Project Title: Surface Mechanical Properties of Bio-Inspired Architectures

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1. Introduction

Many organisms have evolved structures with features that result in remarkable surface mechanical properties such as enhanced, reversible, and tunable adhesion, friction, and contact compliance [1]. Often surface mechanical properties are obtained by manipulation of near-surface architecture, and these rely primarily on non-covalent interactions such as van der Waals, electrostatic, acid-base, and hydrophobic/hydrophilic forces. Combinations difficult to obtain in synthetic materials, such as actively switchable properties and high selectivity, are routinely achieved in nature. Many biomaterials and synthetic biomimetic materials are very “soft” or compliant compared to conventional engineering materials (e.g., metals and ceramics) and consequently phenomena governing their deformation can be quite different. The role of the surface itself in resisting or driving deformation, commonly ignored for conventional stiff materials, plays an important and sometimes dominant role in *all* surface mechanical phenomena for soft materials.

Examples of architectures in nature that determine interesting surface mechanical properties span the length scale from the molecular (shape and charge recognition between folded proteins) to millimeter-scale attachment devices (contacting and attachment surfaces in insects and lizards). One often finds that a very similar architectural motif has evolved across a number of species, using different materials, in response to a given need. Mechanisms have been found for permanent strong adhesion, as in mussels [2, 3], or for strong, but reversible, adhesion suitable for locomotion, as in lizards [4]. Less studied are complementary internal attachment structures such as those that arrest head movement and lock wings in insects and plants that create complementary surfaces to adhere to rough boulders [1]. The idea of building up complex behavior via architecture by using a handful of generic materials properties and non-covalent interactions is particularly relevant to the materials science of bioinspiration and biomimckry because, once motifs and ideas from nature are understood, a similar approach can be followed synthetically. The philosophy of our work has been to design surfaces with controllable surface mechanical properties based on this idea. Structures are designed at the meso-scale (~microns), intermediate between the molecular and macroscopic length scales. In this way one can obtain advantageous coupling between control of properties by surface chemistry and near-surface architecture.

In previous work supported by this grant, we studied surface mechanical properties of a variety of biomimetic surfaces. We demonstrated how highly enhanced and switchable adhesion and static friction can be designed and were able to develop detailed quantitative models for the relationship between geometrical and materials parameters, and properties. The majority of the work in this field, including most of our own early work, has been focused on one-sided materials. More recently, we have focused on two-sided systems, mimicking attachment systems in organisms that use shape complementarity to endow interfaces with highly enhanced and selective adhesion and friction. We discovered the spontaneous appearance of meso-scale dislocations at interfaces between shape-complementary patterned surfaces and studied how their geometry and materials properties govern macroscopic adhesion and friction. Our second major thrust was to study the influence of surface properties, specifically the surface stress, in mechanical phenomenon involving soft materials. We showed that solid surface stress often plays a very significant and pervasive role and this requires a re-thinking of several canonical surface mechanical phenomena such as adhesive contact, wetting, fracture and surface-stress-driven shape change.

2. Background

Enhanced adhesion and selectivity between contact surfaces are highly desirable and have the potential for novel design of high-level functional materials. In nature, biological attachment devices are functional systems for temporary or permanent attachment of an organism to the substrate, to another organism, or temporary interconnection of body parts within an organism. Their design varies enormously in relation to different functional loads [1]. For example, patterns of protuberances of different origin on surfaces play important roles in animals' locomotion, such as in insects, spiders, and lizards [4, 5]. Studies of these structures have shown that the contact mechanical properties (including adhesion and friction) can be modified by near-surface architecture independent of the surface chemistry. Within the last decade, the development of these bio-mimetic and bio-inspired structured surfaces has been pursued actively by many research groups. For the sake of brevity, we do not attempt here to review the subject; it can be found in recent reviews [5, 6].

Although bio-inspired attachment systems have been studied widely, most of the recent work has been on the adhesion and friction of one-sided surface structures against a generic flat surface. There are relatively few studies on the use of surfaces with complementary architectures despite the fact that there are plenty of matched or complementary surfaces in nature. For example, insects use interlocking hard claws to attach to a wide variety of substrates [1, 7]. An interlocking meso-scale structure is responsible for attachments in the dragonfly head-arresting system [8]. At the much smaller length scale of intermolecular associations, it is well-known that two nucleotides on opposite complementary DNA or RNA strands are connected via hydrogen bonds [9] and formation of protein-protein complexes is based on shape complementarity [10]. Selectivity in adhesion can also be achieved by surface chemistry [11, 12]. A celebrated example of achieving adhesion using mechanical complementary is Velcro® which uses a loop-clasp mechanism [13]. Recent studies have shown that complementary structured surfaces have strongly enhanced adhesion [14-16] on *the first separation of an as-molded* shape-complementary interface. The more difficult question is: if shape-complementary patterned substrates are separated and then pressed into contact, will complementary shapes inter-penetrate sufficiently and with high recognition/selectivity? We showed [17] that highly selective adhesion can be achieved between complementary elastic surfaces patterned with ripples after they have been separated and re-pressed together. We also showed that highly selective adhesion, with enhancement of up to a factor of 40 and selectivity of a factor of 160, can be achieved with pillar-channel complementary surfaces [18]. *Misorientation* is accommodated by *line defects* that are essentially twist boundary screw dislocations [19, 20]. These findings connect the science of soft materials to the materials science of crystal dislocations. In particular it raises several intriguing and unanswered questions about whether and how arrays of dislocation line defects on the surface of soft materials can be engineered to control interfacial properties.

The importance of *surface energy* in surface science is well established. However, a closely related but *different* quantity (one is a scalar, the other a *2D* tensor), *surface stress*, is often neglected because its effects are usually felt over a characteristic length scale, the *elastocapillary length*, σ/E, where E is the Young's modulus and σ the magnitude of the surface stress. (For an *isotropic solid surface*, the stress tensor is an isotropic tensor and σ is usually called the *surface tension,* which need not be the same as surface energy of the solid.) For conventional stiff materials (metals and ceramics) its value is generally immeasurably small [21, 22]. However, biomaterials and materials commonly used in biomimetics, such as elastomers like polydimethylsiloxane (PDMS) and hydrogels, are often very "soft" or compliant compared to conventional engineering materials. For example, if we attempt to make a sharp edge in a soft elastic solid, say by molding against a sharp corner in a hard material such as silicon, the radius of curvature to which the sharp edge will relax due to surface stress is on the order of the elastocapillary length [21]. While its value for conventional materials is sub-Angstrom, it is in the tens of *nm* for PDMS and can be tens of microns or larger for hydrogels. Since the importance of surface stress is determined by the ratio of capillary length to the size of a device, small structures are particularly sensitive to it. For these reasons, surface stress can play a significant and sometimes dominant role in *all* surface mechanical phenomena of compliant biomimetic materials and biomaterials.

That the significant role of surface stress requires a re-thinking of all surface mechanical phenomena has sparked many new investigations over the last five years to which our contributions are described in more detail in the next section. Adhesion, locomotion, and proliferation of biological cells depends on surface mechanical properties; cells will propagate from the softer to the stiffer portion of a substrate and exert tractions which results in surface creases. How cells sense the softness of a substrate and use its deformability to generate feedback signals for their intracellular processes is, however, far from understood [23]. Importantly, the role of surface stress of the deformed surface on the response of the cell has generally been ignored but there is new evidence that it can play a significant role in directing cell behavior. The role of surface stresses is much clearer if we look at simpler systems. For example, compliant solid cylinders undergo an instability analogous to the Rayleigh-Plateau instability of a liquid in which surface stress defines the characteristic length scale [24]; surface stress flattens or rounds off solid surfaces by deformation [25-28]. The Hertz and Johnson-Kendall-Roberts theories for adhesion-less and adhesive contact [29], respectively, widely use to interpret indentation data, are no longer applicable and have to be reformulated [30-34]. Jerison et al. [35] showed that solid surface stress influences the elastic substrate deformation due to a contact line. Crosby and co-workers [36] have designed a device to measure mechanical properties of soft tissues by bubble growth under pressure, where both the surface stress and elasticity resist growth. We have recently demonstrated that the contact angle of a liquid drop on a compliant surface is not a material property – it cannot be predicted by Young's equation – but depends on the surface stress of the solid substrate as well as its elasticity [37]. In addition, we have recently shown that the deflection of thin films of relative stiff materials can be substantially affected by surface stress of the film and it is possible to exploit this phenomenon to measure solid surface stress [38, 39].

The intensely investigated role of surface stress addresses only the simplest constitutive behavior that a soft solid surface can have. Compare, for example, the situation in fluids. For simple single-component fluids the dominant surface property is its surface tension. This is analogous to the current understanding of simple soft solids. However, when a strong surfactant adsorbs at the fluid-vapor interface, the complex fluid surface that forms exhibits a full range of rheological behavior [40]. The majority of work reported so far takes the influence of the solid surface to be represented by an isotropic, homogeneous, and strain-independent stress [41]. However, it has long been known that surface stress can be strain dependent [42]. In particular, Gurtin and Ian Murdoch [43] raised the question of whether solid surfaces possess elasticity (surface Lame' constants) in addition to a residual surface stress and this has recently been demonstrated experimentally [44]. Gurtin and Ian Murdoch [43] also raised the possibility that the surface can store energy in bending but this issue has received little attention. This is despite the fact that there exist several systems where this is patently true; we cite two. The first is the lipid bilayer, representative of an interface between two aqueous phases. Thus, if the osmotic pressure across the bilayer is balanced, there is negligible surface stress. Nevertheless, resistance to stretching is high since deformation of the bilayer conserves area and the Hamiltonian of the interface is dominated by bending energy [45, 46]. A second case is where a new phase separates a soft solid from the fluid phase – a well-known example is where a glassy film a few nm thick forms on the surface of an elastomer (e.g., PDMS) exposed to oxygen plasma or UV ozone [47, 48].

3. Report on Work Performed

We focused on two problems:

(a) *What is the geometry of defects between patterned interfaces in soft materials? How are they related to interfacial mechanical properties?* Based on previous discoveries of the spontaneous formation of line defects at the interface between patterned shape-complementary interfaces, we undertook a systematic study of the geometry of these defects and how that affects adhesion and friction.

(b) *What is the role of surface-stress or solid capillarity in soft materials?* We studied by experiment and theory several phenomena in which solid capillarity plays an important and sometimes dominant role in, e.g., shape change due to surface stress, wetting, adhesion, contact mechanics, and fracture.

We made significant progress in and contributions to both these problems as described below.

3.1. Geometry of Line Defects at Shape Complementary Patterned Soft Material Interfaces and Their Effect on Adhesion

3.1.1. Selective Adhesion Enhancement of Ridge/Pillar Shape-Complementary Interfaces

We have investigated biomimetic shape-complementary surfaces. We showed that ridge-channel surfaces (see Fig. 1(a)) can have highly enhanced adhesion (up to a factor of 40) against shape-complementary surfaces. Adhesion enhancement decreases systematically with increasing separation between the ridges. At the same time, adhesion is highly attenuated for non-complementary surfaces [18, 19]. The most interesting discovery was that misorientation is accommodated by meso-scale interfacial screw dislocations. Because the two sides of the elastomer-elastomer interface are patterned by regular arrays of ridges/channels or pillars, when they are brought together the interface behaves like a meso-scale version of an atomistic twist grain boundary. Relative twist and lattice mismatch are accommodated by arrays of dislocations with mixed screw and edge character (e.g., the inclined lines in the optical micrographs in Fig. 1(b). We showed that some aspects of the defect geometry [49] and its energetics [20, 50] can be analyzed by adapting theories developed for crystalline materials. There are some important differences, however. In crystal dislocations, the core is usually invariant and determined by local interatomic bonding energetics. In our case, the dislocation core turns out to be very similar to the Lothe core model in which the Burgers vector is distributed linearly over a finite distance, along with an associated *dilation* in the direction normal to the glide plane. This makes its size susceptible to a crack-like treatment. In particular, the core can be manipulated by external pressure, which manifests strongly in the properties such as friction, as described later. More broadly, our findings connect the subject of structured soft materials to the well-developed materials science of defects in crystals and generates dislocation structures than can be readily examined by optical microscopy (instead of electron microscopy in crystalline solids).

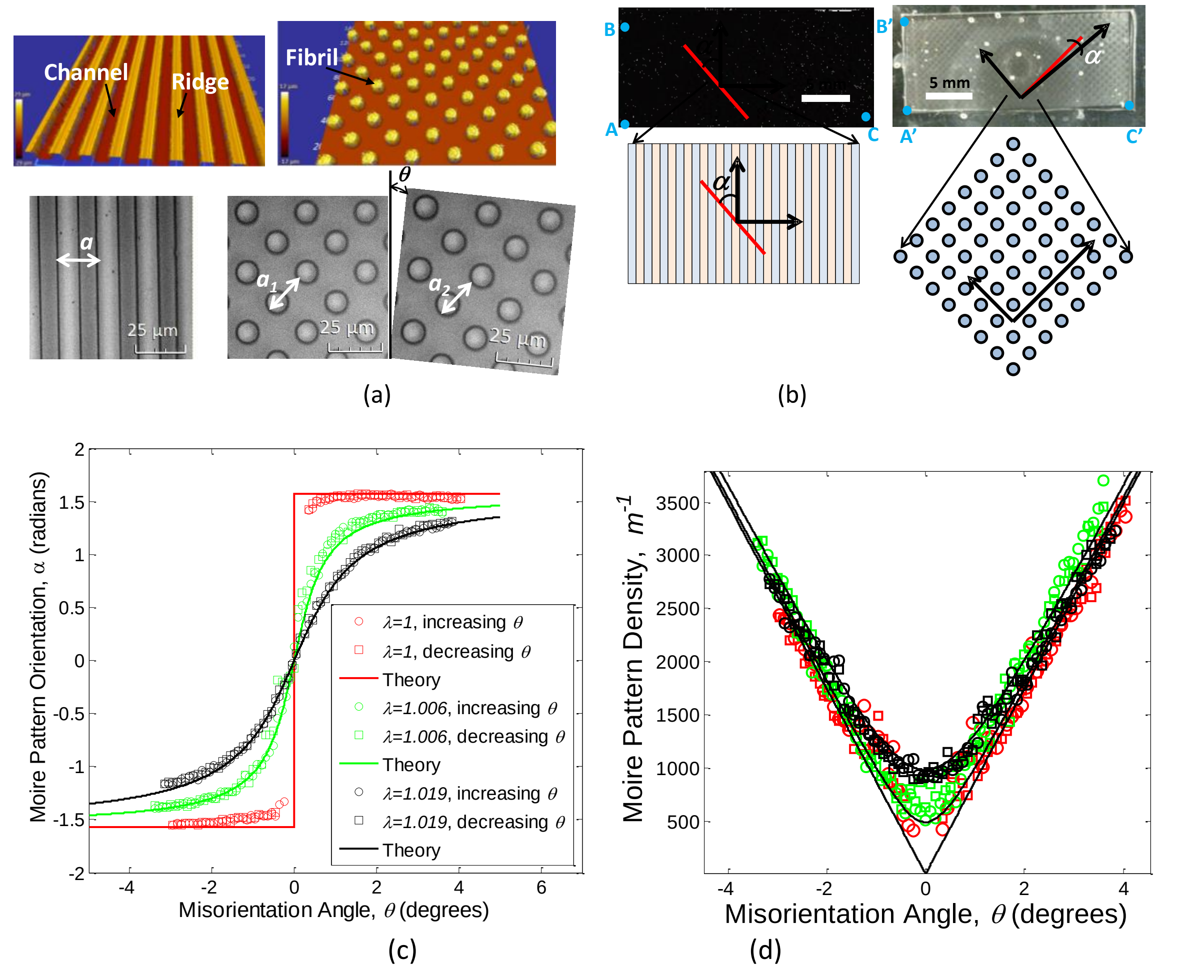
3.1.2. Dislocation arrays at the interface with mixed screw and edge character control adhesion [51]:

We found that relative misorientation is accommodated by interfacial defects that are meso-scale screw dislocations. The arrangement of such dislocations plays a critical role in determining the mechanical properties of the interface. Here we studied the geometric properties of one-dimensional (ridge/channel) and two-dimensional (arrays of pillars) shape-complementary interfaces (Fig. 1(a)) in the presence of both relative misorientation (twist, θ) and difference in lattice spacing (stretch, λ). Relative misorientation without difference in lattice spacing is accommodated by arrays of screw dislocations. Difference in lattice spacing without misorientation is accommodated by arrays of edge dislocations. In general, we observe arrays of dislocations with mixed screw and edge character. The spacing, $1/\rho$, and orientation, α, of these arrays can be predicted accurately using the geometry of Moiré patterns (eqs. 1,2; Fig. 1c,d). (The orientation α is directly related to mixity – edge vs. screw character.) Dislocations carry elastic energy that is released when the interface is opened, thus reducing the effective adhesion energy W_{eff} of the interface. Fig. 1e shows that our analytical model based on this idea (eq. 3) is a good predictor of measured reduction in adhesion with increasing misorientation. In equations (1-3), a is the fibril spacing, W_{ad} is the work of adhesion between two flat surfaces, G is the shear modulus of the material, and β is the factor by which adhesion is enhanced by shape complementarity for a perfectly aligned sample.

$$\alpha = \tan^{-1}\left[\frac{\sin\theta}{\lambda - \cos\theta}\right] \tag{1}$$

$$\rho = \frac{1}{a}\sqrt{1+\lambda^2 - 2\lambda\cos\theta} \tag{2}$$

$$\frac{W_{eff}}{W_{ad}} = \beta\left(1 - \frac{Ga\theta}{4\pi\alpha W_{ad}}\left[\frac{5}{2} - \ln\left(\frac{Ga\theta}{4\pi\alpha W_{ad}}\right)\right]\right) \tag{3}$$



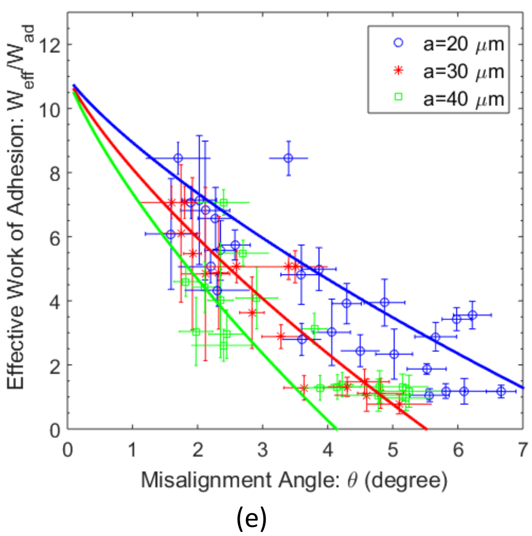


Figure 1. (a) Optical micrographs of ridge/channel and fibrillar samples. Each sample consists of a *pair* of PDMS layers with some difference in lattice parameter and relative twist θ. (b) Typical patterns of approximately parallel lines appears at the interface between two nominally complementary samples (c) Angle of dislocation arrays in the ridge/channel geometry (Moiré patterns). (d) Density of dislocations ρ as a function of misorientation angle. In (c) and (d) the lines are theoretical predictions with no fitting parameters. We have similar agreement between theory and experiment for the pillar-pillar interface. (e) Theoretical prediction for reduction in adhesion with increasing misorientation.

3.1.3. Gel-based material for reversible adhesion to arbitrarily shaped surface by shape recognition. (In collaboration with Prof. Shu Yang's group, University of Pennsylvania.) The shape-complementary strategy we have mainly pursued requires complementary shapes be formed on both sides of the interface being adhered. With the group of Shu Yang we have investigated a gel-based material that extracts the benefit of shape complementarity by adapting to the shape of its counter surface over a large range of length scales when in the soft, hydrated state. This shape can then be locked-in with little residual stress by drying, resulting in very strong adhesion. Moreover, this adhesion can easily be *reversed* by re-hydrating the gel. (A manuscript based on this work is under review.)

3.2. Role of Surface Stress or Solid Capillarity in Soft Materials

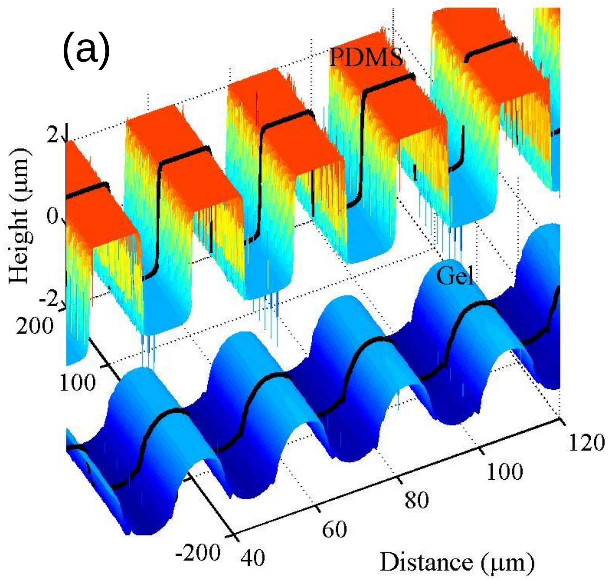
We have studied several aspects of this problem, as also described in the Introduction and Background. Here we first describe our work on flattening of surface features by surface stress and problems related to wetting on compliant substrates.

3.2.1. Flattening of Surface Features on a Compliant Material by Surface Stress.

Nearly all works on creating biomimetic structures for enhanced and controlled surface mechanical properties rely on creating structured surfaces. In many cases, this is accomplished by some form of molding technique. We have shown how, by exerting forces that flatten and round-off surfaces, solid surface stress limits our ability to replicate master shapes by molding [26]. To analyze such deformations, we have developed both analytical models and computational techniques (special surface stress finite elements) [26, 52]. Fig. 2a shows measured 3D profiles of a PDMS master (the higher and sharper features) and a gel (Gelatin in a 70/30 glycerol/water mixture) replica (flattened and rounded features). The gel is much more compliant than the PDMS (Young's modulus of 32.5 kPa versus ~3 MPa, respectively) and its profile is flattened and rounded immediately upon removal of the replica from its mold. We modeled the shape change as being due to elastic deformation driven by an *isotropic* solid surface stress, which can be brought into excellent agreement with experimental profiles using a single fitting parameter, the solid surface stress [25, 26] (Fig. 2). Thus, this experimental set up can also serve as a technique to measure solid surface stress. This work is related to Mullins's classic problem of shape change due to capillarity [53], except that it applies to elastic deformation of solids. In collaboration with the group of Shu Yang at the University of Pennsylvania, we have studied how UV Ozone treated PDMS surfaces carry not only a surface stress but also considerable surface extensional and bending elasticity (manuscript under review). We have also analyzed a similar problem of the recovery of the surface of a viscoelastic material after being subjected to a localized force [54]. Such recovery is observed in solid ridge form ahead of a moving liquid drop on a soft substrate [55].

3.2.2. Wetting of a Compliant Substrate and Spontaneous Droplet Motion on a Periodic Compliant Substrate

The mechanics and physics of wetting of a solid surface is a fundamental problem of broad importance and interest that has been studied nearly exclusively for stiff (nearly rigid) surfaces. The shape of a drop controls a variety of phenomena such as heat transfer, drop penetration versus removal (from clothing or from paper as in printing), moisture collection through condensation, etc. The classic prediction of droplet shape is based on Young's equation [56, 57]. Static wetting of highly compliant substrates, i.e., with increasing elastocapillary number (ratio of surface stress to the product of Young's modulus and droplet size), differs in important ways due to coupling of surface stress and deformability of substrate [35, 37, 38, 58, 59], a subject to which we have previously made contributions. In addition, new aspects of wetting dynamics including droplet motion are emerging [60, 61].



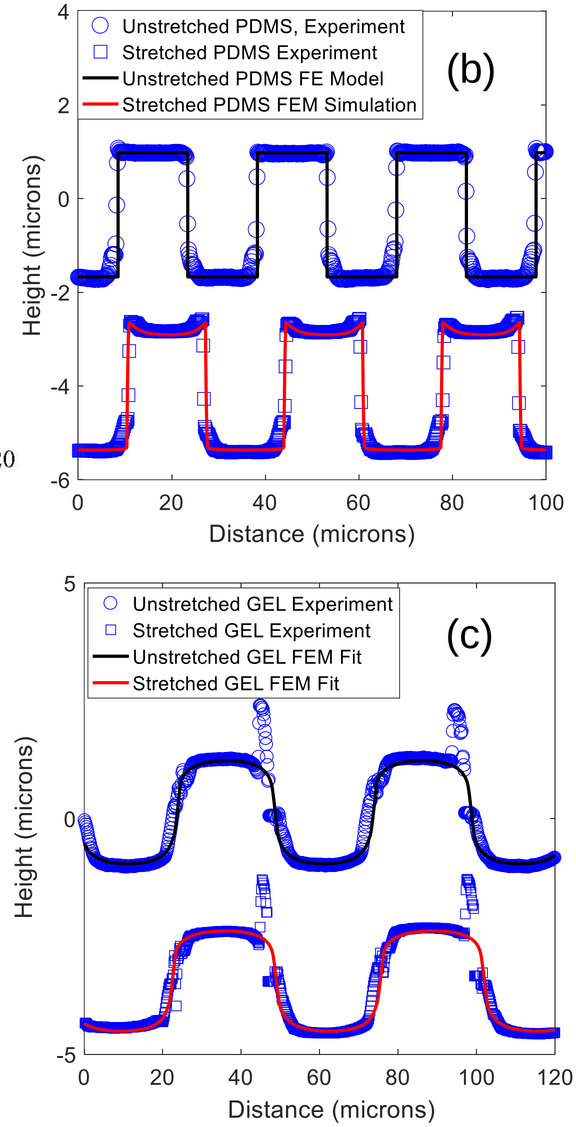


Figure 2. (a) Surface profile of a periodic ridge geometry showing PDMS master (higher and sharper features) and its gel replica (flattened and rounded profile) for gel Young's modulus E = 32.5 kPa, wavelength W ~ 25 µm and initial height h ~ 2.7 µm. (b,c) Profile shape and its change on stretching can be fitted very well by a theoretical finite elment model that includes special elements to account for the influence of the surface-stress. (b) Finite element results capture the change in change on stretching the master mold. (c) Finite element results are in very good agreement with experimental data of the deformed gel profile, stretched and unstretched.

Droplet motion arises in many natural phenomena, ranging from the familiar gravity-driven slip and arrest of raindrops on windows, to the directed transport of droplets for water harvesting by plants and animals under dry conditions. Deliberate transportation and manipulation of droplets is important in many technological applications, such as droplet-based microfluidic chemical reactors and for thermal management. Droplet motion usually requires gradients of surface energy or temperature, or external vibration to overcome contact angle hysteresis. We have discovered a new phenomenon in which a drying droplet placed on a periodically compliant surface (Fig. 3) undergoes spontaneous, erratic motion in the absence of surface energy gradients and external stimuli (Fig. 3a-e). By modeling the droplet as a mass-spring system on a substrate with periodically varying compliance, we show that the energy released during vaporization is partially stored by the compliant surface. It is released periodically via mechanical instabilities to drive the surprisingly large-scale spontaneous and concerted motion of the drop. Our finding offers a novel method by which the droplet motion can be driven [62].

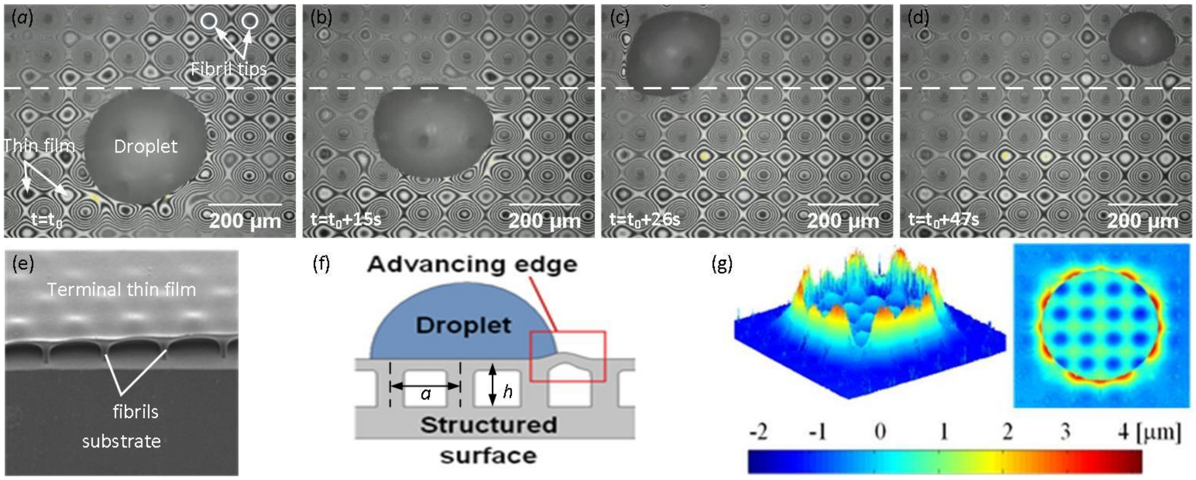


Figure 3 Droplet on a film-terminated fibrillar surface. (a-d) Beginning at $t = t_0$, micrographs of a droplet of de-ionized water placed atop a film-terminated fibrillar surface show (i) significant distortion of interferometric contours, indicating out-of-plane deformation driven by liquid surface tension, and (ii) spontaneous movement of the droplet. In this series of optical micrographs, the droplet moves over a distance much *larger* than its own size and the interfibrillar distance. (e) Scanning electron micrograph image of the film-terminated fibrillar surface. The fibril height is 40 μm, the interfibrillar spacing is 115 μm, and the diameter of the fibrils is 10 μm. (f) A schematic showing a droplet on the structured surface, and the deformation caused by droplet surface tension. The experiments are repeated on samples with height *h* varied from 10 – 40 μm and interfibrillar spacing *a* varied from 20 – 110 μm. (g) Contours and 3D representation of the vertical displacement of the substrate caused by surface tension of the drop.

3.2.3. Interaction of Droplets Separated by an Elastic Film We previously discovered that the Laplace pressure of a droplet placed on one side of an elastic thin film can cause significant deformation in the form of a bulge on its opposite side (Fig.4a) [38]. We show that this deformation can be detected by other droplets suspended on the opposite side of the film, leading to interaction between droplets separated by the solid (but deformable) film (Fig. 4b,c). The interaction is repulsive when the drops have a large overlap and attractive when they have a small overlap. Thus, if two identical droplets are placed right on top of each other (one on either side of the thin film) they tend to repel each other (Fig. 4b), eventually reaching an equilibrium configuration where there is a small overlap (Fig. 4c). This observation has been explained by analyzing the energy landscape of the droplets interacting via an *elastically* deformed film. The system energy here includes the surface energy, the work done by surface stresses (due to stretching of the film) as well as the elastic energy of the deformed film. We further demonstrate this idea by designing a pattern comprising a big central drop with satellite droplets [63]. This is a second novel phenomenon related to wetting of compliant surfaces and can lead to techniques for directed motion of droplets confined to one side of a thin elastic membrane by manipulations on the other side.

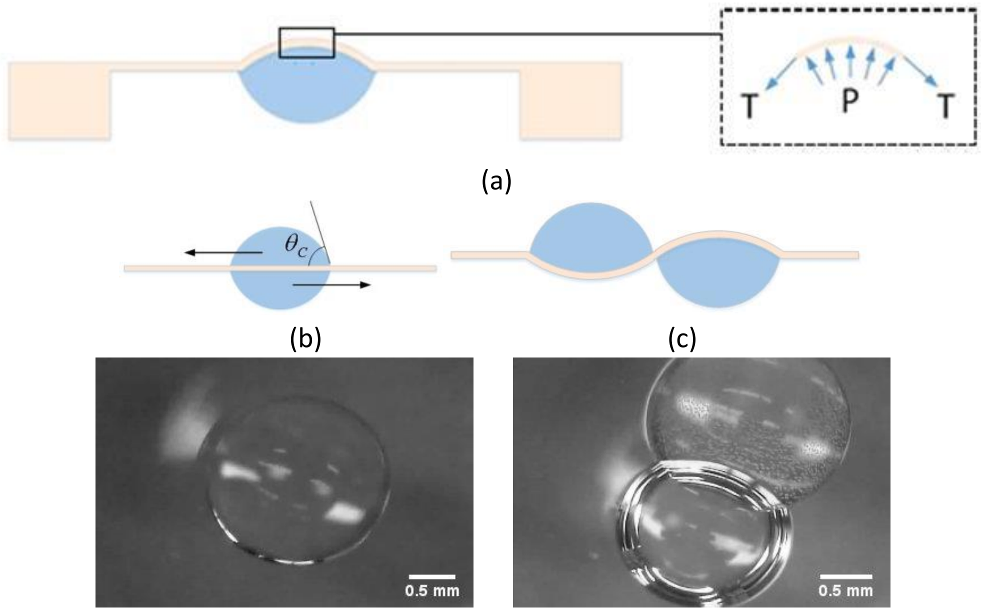


Figure 4. Process of repulsion between two droplets on either side of a suspended film. (a) Using an air displacement pipette, a water droplet was placed underneath the film, and the film bulged out due to the Laplace pressure *P* (see insert). (b) Another droplet of same volume was placed on the top side of the film, overlapping the bottom droplet. (c) The configuration in (b) was unstable and the two droplets separated. (d) Snapshot of the initial (unstable) overlapped configuration (top view). (e) Snapshot of the stable configuration with a small overlap (top view).

3.2.4. Other related studies

o *Role of surface stress in cell fate and proliferation.* It has long been known that the modulus of extracellular matrix (ECM) regulates cell fate and morphogenesis [64]. Cells physically probe the modulus of the ECM using integrin based adhesion complexes. On stiffer substrates, integrin receptors assemble into larger multi-molecular complexes that trigger activation of regulatory signaling cascades. In biomaterials design, tuning integrin-based mechanotransduction is critical for programming desired cellular responses. However, cell behaviors that defy expectations based on ECM rigidity alone have been observed. For example, cells seemingly misinterpret silicone substrates as being rigid, even when the material is highly compliant. While some reports argue that this anomalous behavior can be attributed to how adhesive proteins are tethered to the silicone substrate, others affirm that ECM stiffness regulates cellular behaviors independently of protein tethering. We believe that this paradox can be resolved if surface stress is taken into consideration, since that offers a hitherto ignored agent that resists the deformation of these materials by micrometer-sized cells and their subcellular machinery. The co-PI, C.Y. Hui, has recently collaborated with Matthew Paszek's group at Cornell to study whether indeed surface stresses can direct cell behavior. In a paper currently under revision [65], we report that cells indeed sense solid surface stress through integrins and canonical mechano-transduction pathways. For soft materials with high surface energies, we find that surface stresses can dominate over the elastic modulus in directing cell response. Strikingly, even when the elastic modulus of the material is vanishingly small, surface tension can support cell spreading, the assembly of stable focal adhesions, force-dependent integrin signaling, YAP/TAZ-based mechanotransduction, cell survival, and cell proliferation.

- *Analyzing the Role of Surface Stresses in the Context of Large Deformation.* We and others have established that the role of surfaces stresses becomes important when the material becomes highly compliant, i.e., when the elastocapillary length is on the order of one. However, deformations in this regime tend to be large, a fact that causes significant difficulty in analysis of associated phenomena. We have tackled this problem (we believe we are the only group to do so) for a number of cases:
- How surfaces deform and adhere when brought into contact with a rigid indenter is an important problem in micro or nanoindentation. In soft materials, surface stresses can play an significant role in resisting deformation, and we have been developing models to account for large deformation and surface stress [66].
- Large strain plate bending with surface stress. We have studied pure bending of a finite thickness plate under large deformation with surface stress. We present closed-form solutions and discover a new type of instability [67].
- Full governing equations for droplets on a deformable surface. In the rigid limit the shape of drops on a surface is given by Young's equation representing configurational energy balance. In the highly compliant fluid-like limit, the shape is given by force balance, the so-called Neumann's Triangle. We have now developed a full theory for the shape of droplets on deformable surfaces that accounts for all the surface stresses and large deformation (manuscript under preparation).
- *Wetting of a Partially Immersed Compliant Rod [68]*. The force on a solid rod partially immersed in a liquid is commonly used to determine the liquid-vapor surface tension by equating the measured force required to remove the rod from the liquid to the vertical component of the liquid-vapor surface tension. Here we have studied how this process is affected when the rod is compliant. Our results can be used to extract solid surface stresses from such experiments.
- *Surface tension measurement from indentation of clamped thin films*: We developed an indentation technique to measure the surface tension of relatively stiff solids. In the proposed method, a thin solid film is indented by a rigid sphere and its deflection is measured by optical interferometry. The film deflection is jointly resisted by surface tension, elasticity and residual stress. Using a version of nonlinear von Karman plate theory that includes surface tension, we are able to separate the contribution of elasticity to the total tension in the film. Surface tension is determined by extrapolating the sum of surface tension and residual stress to zero film thickness. We measured surface tension of polydimethylsiloxane (PDMS) using this technique and obtained a value consistent with the surface energy of PDMS reported in the literature [39].
- *Review Article: "Elastocapillarity: Surface tension and the mechanics of soft solids"* [41]: We co-authored a review article on elastocapillarity that aims to summarize the state of the field and to identify open issues.
- *Surface stresses resist fracture in soft solids*: We show theoretically that surface stresses can lower the energy release rate available for crack growth in soft materials [69]. Physically, surface stresses induce curvature forces which resist crack opening, and this reduces the stress field at the crack tip due to external applied load.

References Cited

1. Scherge, M. and S.N. Gorb, *Biological Micro-And Nanotribology: Nature's Solutions*. 2001: Springer.
2. Lin, Q., D. Gourdon, C. Sun, N. Holten-Andersen, T.H. Anderson, J.H. Waite, and J.N. Israelachvili, *Adhesion mechanisms of the mussel foot proteins mfp-1 and mfp-3.* Proceedings of the National Academy of Sciences, 2007. **104**(10): p. 3782-3786.
3. Lee, H., B.P. Lee, and P.B. Messersmith, *A reversible wet/dry adhesive inspired by mussels and geckos* Nature, 2007. **448**(7151): p. 338-U4.
4. Autumn, K., Y.A. Liang, S.T. Hsieh, W. Zesch, W.P. Chan, T.W. Kenny, and R. Fearing, *Adhesive force of a single gecko foot-hair.* Nature, 2000. **405**(8): p. 681–684.
5. Jagota, A. and C.-Y. Hui, *Adhesion, friction, and compliance of bio-mimetic and bio-inspired structured interfaces.* Materials Science and Engineering Reports, 2011. **72**: p. 253-292.
6. Heepe, L. and S.N. Gorb, *Biologically inspired mushroom-shaped adhesive microstructures.* Annual Review of Materials Research, 2014. **44**: p. 173-203.
7. Dai, Z., S.N. Gorb, and U. Schwarz, *Roughness-dependent friction force of the tarsal claw system in the beetle Pachnoda marginata (Coleoptera, Scarabaeidae).* Journal of Experimental Biology, 2002. **205**(16): p. 2479-2488.
8. Gorb, S.N., *Evolution of the dragonfly head-arresting system.* Proceedings of the Royal Society of London. Series B: Biological Sciences, 1999. **266**(1418): p. 525-535.
9. Bruce Alberts, A.J., Julian Lewis, Martin Raff, Keith Roberts, Peter Walter, *Molecular Biology of the Cell, Fourth Edition*. 2002, New York: Garland Science (Taylor & Francis Group).
10. Branden, C. and J. Tooze, *Introduction to protein structure*. Vol. 2. 1991: Garland New York.
11. Koberstein, J.T., *Molecular design of functional polymer surfaces.* Journal of Polymer Science Part B: Polymer Physics, 2004. **42**(16): p. 2942-2956.
12. Kokkoli, E. and C.F. Zukoski, *Surface pattern recognition by a colloidal particle.* Langmuir, 2001. **17**(2): p. 369-376.
13. de Mestral, G., *Adhesive Element in Cloth Form*, in *www.uspto.gov*, USPTO, Editor. 1973, Velcro S.A. (Soulie, Nyon, CH): USA.
14. Lamblet, M., E. Verneuil, T. Vilmin, A. Buguin, P. Silberzan, and L. Léger, *Adhesion enhancement through micropatterning at polydimethylsiloxane-acrylic adhesive interfaces.* Langmuir, 2007. **23**(13): p. 6966-6974.
15. Shahsavan, H. and B. Zhao, *Conformal adhesion enhancement on biomimetic microstructured surfaces.* Langmuir, 2011. **27**(12): p. 7732-7742.
16. Paretkar, D., P. Malhotra, C.-Y. Hui, and A. Jagota, *ADHESION ENHANCEMENT OF A GEL-ELASTOMER INTERFACE BY SHAPE COMPLEMENTARITY*, in *Bio-inspired structured adhesives: biological prototypes, fabrication, adhesive properties, frictional behaviour, and contact mechanics*, L. Xue, L. Heepe, and S. Gorb, Editors. 2015, Springer Thematic Series NanoScience and Technology: Heidelberg.
17. Vajpayee, S., K. Khare, S. Yang, C.-Y. Hui, and A. Jagota, *Adhesion Selectivity Using Rippled Surfaces.* Advanced Functional Materials, 2011. **21**: p. 547-555.
18. Singh, A.K., Y. Bai, N. Nadermann, A. Jagota, and C.-Y. Hui, *Adhesion of Micro-channel Based Complementary Surfaces.* Langmuir, 2012. **28**(9): p. 4313-4222.
19. Jin, C., A. Jagota, and C.Y. Hui, *Structure and Energetics of Dislocations at Micro-Structured Complementary Interfaces Govern Adhesion.* Advanced Functional Materials, 2013.
20. Sutton, A.P. and R.W. Balluffi, *Interfaces in crystalline materials.* 1995.

21. Hui, C.-Y., A. Jagota, Y.Y. Lin, and E.J. Kramer, *Constraints on Micro-Contact Printing Imposed by Stamp Deformation", .* Langmuir, 2002. **18**: p. 1394-1404.
22. Gibbs, J.W., *Collected Works **1** p315*. 1876, London: Longman and Green.
23. Burton, K. and D.L. Taylor, *Traction forces of cytokinesis measured with optically modified elastic substrata.* Nature, 1997. **385**: p. 450-454.
24. Mora, S., T. Phou, J.-M. Fromental, L.M. Pismen, and Y. Pomeau, *Capillarity Driven Instability of a Soft Solid.* Physical Review Letters, 2010. **105** p. 214301.
25. Jagota, A., D. Paretkar, and A. Ghatak, *Surface-tension-induced flattening of a nearly plane elastic solid.* Physical Review E, 2012. **85**: p. 051602.
26. Paretkar, D., X. Xu, C.-Y. Hui, and A. Jagota, *Flattening of a patterned compliant solid by surface stress.* Soft Matter, 2014. **10**(23): p. 4084-4090.
27. Mora, S., C. Maurini, T. Phou, J.-M. Fromental, B. Audoly, and Y. Pomeau, *Solid drops: Large capillary deformations of immersed elastic rods.* Physical Review Letters, 2013. **111**(11): p. 114301.
28. Marchand, A., S. Das, J.H. Snoeijer, and B. Andreotti, *Capillary pressure and contact line force on a soft solid.* Physical Review Letters, 2012. **108**(9): p. 094301.
29. Johnson, K.L., *Contact Mechanics*. 1985, Cambridge: Cambridge University Press.
30. Style, R.W., C. Hyland, R. Boltyanskiy, J.S. Wettlaufer, and E.R. Dufresne, *Surface tension and contact with soft elastic solids.* Nature communications, 2013. **4**.
31. Hui, C.-Y., T. Liu, T. Salez, E. Raphael, and A. Jagota, *Indentation of a rigid sphere into an elastic substrate with surface tension and adhesion.* Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences, 2015. **471**: p. 20140727.
32. Xu, X., A. Jagota, and C.-Y. Hui, *Effects of surface tension on the adhesive contact of a rigid sphere to a compliant substrate.* Soft Matter, 2014. **10**(26): p. 4625-4632.
33. Salez, T., M. Benzaquen, and É. Raphaël, *From adhesion to wetting of a soft particle.* Soft Matter, 2013. **9**(45): p. 10699-10704.
34. Carrillo, J.-M.Y. and A.V. Dobrynin, *Contact mechanics of nanoparticles.* Langmuir, 2012. **28**(29): p. 10881-10890.
35. Jerison, E.R., Y. Xu, L.A. Wilen, and E.R. Dufresne, *Deformation of an Elastic Substrate by a Three-Phase Contact Line.* Physical Review Letters, 2011. **106**(18): p. 186103.
36. Jessica A. Zimberlin, N.S.-D., Gregory N. Tew, Alfred J. Crosby, *Cavitation rheology for soft materials.* Soft Matter, 2007. **3**: p. 763-767.
37. Hui, C.-Y. and A. Jagota, *Planar equilibrium shapes of a liquid drop on a membrane.* Soft Matter, 2015.
38. Nadermann, N., C.-Y. Hui, and A. Jagota, *Solid surface tension measured by a liquid drop under a solid film.* Proceedings of the National Academy of Sciences, 2013. **110**(26): p. 10541-10545.
39. Xu, X., A. Jagota, D. Paretkar, and C.-Y. Hui, *Surface tension measurement from the indentation of clamped thin films.* Soft matter, 2016. **12**(23): p. 5121-5126.
40. Fuller, G.G. and J. Vermant, *Complex fluid-fluid interfaces: rheology and structure.* Annual review of chemical and biomolecular engineering, 2012. **3**: p. 519-543.
41. Style, R.W., A. Jagota, C.-Y. Hui, and E.R. Dufresne, *Elastocapillarity: Surface tension and the mechanics of soft solids.* Annual Review of Condensed Matter Physics, 2017. **8**: p. 99-118.
42. Shuttleworth, R., *The Surface Tension of Solids.* Proceedings of the Physical Society. A, 1950. **63**(5): p. 444.
43. Gurtin, M.E. and A.I. Murdoch, *Surface Stress in Solids.* International Journal of Solids and Structures, 1978. **14**: p. 431-440.

44. Xu, Q., K.E. Jensen, R. Boltyanskiy, R.e. Sarfati, R.W. Style, and E.R. Dufresne, *Direct Measurement of Strain-dependent Solid Surface Stress.* arXiv preprint arXiv:1702.00684, 2017.
45. Helfrich, W., *Elastic properties of lipid bilayers: theory and possible experiments.* Zeitschrift für Naturforschung C, 1973. **28**(11-12): p. 693-703.
46. Jenkins, J., *Static equilibrium configurations of a model red blood cell.* Journal of mathematical biology, 1977. **4**(2): p. 149-169.
47. Stafford, C.M., C. Harrison, K.L. Beers, A. Karim, E.J. Amis, M.R. VanLandingham, H.-C. Kim, W. Volksen, R.D. Miller, and E.E. Simonyi, *A buckling-based metrology for measuring the elastic moduli of polymeric thin films.* Nature materials, 2004. **3**(8): p. 545-550.
48. Lin, P.-C., S. Vajpayee, A. Jagota, C.-Y. Hui, and S. Yang, *Mechanically tunable dry adhesive from wrinkled elastomers.* Soft Matter, 2008. **4**(9): p. 1830-1835.
49. Bollmann, W., *Crystal Defects and Crystalline Interfaces*. 1970, New York: Springer-Verlag.
50. Read, W. and W. Shockley, *Dislocation models of crystal grain boundaries.* Physical Review, 1950. **78**(3): p. 275.
51. Dillen, J., Z. He, C.-Y. Hui, and A. Jagota, *Geometry of defects at shape-complementary soft interfaces.* Extreme Mechanics Letters, 2016. **9**: p. 74-83.
52. Xu, X., A. Jagota, S. Peng, D. Luo, M. Wu, and C.-Y. Hui, *Gravity and surface tension effects on the shape change of soft materials.* Langmuir, 2013. **29**(27): p. 8665-8674.
53. Mullins, W.W., *Flattening of a Nearly Plane Solid Surface due to Capillarity.* Journal of Applied Physics, 1959. **30**(1): p. 77-83.
54. Hui, C.Y. and A. Jagota, *Effect of surface tension on the relaxation of a viscoelastic half-space perturbed by a point load.* Journal of Polymer Science Part B: Polymer Physics, 2015.
55. Kajiya, T., P. Brunet, L. Royon, A. Daerr, M. Receveur, and L. Limat, *A liquid contact line receding on a soft gel surface: dip-coating geometry investigation.* Soft Matter, 2014. **10**(44): p. 8888-8895.
56. Young, T., *An Essay on the Cohesion of Fluids.* Philosophical Transactions of the Royal Society of London, 1805. **95**: p. 65-87.
57. deGennes, P.-G., F. Brochard-Wyart, and D. Quere, *Capillarity and Wetting Phenomena. Drops, Bubbles, Pearls, Waves*. 2002, New York: Springer Science+Business Media, Inc.
58. Hui, C.-Y. and A. Jagota, *Deformation Near a Liquid Contact LIne on an Elastic Substrate.* Proceedings of the Royal Society A: Mathematical, Physical and Engineering Science, 2014. **470**: p. 20140085.
59. Style, R.W. and E.R. Dufresne, *Static wetting on deformable substrates, from liquids to soft solids.* Soft Matter, 2012. **8**(27): p. 7177-7184.
60. Karpitschka, S., A. Pandey, L.A. Lubbers, J.H. Weijs, L. Botto, S. Das, B. Andreotti, and J.H. Snoeijer, *Liquid drops attract or repel by the inverted Cheerios effect.* Proceedings of the National Academy of Sciences, 2016. **113**(27): p. 7403-7407.
61. Jagota, A., *Role reversal: Liquid "Cheerios" on a solid sense each other.* Proceedings of the National Academy of Sciences, 2016. **113**(27): p. 7294-7295.
62. Liu, T., N. Nadermann, Z. He, S.H. Strogatz, C.-Y. Hui, and A. Jagota, *Spontaneous Droplet Motion on a Periodic Compliant Substrate.* Langmuir, 2017. **33**(20): p. 4942-4947.
63. Liu, T., X. Xu, N.K. Nadermann, Z. He, A. Jagota, and C.-Y. Hui, *Interaction of Droplets Separated by an Elastic Film.* Langmuir, 2016. **33**(1): p. 75-81.
64. Engler, A.J., S. Sen, H.L. Sweeney, and D.E. Discher, *Matrix elasticity directs stem cell lineage specification.* Cell, 2006. **126**(4): p. 677-689.

65. Cheng, Z., C.R. Shurer, V.K. Gupta, G. Chuang, C.-Y. Hui, and M.J. Paszek, *Solid Surface Stresses Direct Cellular Behaviors Through Integrin-Based Mechanotransduction.* Nature Materials, 2017(under revision).
66. Liu, T., A. Jagota, and C.-Y. Hui, *Effect of surface tension on the adhesion between a rigid flat punch and a semi-infinite neo-Hookean half-space.* Extreme Mechanics Letters, 2016. **9**: p. 310-316.
67. Liu, T., A. Jagota, and C.-Y. Hui, *A closed form large deformation solution of plate bending with surface effects.* Soft Matter, 2017. **13**(2): p. 386-393.
68. Hui, C.-Y. and A. Jagota, *Wetting of a partially immersed compliant rod.* Journal of Applied Physics, 2016. **120**(19): p. 195301.
69. Hui, C.-Y., T. Liu, and M.-E. Schwaab, *How does surface tension affect energy release rate of cracks loaded in Mode I?* Extreme Mechanics Letters, 2016. **6**: p. 31-36.