

# Wetting and phase separation in soft adhesion

Katharine E. Jensen<sup>a</sup>, Raphael Sarfati<sup>a</sup>, Robert W. Style<sup>b</sup>, Rostislav Boltyanskiy<sup>a</sup>, Aditi Chakrabarti<sup>c</sup>, Manoj K. Chaudhury<sup>c</sup>, and Eric R. Dufresne<sup>a,1</sup>

<sup>a</sup>Department of Mechanical Engineering and Materials Science, Yale University, New Haven, CT 06511; <sup>b</sup>Mathematical Institute, University of Oxford, Oxford, OX1 3LB, United Kingdom; and <sup>c</sup>Department of Chemical Engineering, Lehigh University, Bethlehem, PA 18015

Edited by Joanna Aizenberg, Harvard University, Cambridge, MA, and accepted by the Editorial Board October 13, 2015 (received for review July 22, 2015)

In the classic theory of solid adhesion, surface energy drives deformation to increase contact area whereas bulk elasticity opposes it. Recently, solid surface stress has been shown also to play an important role in opposing deformation of soft materials. This suggests that the contact line in soft adhesion should mimic that of a liquid droplet, with a contact angle determined by surface tensions. Consistent with this hypothesis, we observe a contact angle of a soft silicone substrate on rigid silica spheres that depends on the surface functionalization but not the sphere size. However, to satisfy this wetting condition without a divergent elastic stress, the gel phase separates from its solvent near the contact line. This creates a four-phase contact zone with two additional contact lines hidden below the surface of the substrate. Whereas the geometries of these contact lines are independent of the size of the sphere, the volume of the phase-separated region is not, but rather depends on the indentation volume. These results indicate that theories of adhesion of soft gels need to account for both the compressibility of the gel network and a nonzero surface stress between the gel and its solvent.

wetting | adhesion | soft matter | surface tension | phase separation

**S**olid surfaces stick together to minimize their total surface energy. However, if the surfaces are not flat, they must conform to one another to make adhesive contact. Whether or not this contact can be made, and how effectively it can be made, are crucial questions in the study and development of solid adhesive materials (1, 2). These questions have wide-ranging technological consequence. With applications ranging from construction to medicine, and large-scale manufacturing to everyday sticky stuff, adhesive materials are ubiquitous in daily life. However, much remains unknown about the mechanics of solid adhesion, especially when the solids are very compliant (3–5). This limits our understanding and development of anything that relies on the mechanics of soft contact, including pressure-sensitive adhesives (6, 7), rubber friction (8), materials for soft robotics (9–12), and the mechanical characterization of soft materials, including living cells (13–17).

Adhesion is favorable whenever the adhesion energy,  $W = \gamma_1 + \gamma_2$  $\gamma_2 - \gamma_{12}$ , is positive, where  $\gamma_1$  and  $\gamma_2$  are the surface energies of the free surfaces and  $\gamma_{12}$  is the interfacial energy in contact. When W > 0, the solids are driven to deform spontaneously to increase their area of contact, but at the cost of incurring elastic strain. The foundational and widely applied Johnson-Kendall-Roberts (JKR) theory of contact mechanics (18, 19) was the first to describe this competition between adhesion and elasticity. However, it was recently shown that the JKR theory does not accurately describe adhesive contact with soft materials because it does not account for an additional penalty against deformation due to solid surface stress,  $\Upsilon$  (4). Unlike a fluid, the surface stress of a solid is not always equal to its surface energy,  $\gamma$ . For solids,  $\gamma$  is the work required to create additional surface area by cleaving, whereas  $\Upsilon$  is the work needed to create additional surface area by stretching (20). In general, surface stresses overwhelm elastic response when the characteristic length scale of deformation is less than an elastocapillary length, L, given by the ratio of the surface stress to Young's modulus, L = Y/E (21–25). This has an important implication for soft adhesion (4, 26-30): the geometry of the contact line between a rigid indenter and a soft substrate should be determined by a balance of surface stresses and surface energies, just as the Young–Dupré relation sets the contact angle of a fluid on a rigid solid (31). However, the structure of the contact zone in soft adhesion has not been examined experimentally.

In this article, we directly image the contact zone of rigid spheres adhered to compliant gels. Consistent with the dominance of surface stresses over bulk elastic stresses, we find that the surface of the soft substrate meets each sphere with a constant contact angle that depends on the sphere's surface functionalization but not its size. To satisfy this wetting condition while avoiding a divergent elastic stress, the gel and its solvent phase separate near the contact line. The resulting four-phase contact zone includes two additional contact lines hidden below the liquid surface. The geometries of all three contact lines are independent of the size of the sphere and depend on the relevant surface energies and surface stresses. Surprisingly, these results demonstrate a finite surface stress between the gel and its solvent. The volume of the phase-separated contact zone depends on the indentation volume and the compressibility of the gel's elastic network.

#### Structure of the Adhesive Contact Line

We study the contact between rigid glass spheres and compliant silicone gels. Glass spheres ranging in radius from 7 to 32  $\mu$ m (Polysciences, 07668) are used as received or surface functionalized with 1H,1H,2H,2H-Perfluorooctyl-trichlorosilane (Sigma-Aldrich, 448931), as described in the *Supporting Information*. We prepare silicone gels by mixing liquid (1 Pa · s) divinyl-terminated polydimethylsiloxane (PDMS) (Gelest, DMS-V31) with a chemical cross-linker (Gelest, HMS-301) and catalyst (Gelest, SIP6831.2). The silicone mixture is degassed in vacuum, put into

### Significance

Modern contact mechanics was originally developed to describe adhesion to relatively stiff materials like rubber, but much softer sticky materials are ubiquitous in biology, medicine, engineering, and everyday consumer products. By studying adhesive contact between compliant gels and rigid objects, we demonstrate that soft materials adhere very differently than their stiffer counterparts. We find that the structure in the region of contact is governed by the same physics that sets the geometry of liquid droplets, even though the material is solid. Furthermore, adhesion can cause the local composition of a soft material to change, thus coupling to its thermodynamic properties. These findings may substantially change our understanding of the mechanics of soft contact.

Author contributions: K.E.J., R.S., M.K.C., and E.R.D. designed research; K.E.J., R.S., R.B., A.C., and M.K.C. performed research; R.W.S. contributed new reagents/analytic tools; K.E.J., R.W.S., and E.R.D. analyzed data; and K.E.J., R.W.S., A.C., M.K.C., and E.R.D. wrote the paper. The authors declare no conflict of interest.

This article is a PNAS Direct Submission. J.A. is a guest editor invited by the Editorial Board.

<sup>&</sup>lt;sup>1</sup>To whom correspondence should be addressed. Email: eric.dufresne@yale.edu.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10. 1073/pnas.1514378112/-/DCSupplemental.

the appropriate experimental geometry, and cured at 68° C for 12–14 h. The resulting gel is an elastic network of cross-linked polymers swollen with free liquid of the same un- or partiallycross-linked polymer. The fraction of liquid PDMS in these gels is 62% by weight, measured by solvent extraction. The gel has a shear modulus of G' = 1.9 kPa, measured by bulk rheology. The Poisson ratio of the gel's elastic network is  $\nu = 0.48$ , measured using a compression test in the rheometer as described in ref. 32. As this is an isotropic, elastic material, this gives a Young modulus E = 5.6 kPa and a bulk modulus K = 47 kPa. All rheology data are included in the *Supporting Information*.

We directly image the geometry of the contact between the gel and sphere using optical microscopy. To prepare the gel substrates, we deposit an  $\sim$  300-µm-thick layer of PDMS along the millimeter-wide edge of a standard microscope slide. The silicone surface is flat parallel to the edge of the slide and slightly curved in the orthogonal direction with a radius of curvature  $\sim 700 \ \mu\text{m}$ . We distribute silica spheres sparsely on the surface of the gel and image only those spheres that adhere at the thickest part of the gel. Using an inverted optical microscope, we illuminate the sample with a low-N.A. condenser and image using a  $40 \times$  (N.A. 0.60) air objective. Example images for fluorocarbon-functionalized and plain silica spheres having radii of about 18 µm are shown in Fig. 1 A and B, respectively. All of the images analyzed for this work are included in the Supporting Information. In all cases, the rigid particles spontaneously indent into the gel as they adhere. Plain silica spheres indent more deeply than fluorocarbon-functionalized spheres of the same size.

To test whether surface stresses dominate over elasticity at the contact line, we measure the contact angle between the free surface of the gel and the sphere. Starting with the raw image data, we map the position of the dark edge in the images with 100-nm resolution using edge detection in MATLAB, as described in the *Supporting Information*. Example profiles for fluorocarbon-functionalized (blue points) and plain silica (red points) spheres are shown in Fig. 1*C*. We fit the central region of the sphere, indicated by the gray lines in Fig. 1*C*.

The approach to contact is qualitatively different for the two types of spheres: the substrate meets the plain spheres at a much shallower angle than the fluorocarbon-functionalized ones. We fit the substrate surface profile near the contact line to a surface of constant total curvature, which is the shape expected when surface stresses completely overwhelm elastic effects (31). The fitting procedure is described in the *Supporting Information*. Fit results for the profiles shown in Fig. 1*C* are plotted in Fig. 1*D*, zoomed in close to the contact line on one side. Note that we do not fit to the profile data within 1  $\mu$ m of the contact line, because diffraction tends to round off sharp corners. The resulting contact angles and curvatures are plotted as a function of sphere size for both fluorocarbon-functionalized and plain spheres ranging in radius from 12 to 27  $\mu$ m in Fig. 1*E* and *F*.

The contact angle of the substrate on the sphere is independent of the sphere size, but depends on the sphere's surface functionalization. The gel establishes a contact angle of  $\theta = 55 \pm 5^{\circ}$ with the fluorocarbon-functionalized spheres, and  $\theta = 7 \pm 8^{\circ}$  with the plain spheres. We also see no size dependence of the curvature of the gel near the contact line, and little difference with surface functionalization:  $\kappa_{plain} = -0.14 \pm 0.03 \ \mu m^{-1}$  and  $\kappa_{fc} = -0.17 \pm$  $0.02 \ \mu m^{-1}$ . Assuming that the surface tension of the solid is close to that of the liquid, 20 mN/m, these constant curvature values are comparable to the inverse of the elastocapillary length of the substrate  $E/\Upsilon = 0.28 \ \mu m^{-1}$ .

For comparison, we measure the contact angle between the spheres and uncured PDMS liquid. See the *Supporting Information* for a description of this measurement, raw images, and a histogram of measured contact angles. In this case, the contact angles should be set by the surface energies through the classic



**Fig. 1.** Contact angle measurements. (*A* and *B*) Side views of (*A*) an 18.2-µmradius fluorocarbon-functionalized silica sphere and (*B*) a 17.7-µm-radius plain silica sphere, each adhered to an E = 5.6 kPa silicone gel. (Scale bars, 10 µm.) (*C*) Mapped profiles of the spheres in *A* and *B* overlaid, with fit circles drawn to outline each sphere's position. The undeformed plane far from the adhered particles defines z = 0. (*D*) Close-up of the profiles in *C* superimposed on the raw data, focusing on the approach to contact. The constant curvature fits are overlaid as orange curves, as well as straight dashed lines indicating the measured contact angles. (*E* and *F*) Measured contact angle, *θ*, and measured curvature,  $-\kappa$ , respectively, versus sphere radius for both the fluorocarbon-functionalized (blue triangles) and plain silica (red circles) spheres. Dashed lines indicate the mean values. Histograms of the measurements are shown at right, with mean and SD indicated.

Young–Dupré relation. We find that the plain silica spheres are completely engulfed by the silicone liquid, corresponding to a contact angle  $\theta = 0^{\circ}$ . On the fluorocarbon-functionalized spheres, the uncured liquid makes a contact angle  $\theta = 54 \pm 4^{\circ}$ . These contact angles are also very close to what we measure for the silicone liquid on flat glass:  $\theta = 0^{\circ}$  on plain glass, and  $\theta = 57^{\circ}$  on fluorocarbon-functionalized flat glass.

The contact angles made by the silicone gel on the spheres are the same as the contact angles made by the silicone liquid. This suggests that the Young–Dupré relation governs the contact line of a soft adhesive. However, achieving the contact angle prescribed by Young–Dupré presents a serious difficulty for the gel's elastic network, especially during contact with surfaces that demand total wetting. As the contact angle of the gel approaches zero, the tensile strain on the elastic network diverges. How does the gel satisfy the wetting condition without creating an elastic singularity?



**Fig. 2.** Structure of the gel's elastic network near contact. (A) Confocal profiles of the surface of the silicone elastic network adhered to an 18.3-µm-radius plain silica sphere (red) and an 18.5-µm-radius fluorocarbon-functionalized sphere (blue). (B) Contact angle,  $\phi$ , made by the elastic network as it abruptly changes direction during approach to contact. (C) Contact angle,  $\psi$ , made by the elastic network as it contacts the sphere. Both  $\phi$  and  $\psi$  are plotted versus sphere radius for both the fluorocarbon-functionalized (blue triangles) and plain silica (red circles) spheres. Dashed lines indicate the mean contact angle. Histograms of the measured contact angles are shown at right, with mean and SD indicated.

## **Deformation of the Elastic Network**

To quantify the deformation of the gel's elastic network, we embed fluorescent tracers in the elastic network at the surface of the gel and image them using confocal microscopy. For this experiment, we prepare flat, ~ 120-µm-thick, silicone substrates on glass coverslips by spin-coating. After curing, we adsorb 48-nmdiameter fluorescent spheres (Life Technologies, F-8795) from an aqueous suspension onto the PDMS. This procedure is identical to that described in ref. 32 except that we do not chemically modify the silicone surface. Then, following the procedure of ref. 4, we sprinkle silica spheres onto the substrates and map the surface of the deformed elastic network by locating the fluorescent makers in 3D from confocal microscope images (33). Examples of azimuthally collapsed deformation profiles for each type of sphere are shown in Fig. 2A. Confocal profiles for 146 spheres ranging from 7 to 32 µm in radius are included in the Supporting Information. We find that the dependence of indentation depth on particle size is consistent with our earlier study of the transition from elastic-dominated to capillary-dominated adhesion (4); these data and fits to theory are also included in the Supporting Information, Fig. S13.

As expected, the elastic network rises gradually toward contact from the far field and conforms to the surface of the spheres underneath the particles. However, the surface of elastic network in the contact zone (Fig. 2A) looks nothing like the free surface of the substrate (Fig. 1). Specifically, the elastic network does not rise smoothly to contact the sphere with the expected contact angle and curvature. Instead, it has a kink of angle  $\phi$  a few micrometers from the sphere. Eventually the elastic network comes into contact with the sphere with an angle  $\psi$  well below the expected contact point. A series of control experiments, described in the *Supporting Information*, ruled out the possibility that the discrepancies between the structure of the contact zone in the bright-field and confocal experiments could be due to imaging artifacts. Just like the contact angle of the free surface  $\theta$ (Fig. 1*E*), the angles  $\phi$  and  $\psi$  are independent of sphere radius, as shown in Fig. 2 *B* and *C*.

#### **Adhesion-Induced Phase Separation**

Comparison of the bright-field images in Fig. 1A and B with the confocal images in Fig. 2A suggests that liquid PDMS fills the



**Fig. 3.** Structure and size of the four-phase contact zone. (*A*) Schematic of the four-phase contact zone. (*Inset*) Schematic of the surface tension balance at each of the contact lines **A**, **B**, and **C**. (*B*) Plot of the volume of phase-separated liquid,  $V_{\text{liquid}} = (V_{\text{indent}} - V_{\text{ridge}})$ , vs. indented volume,  $V_{\text{indent}}$ , measured by integrating the confocal profiles. The data for plain spheres in air are plotted as red circles, for fluorocarbon-functionalized spheres in air as blue triangles, and for plain spheres under glycerol as orange circles. A dashed line of slope 4/3 is shown as a guide to the eye. (*Inset*) The same data plotted vs. sphere radius, with a dashed line of slope 3.

space between the elastic network and the free surface, as shown schematically in Fig. 3A. In this way, the fluid can satisfy the Young-Dupré wetting condition while the elastic network avoids an elastic singularity. This adhesion-induced phase separation makes the zone of adhesive contact between a soft gel and a rigid object more complex than in adhesion to stiffer single-phase solids. Instead of a single three-phase contact line, phase separation creates a four-phase contact zone in which air, silica, silicone liquid, and silicone gel meet, as shown in Fig. 3A. In addition to the standard contact line at A, the confocal experiments reveal two additional contact lines at B and C. The existence of particle-size-independent contact angles  $\phi$  and  $\psi$  at these contact lines strongly indicates that their geometry is governed by surface stresses and/or surface energies, as indicated in Fig. 3A, Inset. The contact line at A is a conventional rigid solid-liquid-vapor contact line which satisfies the Young-Dupré relation, as discussed above. The contact line at **B** follows a Neumann triangle construction at this soft solid-liquid-vapor contact line, as in refs. 34, 35. Finally, we expect the contact line at C to be described by a modified Young–Dupré relation for a soft solid in contact with a rigid solid, as in ref. 4.

The structures of the contact lines at **B** and **C** therefore provide information about the relevant surface stresses and surface energies (20). For an ideal gel (36), the liquid phase dominates and the surface stress and surface energy of the gel are identical and equal to the surface tension of the solvent (36, 37). However, recent measurements of the surface stress of gels have sometimes differed significantly from the surface tension of their fluid phases (4, 34, 38, 39). If our silicone gel were ideal, we would expect the surface of the gel to be equivalent to the surface of its solvent, such that  $\Upsilon_{gl} = 0$ . In that case, there would be no constraint on the contact angles,  $\psi$  or  $\phi$ . However, the existence of well-defined, size-independent values of  $\psi$  and  $\phi$ implies that  $\Upsilon_{gl} > 0$ . Furthermore, we observe that  $\psi > 90^\circ$ , implying that  $\gamma_{pg} > \gamma_{pl}$ . This means that the particle has a preference for making contact with the pure liquid over the gel. This preference is only slightly changed by fluorocarbon functionalization of the particle surface.

At contact line **B**, the surface tension of the liquid  $\gamma_{lv}$  must balance the surface stresses of the gel,  $Y_{gl}$  and  $Y_{gv}$ , through the Neumann construction. To fully determine all of the surface tensions, we also need to measure the difference in angle between the gel and the liquid free surfaces,  $\alpha$ , as indicated in Fig. 3A, Inset. In principle,  $\alpha$  should be measurable as a discontinuity in the free surface at **B**. However, our bright-field images do not reveal such a discontinuity (Fig. 1 and Supporting In*formation*). This suggests that the angle  $\alpha$  is small and cannot be resolved due to diffraction effects (as seen in Fig. 1D). Small values of  $\alpha$  are expected when  $\Upsilon_{gl}$  and/or  $(\Upsilon_{gv} - \gamma_{lv})$  are small. Simplifying the Neumann condition for  $\gamma_{gl}/\gamma_{lv} \ll 1$ , we obtain  $\alpha = (\Upsilon_{gl}/\gamma_{lv})\sin\phi \ll 1$ . Further, by expanding both the horizontal and vertical force balances at **B** for  $\epsilon = (\Upsilon_{gv} - \gamma_{lv})/\gamma_{lv} \ll 1$ , we find that  $1 + \epsilon = \cos \alpha - \sin \alpha \cot \phi$ , which also results in small values of  $\alpha$  for small  $\varepsilon$ .

Although we cannot measure  $\alpha$  directly in these experiments, we can put a rough upper bound on its magnitude by combining our bright-field and confocal results for the geometry of the contact zone. These observations allow us to constrain  $\alpha$  between 0° and 10°. This bounds the values of the solid surface stresses such that  $0 < \Upsilon_{gl} \leq 0.4\gamma_{lv}$  and  $\gamma_{lv} < \Upsilon_{gv} \leq 1.3\gamma_{lv}$ . More precise measurements of the free-surface profile at contact line **B** will be required for precise measurement of the solid surface stresses.

Surface stresses and energies fix the geometries of the corners of the phase-separated liquid region at **A**, **B**, and **C**, but this is not sufficient to determine its overall size,  $V_{\text{liquid}}$ . Because the liquid is incompressible but the elastic network is not (40, 41),  $V_{\text{liquid}}$  must equal the change in volume of the elastic network due to the adhesion of the sphere. We define  $V_{\text{indent}}$  as the volume occupied by the sphere below the plane of the undeformed silicone surface, and  $V_{\text{ridge}}$  as the volume of the elastic network displaced above the undeformed surface, as indicated in Fig. 3*A*. Thus, we can measure  $V_{\text{liquid}}$  from our confocal profiles as  $V_{\text{indent}} - V_{\text{ridge}}$ . We compute these volumes by numerical integration of the axisymmetric confocal profiles.

We plot  $V_{\text{liquid}}$  vs. sphere radius in Fig. 3B, Inset. We see that the dependence of  $V_{\text{liquid}}$  on sphere size differs for the different surface functionalizations, but scales approximately as  $R^3$ . This suggests that  $V_{\text{liquid}}$  may be related to volume, rather than surface effects. We find that all of the data collapse if we instead plot  $V_{\text{liquid}}$  versus  $V_{\text{indent}}$ , as shown in the main panel of Fig. 3B. The volume of the phase-separated contact zone scales as a power law with exponent 4/3 over this range of indentation volumes. The more the elastic network is compressed by the spontaneous indentation of the particle, the larger the volume of incompressible liquid that phase-separates from the elastic network. This collapse is robust not only for the fluorocarbon-functionalized and plain silica spheres, but also after changing the balance of surface energies by covering the sphere and substrate with glycerol. It can even work when the system is out of equilibrium, as some of the glycerol-covered data points were not given enough time to equilibrate fully to their new indentation depth. Dimensionally, the prefactor for this power-law collapse must have dimensions of 1/[length]. Fitting to  $V_{liquid} =$  $(1/L')V_{\text{indent}}^{4/3}$ , we measure  $L' = 38 \,\mu\text{m}$ , which is about 10 times the elastocapillary length.

#### Conclusions

We have seen that during adhesion with a rigid object, a compliant gel phase-separates near the contact line to create a fourphase contact zone with three distinct contact lines. The total volume of the phase-separated region is set by the extent of indentation and the compressibility of the gel's elastic network. The geometries of the contact lines are independent of the size of the particles and suggest that the gel-vapor-solid surface stress,  $T_{gv}$ , and the liquid-vapor surface tension,  $\gamma_{hv}$ , are different, and that the solid surface stress between the gel and the liquid,  $T_{gl}$ , is nonzero.

These findings qualitatively change our understanding of the contact zone. This understanding of the geometry of contact and the balance of forces at work should inform both future theoretical work and engineering design of soft interfaces. Future studies will address adhesion-induced phase separation in different types of gels having varying compressibility of the elastic network. In many situations, a gel can be considered a single, homogeneous material. However, our results demonstrate that under extreme conditions-such as near a contact line-the nature of a gel as a multiphase material becomes important. This may have important implications not just for silicone materials, but also for materials like hydrogels, which have recently been the subject of significant research efforts (42-44). Because elastic networks in hydrogels can be much more compressible than the silicone gel studied here (40, 41), it is possible that they will be even more susceptible to phase separation during contact.

ACKNOWLEDGMENTS. We thank Manjari Randeria and Ross Bauer for help with sample preparation, and Dominic Vella for useful discussions and for help with the MATLAB code for the constant-curvature analyses. We acknowledge funding from the National Science Foundation (CBET-1236086). R.W.S. also received funding from the John Fell Oxford University Press Research Fund.

- 1. Johnson K (1987) Contact Mechanics (Cambridge Univ Press, Cambridge, UK).
- Creton C, Papon E (2003) Materials science of adhesives: How to bond things together. MRS Bull 28(6):419–421.
- Shull K, Ahn D, Chen W, Flanigan C, Crosby A (1998) Axisymmetric adhesion tests of soft materials. *Macromol Chem Phys* 199(4):489–511.
- Style RW, Hyland C, Boltyanskiy R, Wettlaufer JS, Dufresne ER (2013) Surface tension and contact with soft elastic solids. Nat 4:2728.
- Pastewka L, Robbins MO (2014) Contact between rough surfaces and a criterion for macroscopic adhesion. Proc Natl Acad Sci USA 111(9):3298–3303.
- Crosby A, Shull K (1999) Adhesive failure analysis of pressure-sensitive adhesives. J Polym Sci, B, Polym Phys 37(24):3455–3472.
- Creton C (2003) Pressure-sensitive adhesives: An introductory course. MRS Bull 28(6): 434–439.
- Persson B (2001) Theory of rubber friction and contact mechanics. J Chem Phys 115(8): 3840–3861.
- Kao I, Yang F (2004) Stiffness and contact mechanics for soft fingers in grasping and manipulation. *IEEE Trans Robot Autom* 20(1):132–135.
- Kim S, et al. (2007) Whole body adhesion: Hierarchical, directional and distributed control of adhesive forces for a climbing robot. 2007 IEEE International Conference on Robotics and Automation (IEEE, Rome), pp 1268–1273.
- 11. Martinez RV, et al. (2013) Robotic tentacles with three-dimensional mobility based on flexible elastomers. Adv Mater 25(2):205–212.
- 12. Kim S, Laschi C, Trimmer B (2013) Soft robotics: A bioinspired evolution in robotics. *Trends Biotechnol* 31(5):287–294.
- Mowery C, Crosby A, Ahn D, Shull K (1997) Adhesion of thermally reversible gels to solid surfaces. *Langmuir* 13(23):6101–6107.
- Van Vliet K, Bao G, Suresh S (2003) The biomechanics toolbox: Experimental approaches for living cells and biomolecules. Acta Mater 51(19):5881–5905.
- Suresh S (2007) Biomechanics and biophysics of cancer cells. Acta Biomater 3(4): 413–438.
- Li QS, Lee GYH, Ong CN, Lim CT (2008) AFM indentation study of breast cancer cells. Biochem Biophys Res Commun 374(4):609–613.
- Gonzalez-Rodriguez D, Guevorkian K, Douezan S, Brochard-Wyart F (2012) Soft matter models of developing tissues and tumors. Science 338(6109):910–917.
- Johnson K, Kendall K, Roberts A (1971) Surface energy and contact of elastic solids. Proc R Soc Lond A Math Phys Sci 324(1558):301–313.
- 19. Maugis D (1995) Extension of the Johnson-Kendall-Roberts theory of the elastic contact of spheres to large contact radii. *Langmuir* 11(2):679–682.
- Cammarata RC, Sieradzki K (1994) Surface and interface stresses. Annu Rev Mater Sci 24(1):215–234.
- Long D, Ajdari A, Leibler L (1996) Static and dynamic wetting properties of thin rubber films. Langmuir 12(21):5221–5230.
- 22. Jerison ER, Xu Y, Wilen LA, Dufresne ER (2011) Deformation of an elastic substrate by a three-phase contact line. *Phys Rev Lett* 106(18):186103.
- Jagota A, Paretkar D, Ghatak A (2012) Surface-tension-induced flattening of a nearly plane elastic solid. Phys Rev E Stat Nonlin Soft Matter Phys 85(5):051602.

- Paretkar D, Xu X, Hui CY, Jagota A (2014) Flattening of a patterned compliant solid by surface stress. Soft Matter 10(23):4084–4090.
- Mora S, Phou T, Fromental JM, Pismen LM, Pomeau Y (2010) Capillarity driven instability of a soft solid. Phys Rev Lett 105(21):214301.
- Xu X, Jagota A, Hui CY (2014) Effects of surface tension on the adhesive contact of a rigid sphere to a compliant substrate. Soft Matter 10(26):4625–4632.
- Liu T, Jagota A, Hui CY (2015) Adhesive contact of a rigid circular cylinder to a soft elastic substrate-the role of surface tension. Soft Matter 11(19):3844–3851.
- Cao Z, Stevens MJ, Dobrynin AV (2014) Adhesion and wetting of nanoparticles on soft surfaces. Macromolecules 47(9):3203–3209.
- Salez T, Benzaquen M, Raphaël É (2013) From adhesion to wetting of a soft particle. Soft Matter 9(45):10699–10704.
- Hui CY, Liu T, Salez T, Raphael E, Jagota A (2015) Indentation of a rigid sphere into an elastic substrate with surface tension and adhesion. *Proc Math Phys Eng Sci* 471(2175): 20140727.
- De Gennes PG, Brochard-Wyart F, Quéré D (2013) Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves (Springer Science & Business Media, New York).
- Style RW, et al. (2014) Traction force microscopy in physics and biology. Soft Matter 10(23):4047–4055.
- Gao Y, Kilfoil ML (2009) Accurate detection and complete tracking of large populations of features in three dimensions. Opt Express 17(6):4685–4704.
- Style RW, et al. (2013) Universal deformation of soft substrates near a contact line and the direct measurement of solid surface stresses. *Phys Rev Lett* 110(6):066103.
- Lubbers LA, et al. (2014) Drops on soft solids: Free energy and double transition of contact angles. J Fluid Mech 747:R1.
- Hui CY, Jagota A (2013) Surface tension, surface energy, and chemical potential due to their difference. Langmuir 29(36):11310–11316.
- Shuttleworth R (1950) The surface tension of solids. Proc Phys Soc A 63(5):444–457.
  Nadermann N, Hui CY, Jagota A (2013) Solid surface tension measured by a liquid
- drop under a solid film. *Proc Natl Acad Sci USA* 110(26):10541–10545. 39. Chakrabarti A, Chaudhury MK (2013) Direct measurement of the surface tension of a
- Chakrabaru A, Chaudhury MK (2013) Direct measurement of the surface tension of a soft elastic hydrogel: exploration of elastocapillary instability in adhesion. *Langmuir* 29(23):6926–6935.
- Geissler E, Hecht A (1980) The Poisson ratio in polymer gels. *Macromolecules* 13(5): 1276–1280.
- Cai S, Hu Y, Zhao X, Suo Z (2010) Poroelasticity of a covalently crosslinked alginate hydrogel under compression. J Appl Phys 108(11):113514-1–113514-8.
- 42. Lee KY, Mooney DJ (2001) Hydrogels for tissue engineering. Chem Rev 101(7): 1869–1879.
- Drury JL, Mooney DJ (2003) Hydrogels for tissue engineering: Scaffold design variables and applications. *Biomaterials* 24(24):4337–4351.
- 44. Sun JY, et al. (2012) Highly stretchable and tough hydrogels. *Nature* 489(7414):133–136. 45. Río Ol, Neumann AW (1997) Axisymmetric drop shape analysis: Computational
- 45. Rio Oi, Neumann AW (1997) Axisymmetric drop shape analysis: Computational methods for the measurement of interfacial properties from the shape and dimensions of pendant and sessile drops. J Colloid Interface Sci 196(2):136–147.