network. The complete lack of gelatin-to-tip transfer in stage D indicates that essentially all molecules are strongly linked to the network. The development of crystalline cross-links has proceeded nearly to completion, and the overall modulus is perhaps

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similar to that of a highly cross-linked rubber. The shrinking and final disappearance of the circular deformation from stage C to E presumably reflects the slow increase in the number and size of physical cross-links (and perhaps a concomitant decrease in free volume). Increased modulus as a function of increased cross-linking is a general property of polymer networks. In our case the increase of mechanical stiffness with age must necessarily decrease the volume of the deformed film for a given magnitude of the attractive force during approach.

4.2. Delamination Model. Our earlier work indicated that the amount of friction on gelatin is strongly related to the degree of crystallinity, that is, the amount of triple-helical content. This affects the film stiffness and thus the tip-sample contact area, i.e., extensive friction: the greater the decrease in the diameter dissipation energy, the greater the frictional force. One finding, however, was that contact area is of secondary importance. The dramatic reduction in friction on highly crystalline gelatin is due primarily to interfacial differences, i.e., a reduction in the dissipative character of the film. Likewise, the reduction of friction within the perturbed circular regions of present focus cannot be explained simply in terms of a reduction in contact area (implicit in slightly elevated stiffness). Thus we infer that lesser friction on the deformed film regions relates to a reduction in intensive friction, the latter caused by stretching (stiffening) of polymer chains and the resultant decrease in the freedom to dissipate energy viscoelastically (i.e., via molecular relaxations).

We have determined that the amount of friction reduction is precisely proportional to the distance the surface is raised (Figure 4b). The question arises whether the deformed film has simply stretched vertically and nothing more, by 4.1 nm in the case of Figure 4b. Such an effect certainly is not intuitive, because the initial tip-sample attraction was localized to a small region near the center of the circle. A simple analysis employing Hooke's law quantifies this model. We first compute the area of the affected region for the case of a rather small deformation induced by a single approach:

\[ A = \pi R^2 = (3.14)(2 \mu m)^2 \approx 10^{-1} \text{ m}^2 \]

The Young's modulus for the film is strongly dependent on water content and the cross-link density (i.e., the extent to which gelatin has polymerized). Here we use a lower-bound estimate assuming a water-plasticized, rubbery film: \( E \approx 10^7 \text{ N/m}^2 \). The strain in the deformed film in this model, i.e., change in thickness divided by initial thickness, is on the order of 0.1 (and as high as 0.4). Inserting these values into Hooke's law, \( \sigma = E \gamma \), we obtain

\[ F = AE \gamma \approx (10^{-11} \text{ m}^2)(10^7 \text{ N/m}^2)(0.1) = 10^{-5} \text{ N} = 10,000 \text{ nN} \]

The force required, in this conservative estimate, is at least 2 orders of magnitude greater than typically observed. Thus the above model cannot possibly be correct.

To explain the raised surface, we must propose delamination between film and substrate. This is illustrated in Figure 11. The distance that the film is deformed upward is exaggerated; the maximum amount observed among the films studied is 40% of the original film thickness.

Figure 11. Illustration of the proposed delamination model at the end of the event. The distance that the film is displaced upward is exaggerated; the maximum amount observed among the films studied is 40% of the original film thickness.

Figure 11. Illustration of the proposed delamination model at the end of the event. The distance that the film is displaced upward is exaggerated; the maximum amount observed among the films studied is 40% of the original film thickness.

Under repeated deformations the affected area does not increase linearly with the increasing number of cycles but rather seems to plateau after some number (which we have not quantified). This result verifies that the work done by attractive forces during approach does not continually translate into delaminated area. Rather, the role of delamination in successive approaches diminishes as the deformation region enlarges. Similarly, the fraction of mechanical energy retained in the form of irreversible lateral stretching must approach a constant as the deformation region ceases to grow. The only remaining repository in which the energy of attraction may reside during continual approach—withdrawal cycles is in reversible degrees of freedom. Thus, reversible deformations must comprise a greater fraction of the total deformation energy during repeated approach—withdrawal cycles, as

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(44) Film thickness is measured by removing all gelatin from a small region via high-force scanning and then imaging the depth of this region.

(45) We know very little about the strength of adhesion but assume that it is very small, perhaps due to a small areal concentration of adsorbing groups.
irreversible effects are diminished. Such elastic deformations by definition are not visible in subsequent images.

We assume that irreversible deformations always occur, even during the first approach and may produce strains much greater than evident in the residual deformation. Indeed large, nonlinear deformations may be the source of irreversible effects. Presumably there is a perimeter strain threshold below which delamination and associated irreversible stretching does not occur. As the deformed, stiffened film grows during repeated cycles, the reversible strain is distributed over a larger volume and thus attains smaller local values (because of increased modulus), until it no longer reaches the threshold for delamination at the perimeter. Alternatively, desiccating the film removes the plasticizing effects of water molecules, thereby stiffening the film. In this case the strain threshold may no longer be reached, even during the first approach, and hence irreversible deformation is precluded (Figure 7). One might investigate the generality of this concept as an analytical tool for a variety of amorphous and semicrystalline polymer films. We expect that plasticization will be more substantial in some materials, and in some phases of the same material, than in others. Hence one might exploit this phenomenon to identify phases in a phase-separated blend, for example.

In the above delamination model a portion of the initial tip-sample energy of attraction is stored mechanically in the deformed film. The slow dissipation of this energy enables imaging as a function of elapsed time (Figures 8 and 9) with some degree of quantification (Figure 10). The relaxation data in Figure 10 are too few and scattered, however, to infer the detailed nature of the relaxation based on the stretched-exponential fitting parameters $\tau$ and $\beta$. Nonetheless, we find that of the two functional forms examined, only the stretched exponential provides adequate agreement with the data in (a) or (b). Such empirical results are ubiquitous to studies of relaxation dynamics in disordered systems, in particular mechanical relaxations in polymers. The departure from a simple exponential decay generally signifies a distribution of relaxation times (which are described by the stretched exponential or other forms). In polymeric materials this may reflect variations in both the local conformation and the entanglement environment.

### 4.3. Additional Effects and Practical Relevance

Because it may play a role of some importance, it is necessary to address capillary condensation and the potential for transfer of water between tip and sample. The humidity dependence and lubricating character of adsorbed water on mica has been reported. Following others’ work, we have examined the transfer of water in the vicinity of the initial contact between an SFM tip and the mica surface, and the changes in the frictional signature of this region. In particular, we have observed that brief contact of the SFM tip with freshly deaved mica at 1–3% relative humidity (but not at ambient humidities) leaves a 2-μm circular region, centered at the site of approach, exhibiting slightly elevated height and slightly reduced friction. We concur with the interpretations of the first investigators of this phenomenon by attributing these observations to the transfer of water from the oxidized Si$_3$N$_4$ tip to the mica surface at low RH.

At first glance the above signature of water transfer appears similar to the phenomenon presently under investigation. We cannot rule out that water transfer between the SFM tip and gelatin film may play a role in the deformation/delamination process identified above. For water transfer alone to produce the phenomenology of the present study on gelatin films, however, would require (1) transfer only at high humidities, apparently from film to tip (given the fact that SFM-measured friction decreases with decreasing water content in gelatin films), (2) height increase upon water removal, (3) water depletion by a continuously decreasing amount as a function of distance from the point of approach, (4) depletion during the first several contacts but not during additional contacts, (5) extremely slow additional depletion of water from previously unperturbed surrounding regions as water is regained in the perturbed region, (6) decreasing range of water transfer (and ultimately negligible transfer) as gelatin films age, (7) transfer only from films prepared in a particular way, and (8) relaxation to initial water content with stretched exponential kinetics. Alone these points would comprise a convoluted and ad hoc explanation of our results.

Whether or not water transfer plays some role, the deformation phenomenon identified herein is clearly of practical importance to gelatin technology, and perhaps polymer-film products in general. The drying of processed photographic, for example, the movement of sheets of gelatin-coated structures over rollers involves numerous microasperity contacts between roller and film. Typically, such films are far from glassy at this stage and highly solvent plasticized. The presence of micron-scale regions of local strain, due to deformations of the type reported here, presumably would affect the homogeneity of the drying film and cause variations in the silver metal density deposited in development. Also, in the manufacture of coated photographic emulsions, contact after initial drying in windup and finishing at elevated humidity may induce deleterious changes in the suspended entities (e.g., silver halide crystals), producing effects such as printout, fog, bleaching, etc.

### Conclusions

We have presented the first SFM images (to our knowledge) of outward sample deformation induced by attractive forces upon close approach of the SFM tip. In gelatin films these deformations can extend microns beyond the tip-sample contact zone and apparently involve delamination of film from substrate. We expect this phenomenon to be restricted to soft films with strong in-plane cohesion and very weak adhesion to substrate. It may be unique to cross-linked polymer networks.

It was possible to identify the above because (1) force microscopy is uniquely capable of imaging both structural and mechanical changes, and (2) the deformations were not purely elastic, but rather viscoelastic with relaxation times on the order of minutes, allowing “shapshots” of the affected zone to be acquired seconds to minutes after the deforming event. One expects residual effects in general in viscoelastic materials having relaxation times on the order of experimental times (or longer) and of course if plastic deformation has occurred. We were able to augment topographic images of deformations with more sensitive friction force images because viscoelastic dissipation (friction) was reduced in the deformed film. Apparently, this results from stretching of polymer—colloids. These findings (together with earlier studies) imply that friction is sensitive to molecular conformation.

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(46) In addition to histogram breadth, the uncertainty in the determined values of frictional force arises from the variable image background (variations within a single image and between images).
and thus underscore the notion that a fundamental theory of interfacial friction must address the mechanisms of energy dissipation, not just the parameters of friction (e.g., contact area or interfacial energies). In general, strain-induced modifications of secondary (or perhaps even tertiary) structure may be necessary for deformation-dependent frictional response. This might only occur on materials that organize to form complex structures, i.e., biologically derived materials such as gelatin or materials designed to have such structures.

We have developed “annular histogram analysis” of images to quantify deformation effects precisely. In particular, this allowed us to address the relationship between topographic and frictional data, the dependence of height and friction on distance from the deformation center, the roles of reversible versus irreversible processes in the deformation phenomenon, and spatial variations of the relaxation of the film to its unstressed state. Annular histogram analysis will apply in general to the study of residual perturbative effects (viscoelastic, plastic) having point symmetry, the natural symmetry for the approximate sphere-on-flat geometry of SFM. The method also applies to intrinsic surface features having point symmetry.

In gelatin films the outward deformations do not relax with a single (Debye) relaxation time. This is expected in a semicrystalline, polymeric material that presumably deforms with a distribution of relaxation times. Relaxation further varies with distance from the deformation center, apparently due to stresses beyond the visual deformation perimeter. These stresses cause the deformed region to expand laterally with elapsed time. The ability to quantify time-dependent behavior requires not only a residual signature but also the ability to image it with minimal perturbation.

The lateral range of deformations on gelatin films depends strongly on film age on the scale of days. This is consistent with the understanding that the number and/or size of triple-helical physical cross-links in gelatin increases slowly over a long time scale. We speculate that if the relationship between cross-link concentration and deformation could be quantified, one might conversely use deformation imaging to determine cross-link concentration.

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