

Wetting and phase separation in soft adhesion

Katharine E. Jensen^a, Raphael Sarfati^a, Robert W. Style^b, Rostislav Boltyskiy^a, Aditi Chakrabarti^c,
 Manoj K. Chaudhury^c, and Eric R. Dufresne^{a,1}

^aDepartment of Mechanical Engineering and Materials Science, Yale University, New Haven, CT 06511; ^bMathematical Institute, University of Oxford, Oxford, OX1 3LB, United Kingdom; and ^cDepartment of Chemical Engineering, Lehigh University, Bethlehem, PA 18015

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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

Solid 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 consequences. 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, $W = \gamma_1 + \gamma_2 - \gamma_{12}$, is positive, where γ_1 and γ_2 are the surface energies of the free surfaces and γ_{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, Υ (4). Unlike a fluid, the surface stress of a solid is not always equal to its surface energy, γ . For solids, γ is the work required to create additional surface area by cleaving, whereas Υ 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, $L = \Upsilon/E$ (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 μm (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.

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¹To whom correspondence should be addressed. Email: eric.dufresne@yale.edu.

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